Reactions of alkynes with *cis*-$RuCl_2(dppm)_2$: exploring the interplay of vinylidene, alkynyl and η^3-butenynyl complexes

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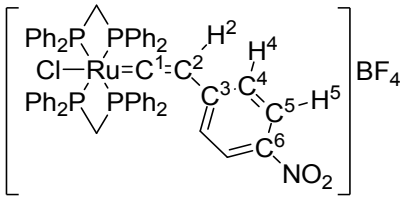
S1 General Conditions

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Dichloromethane was dried over CaH_2, all other solvents were standard reagent grade and used as received. No special precautions were taken to exclude air or moisture during workup. The compounds *cis*-[$RuCl_2(dppm)_2$];[1] $HC{\equiv}CC_6H_4$-4-NO_2;[2] $HC{\equiv}CC_6H_4$-4-COOMe;[2] $HC{\equiv}CC_6H_4$-4-$C{\equiv}CSiMe_3$[3] and $TlBF_4$[4] were synthesised by literature methods. All other reagents were commercially available and used as received. NMR spectra were recorded at 25 ºC either on a Varian Inova 300 (^{1}H, 300.2 MHz; ^{31}P, 121.5 MHz), Jeol 400 (^{1}H, 399.78 MHz; ^{13}C, 100.53 MHz; ^{19}F, 376.17 MHz; ^{11}B, 128.27 MHz), Varian Mercury-400 (^{1}H, 399.97 MHz; ^{31}P, 161.10 MHz), Bruker AV500 (^{1}H, 500.23 MHz; ^{31}P, 202.50 MHz; ^{13}C, 125.77 MHz), Bruker Avance 600 (^{1}H, 600.1 MHz; ^{13}C, 150.9 MHz; ^{19}F, 564.6 MHz; ^{31}P, 242.9 MHz) or a Varian VNMRS-700 (^{1}H, 699.73 MHz; ^{13}C, 175.95 MHz ; ^{31}P, 279.89 MHz) spectrometer using $CDCl_3$ or CD_2Cl_2 as the solvent. Chemical shifts were determined relative to internal residual solvent signals (^{1}H, δ = 7.26 ppm, 5.32 ppm; ^{13}C, δ = 77.2 ppm, 54.2 ppm) or external 85% H_3PO_4 (^{31}P, δ = 0.0 ppm).[5] FT-IR spectra were measured on an Agilent Technologies Cary 660 spectrometer or a Nicolet Avatar 360 spectrometer from solutions in CH_2Cl_2 in a thin layer cell fitted with CaF_2 windows. ESI-MS and APCI-MS were recorded on a Waters LCT Premier XE mass spectrometer in positive or negative ion mode from solutions in methanol. MALDI-MS were recorded using an Autoflex II TOF / TOF mass spectrometer (Bruker Daltonik, GmbH) equipped with a 337 nm laser. Cyclic voltammetry was carried out using Autolab PGSTAT 30 or Princeton Applied Research Versastat 3 potentiostats, with a platinum disc working electrode, a platinum wire counter electrode and a platinum wire pseudo-reference electrode from solutions in CH_2Cl_2 containing 0.1 M $[N^nBu_4]PF_6$ as the electrolyte. Potentials are reported *vs.* ferrocene / ferrocenium ($[FeCp_2]$ / $[FeCp_2]^+$ = 0 V)[6] using a decamethylferrocene / decamethylferrocenium internal standard ($[FeCp^*_2]$ / $[FeCp^*_2]^+$ = – 0.48 V).

S1. Synthesis of characterisation of *mono*-vinylidene complexes

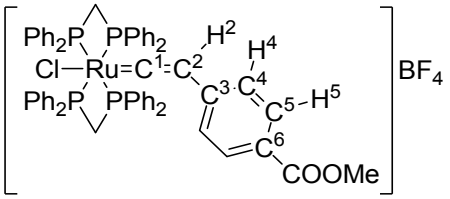
S1.1 Synthesis of *trans*-[RuCl(=C=CHC$_6$H$_4$-4-NO$_2$)(dppm)$_2$]BF$_4$ [1a]BF$_4$



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.05 mmol) and HC≡CC$_6$H$_4$-4-NO$_2$ (0.0082 g, 0.05 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for two hours. The solution colour changed from yellow to red and a white solid (TlCl) precipitated. The TlCl was removed by filtration through a HPLC Teflon filter (20 μm pores) and the filtrate concentrated to *ca.* 1 ml by rotary evaporation. Excess diethyl ether was then added to the red solution, resulting in the instantaneous precipitation of a red solid which was collected by filtration, washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml), and then dried in air (0.049 g, 80 %).

IR (CH$_2$Cl$_2$, cm^{-1}): 1635 ν(Ru=C=C), 1550 ν(N=O), 1340 ν(N-O). ^{1}H NMR (CDCl$_3$, 400 MHz) δ / ppm: 3.36 (quin., J_{HP} = 3 Hz, 1H, H^2), 5.21 (dt, J_{HP} = 16 Hz, J_{HH} = 5 Hz, 2H, CH$_2$, dppm), 5.42 (dt, J_{HP} = 16 Hz, J_{HH} = 5 Hz, 2H, CH$_2$, dppm), 5.65 (d, J_{HH} = 8 Hz, 2H, H^4), 7.23 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.25 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.31 – 7.38 (m, 8H, H$_o$, dppm), 7.42 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.45 (d, J_{HH} = 8 Hz, 2H, H^5), 7.44 – 7.50 (m, 12H, H$_o$ and H$_p$, dppm). ^{31}P{^{1}H} NMR (CDCl$_3$, 400 MHz) δ / ppm: − 17.3 (s, Ru(dppm)$_2$). ^{19}F NMR (CDCl$_3$, 400 MHz) δ / ppm: − 155.3 (s, BF$_4$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 400 MHz) δ / ppm: 46.2 (t, J_{CP} = 12 Hz, CH$_2$, dppm), 110.4 (s, C^2), 124.2 (s, C^5), 127.2 (s, C^4), 128.8 (s, C$_m$, dppm), 129.4 (s, C$_m$, dppm), 131.6 (s, C$_p$, dppm), 131.8 (s, C$_p$, dppm), 132.4 (quin., J_{CP} = 13 Hz, C$_i$, dppm), 132.7 (s, C$_o$, dppm), 133.5 (quin., J_{CP} = 13 Hz, C$_i$, dppm), 133.6 (s, C$_o$, dppm), 136.2 (s, C^3), 145.8 (s, C^6), 352.5 (quin., J_{CP} = 14 Hz, C^1). ASAP (+)-MS (*m/z*): 1052 [RuCl(=C=CHC$_6$H$_4$-4-NO$_2$)(dppm)$_2$]$^+$. Anal. Found: C, 60.94; H, 4.28; N, 1.34. Calc. for C$_{58}$H$_{49}$BClF$_4$NO$_2$P$_4$Ru: C, 61.10; H, 4.34; N, 1.23.

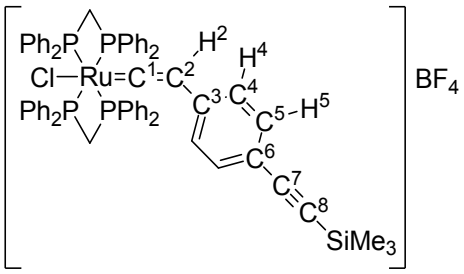
S1.2 Synthesis of *trans*-[RuCl(=C=CHC$_6$H$_4$-4-COOMe)(dppm)$_2$]BF$_4$ [1b]BF$_4$



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.05 mmol) and HC≡CC$_6$H$_4$-4-COOMe (0.0087 g, 0.05 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for one hour. The solution colour changed from yellow to orange / brown and a white solid (TlCl) precipitated. The TlCl was removed by filtration through a HPLC Teflon filter (20 μm pores) and the filtrate concentrated to *ca.* 1 ml by rotary evaporation. Excess diethyl ether was then added to the orange / brown solution, resulting in the instantaneous precipitation of a pale brown solid which was collected by filtration, washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml), and then dried in air (0.046 g, 75 %).

IR (CH$_2$Cl$_2$, cm^{-1}): 1717 ν(C=O), 1635 ν(Ru=C=C). ^{1}H NMR (CD$_2$Cl$_2$, 700 MHz) δ / ppm: 3.13 (quin., J_{HP} = 3 Hz, 1H, H^2), 3.90 (s, 3H, CH$_3$), 5.14 (dt, J_{HP} = 15 Hz, J_{HH} = 5 Hz, 2H, CH$_2$, dppm), 5.36 (dt, J_{HP} = 15 Hz, J_{HH} = 5 Hz, CH$_2$, dppm), 5.58 (d, J_{HH} = 8 Hz, 2H, H^4), 7.25 (t, J_{HH} = 7 Hz, 16H, H$_m$, dppm), 7.31 – 7.36 (m, 8H, H$_o$, dppm), 7.40 – 7.46 (m, 16H, H$_o$ and H$_p$, dppm), 7.41 (d$_{HH}$, J = 8 Hz, 2H, H^5). ^{11}B NMR (CD$_2$Cl$_2$, 500 MHz) δ / ppm: – 2.0 (s, BF$_4$). ^{19}F NMR (CD$_2$Cl$_2$, 500 MHz) δ / ppm: – 152.5 (s, BF$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$, 700 MHz) δ / ppm: – 16.6 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 500 MHz) δ / ppm: 46.4 (t, J_{CP} = 13 Hz, CH$_2$, dppm), 52.6 (s, CH$_3$), 110.7 (s, C^2), 127.2 (s, C^4), 128.2 (s, C^3), 129.1 (t, J_{CP} = 3 Hz, C$_m$, dppm), 129.7 (t, J_{CP} = 3 Hz, C$_m$, dppm), 129.8 (quin., J_{CP} = 12 Hz, C$_i$, dppm), 130.2 (s, C^5), 131.3 (quin., J_{CP} = 12 Hz, C$_i$, dppm), 132.0 (s, C$_p$, dppm), 132.3 (s, C$_p$, dppm), 132.6 (s, C^6), 132.9 (quin., J_{CP} = 3 Hz, C$_o$, dppm), 133.9 (quin., J_{CP} = 3 Hz, C$_o$, dppm), 166.9 (s, C=O), 355.4 (quin., J_{CP} = 14 Hz, C^1). ASAP (+)-MS (*m/z*): 1065 [RuCl(=C=CHC$_6$H$_4$-4-COOMe)(dppm)$_2$]$^+$, 521 [RuCl(dppm)]$^+$. A satisfactory elemental analysis was not obtained.

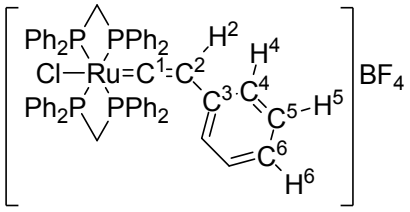
S1.3 Synthesis of *trans*-[RuCl(=C=CHC$_6$H$_4$-4-C≡CSiMe$_3$)(dppm)$_2$]BF$_4$ [1c]BF$_4$



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.049 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.06 mmol) and HC≡CC$_6$H$_4$-4-C≡CSiMe$_3$ (0.011 g, 0.06 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for two hour. The solution colour changed from yellow to brown and a white solid (TlCl) precipitated. The TlCl was removed by filtration through a HPLC Teflon filter (20 μm pores) and the filtrate concentrated to *ca.* 1 ml by rotary evaporation. Excess diethyl ether was then added to the brown solution, resulting in the instantaneous precipitation of a brown solid which was collected by filtration, washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml), and then dried in air (0.041 g, 66 %).

IR (CH$_2$Cl$_2$, cm^{-1}): 1605 ν(Ru=C=C). ^{1}H NMR (CDCl$_3$, 600 MHz) δ / ppm: 0.25 (s, 9H, SiMe$_3$), 3.00 (quin., J_{HP} = 3 Hz, 1H, H^2), 5.14 (dt, J_{HP} = 15 Hz, J_{HH} = 4 Hz, 2H, CH$_2$, dppm), 5.42 (dt, J_{HP} = 15 Hz, J_{HH} = 4 Hz, 2H, CH$_2$, dppm), 5.43 (d, J_{HH} = 8 Hz, 2H, H^4), 6.82 (d, J_{HH} = 8 Hz, 2H, H^5), 7.21 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.22 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.32 – 7.35 (m, 8H, H$_o$, dppm), 7.35 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.38 – 7.44 (m, 12H, H$_o$ and H$_p$, dppm). ^{31}P{^{1}H} NMR (CDCl$_3$, 600 MHz) δ / ppm: – 16.3 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 600 MHz) δ / ppm: 0.19 (s, SiMe$_3$), 46.2 (quin., J_{CP} = 13 Hz, CH$_2$, dppm), 94.6 (s, C^8), 105.0 (s, C^7), 110.1 (s, C^2), 120.5 (s, C^3), 126.9 (s, C^4), 127.7 (s, C^6), 128.7 (s, C$_m$, dppm), 129.3 (s, C$_m$, dppm), 129.6 (quin., J_{CP} = 13 Hz, C$_i$, dppm), 131.1 (quin., J_{CP} = 13 Hz, C$_i$, dppm), 131.4 (s, C$_p$, dppm), 131.7 (s, C$_p$, dppm), 132.1 (s, C^5), 132.7 (s, C$_o$, dppm), 133.6 (s, C$_o$, dppm), 355.9 – 356.1 (m, C^1). ESI (+)-MS (*m/z*): 1103 [RuCl(=C=CHC$_6$H$_4$-4-C≡CSiMe$_3$)(dppm)$_2$]$^+$, 905 [Ru(dppm)$_2$]$^+$. A satisfactory elemental analysis was not obtained.

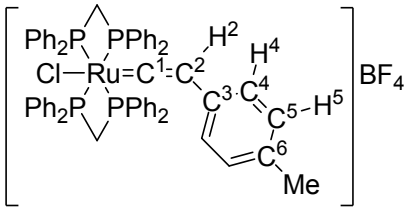
S1.4 Synthesis of *trans*-[RuCl(=C=CHC$_6$H$_5$)(dppm)$_2$]BF$_4$ [1d]BF$_4$



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.05 mmol) and HC≡CC$_6$H$_5$ (6 µL, 0.06 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for one hour. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The TlCl was removed by filtration through a HPLC Teflon filter (20 µm pores) and the filtrate concentrated to *ca.* 1 ml by rotary evaporation. Excess diethyl ether was then added to the orange / brown solution, resulting in the instantaneous precipitation of a pale yellow / brown solid which was collected by filtration, washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml), and then dried in air (0.047 g, 82 %).

IR (CH$_2$Cl$_2$, cm^{-1}): 1605 ν(Ru=C=C). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz) δ / ppm: 3.10 (quin., J_{HP} = 3 Hz, 1H, H^2), 5.03 – 5.10 (m, 2H, CH$_2$, dppm), 5.11 – 5.18 (m, 2H, CH$_2$, dppm), 5.56 (d, J_{HH} = 8 Hz, 2H, H^4), 6.79 (t, J_{HH} = 8 Hz, 2H, H^5), 6.92 (t, J_{HH} = 8 Hz, 1H, H^6), 7.22 – 7.32 (m, 16H, H$_m$, dppm), 7.32 – 7.42 (m, 16H, H$_o$, dppm), 7.48 (t, J_{HH} = 8 Hz, 8H, H$_p$, dppm). ^{19}F NMR (CD$_2$Cl$_2$, 400 MHz) δ / ppm: – 152.8 (s, BF$_4$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 400 MHz) δ / ppm: – 15.4 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 400 MHz) δ / ppm: 46.7 (t, J_{CP} = 12 Hz, CH$_2$, dppm), 111.1 (s, C^2), 126.9 (s, C^3), 127.9 (s, C^4), 129.5 (s, C$_m$, dppm), 130.0 (s, C$_m$, dppm), 131.3 – 131.8 (m, C$_i$, dppm), 132.14 (s, C^6), 132.4 (s, C^5), 132.3 (s, C$_p$, dppm), 132.7 (s, C$_p$, dppm), 132.9 (s, C$_o$, dppm), 134.0 (s, C$_o$, dppm), 358.2 (quin., J_{CP} = 13 Hz, C^1). ESI (+)-MS (*m/z*): 1007 [RuCl(=C=CHC$_6$H$_5$)(dppm)$_2$]$^+$. ESI (–)-MS (*m/z*): 87 [BF$_4$]$^-$. Anal. Found: C, 63.01; H, 4.55. Calc. for C$_{58}$H$_{50}$BClF$_4$P$_4$Ru: C, 63.67; H, 4.52.

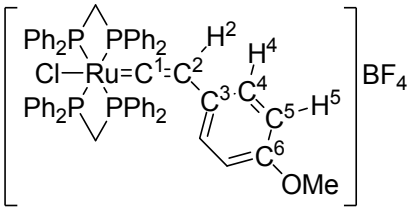
S1.5 Synthesis of *trans*-[RuCl(=C=CHC$_6$H$_4$-4-Me)(dppm)$_2$]BF$_4$ [1e]BF$_4$



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.047 g, 0.05 mmol), TlBF$_4$ (0.015 g, 0.05 mmol) and HC≡CC$_6$H$_4$-4-Me (7 μL, 0.06 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for one hour. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The TlCl was removed by filtration through a HPLC Teflon filter (20 μm pores) and the filtrate concentrated to *ca.* 1 ml by rotary evaporation. Excess diethyl ether was then added to the orange / brown solution, resulting in the instantaneous precipitation of a pale orange / brown solid which was collected by filtration, washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml), and then dried in air (0.046 g, 83 %).

IR (CH$_2$Cl$_2$, cm^{-1}): 1646 ν(Ru=C=C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ / ppm: 2.16 (s, 3H, CH$_3$), 2.94 (quin., J_{HP} = 3 Hz, 1H, C=CH), 5.11 (dt, J_{HP} = 15 Hz, J_{HH} = 5 Hz, 2H, CH$_2$, dppm), 5.41 (dt, J_{HP} = 15 Hz, J_{HH} = 5 Hz, 2H, CH$_2$, dppm), 5.36 (d, J_{HH} = 8 Hz, 2H, H^4), 6.50 (d, J_{HH} = 8 Hz, 2H, H^5), 7.12 – 7.26 (m, 16H, H$_m$, dppm), 7.26 – 7.37 (m, 16H, H$_o$, dppm), 7.37 – 7.45 (m, 8H, H$_p$, dppm). ^{19}F NMR (CDCl$_3$, 400 MHz) δ / ppm: –152.4 (s, BF$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$, 400 MHz) δ / ppm: – 15.9 (s, dppm). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 500 MHz) δ / ppm: 21.2 (s, CH$_3$), 46.5 (t, J_{CP} = 12 Hz, CH$_2$, dppm), 110.6 (s, C^2), 123.8 (s, C^3), 127.6 (s, C^4), 129.2 (t, J_{CP} = 3 Hz, C$_m$, dppm), 129.8 (t, J_{CP} = 3 Hz, C$_m$, dppm), 129.6 (s, C^5), 130.4 (quin., J_{CP} = 13 Hz, C$_i$, dppm), 131.6 (quin., J_{CP} = 13 Hz, C$_i$, dppm), 132.0 (s, C$_p$, dppm), 132.3 (s, C$_p$, dppm), 133.2 (quin., J_{CP} = 3 Hz, C$_o$, dppm), 134.1 (quin., J_{CP} = 3 Hz, C$_o$, dppm), 136.6 (s, C^6), 359.5 (quin., J_{CP} = 15 Hz, C^1). ASAP (+)-MS (m/z): 1021 [RuCl(=C=CHC$_6$H$_4$-4-Me)(dppm)$_2$]$^+$. Anal. Found: C, 62.65; H, 4.28. Calc. for C$_{59}$H$_{52}$BClF$_4$P$_4$Ru: C, 63.89; H, 4.73.

S1.6 Synthesis of *trans*-[RuCl(=C=CHC$_6$H$_4$-4-OMe)(dppm)$_2$]BF$_4$ [1f]BF$_4$

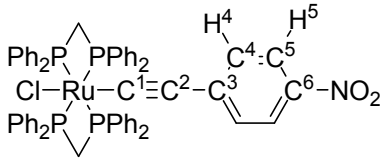


A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.05 mmol) and HC≡CC$_6$H$_4$-4-OMe (7 μL, 0.05 mmol) in CH_2Cl_2 (5 ml) was stirred under N_2 for one hour. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The TlCl was removed by filtration through a HPLC Teflon filter (20 μm pores) and the filtrate concentrated to *ca.* 1 ml by rotary evaporation. Excess diethyl ether was then added to the orange / brown solution, resulting in the instantaneous precipitation of a pale yellow / brown solid which was collected by filtration, washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml), and then dried in air (0.050 g, 83 %).

IR (CH_2Cl_2, cm^{-1}): 1653 ν(Ru=C=C). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ / ppm: 3.05 – 3.12 (m, 1H, H^2), 3.71 (s, 3H, CH_3), 5.09 (dt, J_{HP} = 16 Hz, J_{HH} = 4 Hz, 2H, CH_2, dppm), 5.16 (dt, J = 16 Hz, J_{HH} = 4 Hz, 2H, CH_2, dppm), 5.49 (d, J_{HH} = 8 Hz, 2H, H^4), 6.35 (d, J_{HH} = 8 Hz, 2H, H^5), 7.24 – 7.32 (m, 16H, H_m, dppm), 7.33 – 7.41 (m, 16H, H_o, dppm), 7.45 – 8.41 (m, 8H, H_p, dppm). ^{11}B NMR (CD_2Cl_2, 400 MHz) δ / ppm: – 2.0 (s, BF_4). ^{19}F NMR (CD_2Cl_2, 400 MHz) δ / ppm: – 152.6 (s, BF_4). ^{31}P{^{1}H} NMR (CD_2Cl_2, 500 MHz) δ / ppm: – 15.9 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 500 MHz) δ / ppm: 46.7 (t, J_{CP} = 13 Hz, CH_2, dppm), 56.0 (s, CH_3), 110.5 (s, C^2), 114.7 (s, C^5), 118.7 (s, C^3), 129.2 (s, C^4), 129.6 (t, J = 3 Hz, C_m, dppm), 130.2 (t, J = 3 Hz, C_m, dppm), 130.8 (quin., J_{CP} = 13 Hz, C_i, dppm), 132.2 (quin., J_{CP} = 13 Hz C_i, dppm), 132.7 (s, C_p, dppm), 133.0 (s, C_p, dppm), 133.6 (quin., J_{CP} = 3 Hz, C_o, dppm), 134.5 (quin., J_{CP} = 3 Hz, C_o, dppm), 158.8 (s, C^6), 362.5 – 362.6 (m, C^1). ASAP (+)-MS (*m/z*): 1037 [RuCl(=C=CHC$_6$H$_4$-4-OMe)(dppm)$_2$]$^+$. Anal. Found: C, 62.90; H, 4.57. Calc. for $C_{59}H_{52}BClF_4OP_4Ru$: C, 62.98; H, 4.66.

S2. Synthesis of Ruthenium *mono*-Alkynyl Complexes

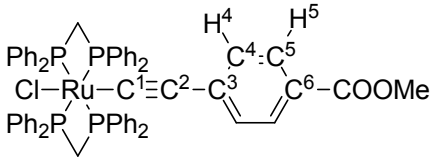
S2.1 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_4$-4-NO$_2$)(dppm)$_2$] [2a]



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.05 mmol) and HC≡CC$_6$H$_4$-4-NO$_2$ (0.0083 g, 0.05 mmol) in CH_2Cl_2 (5 ml) was stirred under N_2 for two hour. The solution colour changed from yellow to red and a white solid (TlCl) precipitated. The solution was then transferred, via cannula filtration (– TlCl), into a separate dry degassed flask containing 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.046 g, 0.21 mmol) in CH_2Cl_2 (2 ml), where the red solution colour darkened instantly. The solution was stirred for a further ten minutes, then filtered through celite to remove reaction salts. The red filtrate is concentrated to *ca.* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a red solid. The solid is collected by filtration, washed with hexanes (3 × 20 ml) and dried in air (0.049 g, 88 %). Crystals of the complex were obtained from CH_2Cl_2 / hexanes layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 2058 ν(C≡C), 1579 ν(N=O), 1322 ν(N-O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ / ppm: 4.86 – 5.05 (m, 4H, CH_2, dppm), 5.95 (d, J_{HH} = 8 Hz, 2H, H^4), 7.09 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.18 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.26 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.31 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.36 – 7.41 (m, 8H, H$_o$, dppm), 7.42 – 7.46 (m, 8H, H$_o$, dppm), 7.78 (d, J = 8 Hz, 2H, H^5). ^{31}P{^{1}H} NMR ($CDCl_3$, 400 MHz) δ / ppm: – 7.1 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 500 MHz) δ / ppm: 50.2, (t, J_{CP} = 11 Hz, CH_2, dppm), 115.8 (s, C^2), 122.9 (s, C^5), 127.7 (s, C$_m$, dppm), 127.8 (s, C$_m$, dppm), 129.5 (s, C$_p$, dppm) 129.7 (s, C$_p$, dppm), 129.8 (s, C^4), 133.3 (t, J_{CP} = 3 Hz, C$_o$, dppm) 133.8 (t, J_{CP} = 3 Hz, C$_o$, dppm), 133.9 (quin., J_{CP} = 11 Hz, C$_i$, dppm), 134.7 (quin., JCP = 11 Hz, C$_i$, dppm), 137.6 (s, C^3), 141.9 (s, C^6), 147.6 (quin., J_{CP} = 16 Hz, C^1). MALDI (+)-MS (*m/z*): 1051 [RuCl(C≡CC$_6$H$_4$-4-NO$_2$)(dppm)$_2$ + H]$^+$, 870 [Ru(dppm)$_2$]$^+$. Anal. Found: C, 66.30; H, 4.48; N, 1.39. Calc. for $C_{58}H_{48}ClNO_2P_4Ru$: C, 66.21; H, 4.60; N, 1.33.

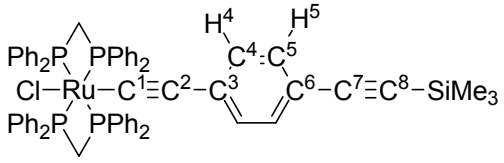
S2.2 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_4$-4-COOMe)(dppm)$_2$] [2b]



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.017 g, 0.06 mmol) and HC≡CC$_6$H$_4$-4-COOMe (0.0086 g, 0.05 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for one hour. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The solution was then transferred, via cannula filtration (– TlCl), into a separate dry degassed flask containing 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.045 g, 0.21 mmol) in CH$_2$Cl$_2$ (2 ml), where solution colour immediately changed from orange to yellow. The solution was stirred for a further ten minutes, then filtered through celite to remove reaction salts. The yellow filtrate is concentrated to *ca.* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a yellow solid. The solid is collected by filtration, washed with hexanes (3 × 20 ml) and dried in air (0.048 g, 86 %). Crystals of the complex were obtained from CH$_2$Cl$_2$ / pentane layer diffusion.

IR (CH$_2$Cl$_2$, cm^{-1}): 2073 ν(C≡C), 1705 ν(C=O), 1590 ν(C-O). ^{1}H NMR (CDCl$_3$, 400 MHz) δ / ppm: 3.84 (s, 3H, CH$_3$), 4.86 – 4.95 (m, 4H, CH$_2$, dppm), 6.00 (d, J_{HH} = 8 Hz, 2H, H^4), 7.06 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.72 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.23 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.29 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.37 – 7.43 (m, 8H, H$_o$, dppm), 7.43 – 7.49 (m, 8H, H$_o$, dppm), 7.48 (d, J_{HH} = 8 Hz, 2H, H^5). ^{31}P{^{1}H} NMR (CDCl$_3$, 400 MHz) δ / ppm: – 6.8 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 600 MHz) δ / ppm: 50.4 (quin., J = 10 Hz, CH$_2$, dppm), 51.8 (s, CH$_3$), 113.9 (s, C^2), 123.2 (s, C^3), 127.7 (s, C$_m$, dppm), 128.5 (s, C^5), 129.3 (s, C$_p$, dppm), 129.5 (s, C$_p$, dppm), 129.9 (s, C^4), 133.5 (s, C$_o$, dppm), 133.8 (s, C$_o$, dppm), 134.2 (quin., J_{CP} = 10 Hz, C$_i$, dppm), 134.9 (quin., J_{CP} = 10 Hz, C$_i$, dppm), 135.6 (s, C^6), 144.7 – 145.0 (m, C^1), 167.8 (s, C=O). MALDI (+)-MS (*m/z*): 1189 [RuCl(C≡CC$_6$H$_4$-4-COOMe)(dppm)$_2$ + H]$^+$, 870 [Ru(dppm)$_2$]$^+$. Anal. Found: C, 62.96; H, 4.67. Calc. for C$_{60}$H$_{51}$ClO$_2$P$_4$Ru × CH$_2$Cl$_2$: C, 63.76; H, 4.65.

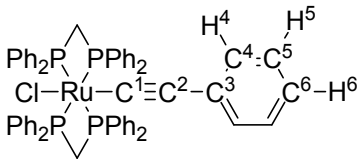
S2.3 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_4$C≡CSiMe$_3$)(dppm)$_2$] [2c]



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.11 g, 0.12 mmol), TlBF$_4$ (0.035 g, 0.12 mmol) and HC≡CC$_6$H$_4$-4-C≡CSiMe$_3$ (0.035 g, 0.12 mmol) in CH_2Cl_2 (5 ml) was stirred under N_2 for 75 minutes. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The solution was then transferred, via cannula filtration (– TlCl), into a separate dry degassed flask containing 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.088 g, 0.48 mmol) in CH_2Cl_2 (2 ml), where solution colour immediately changed from orange to yellow. The solution was stirred for a further ten minutes, then filtered through celite to remove reaction salts. The yellow filtrate is concentrated to *ca.* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a yellow solid. The solid is collected by filtration, washed with hexanes (3 × 20 ml) and dried in air (0.11 g, 80 %). Crystals of the complex were obtained from CH_2Cl_2 / MeOH layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 2146 ν(C≡CSiMe$_3$), 2073 ν(C≡C). ^{1}H NMR (CD_2Cl_2, 700 MHz) δ / ppm: 0.23 (s, 9H, SiMe$_3$), 4.88 – 4.98 (m, 4H, CH_2, dppm), 5.95 (d, J_{HH} = 8 Hz, 2H, H^4), 6.96 (d, J_{HH} = 8 Hz, 2H, H^5), 7.04 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.17 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.21 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.28 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.36 – 7.44 (m, 8H, H$_o$, dppm), 7.44 – 7.50 (m, 8H, H$_o$, dppm). ^{31}P{^{1}H} NMR ($CDCl_3$, 400 MHz) δ / ppm: – 6.6 ppm (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 700 MHz) δ / ppm: – 0.3 (s, SiMe$_3$), 49.8 (t, J_{CP} = 10 Hz, CH_2, dppm), 93.2 (s, C^8), 106.0 (s, C^7), 112.9 (s, C^2), 116.0 (s, C^3), 128.3 (t, J_{CP} = 3 Hz, C$_m$, dppm), 128.4 (t, J_{CP} = 3Hz, C$_m$, dppm), 129.9 (s, C$_p$, dppm), 130.1 (s, C$_p$, dppm), 130.4 (s, C^4), 130.8 (quin., J_{CP} = 15 Hz, C^1), 131.1 (s, C^5), 131.4 (s, C^6), 134.0 (t, J_{CP} = 3 Hz, C$_o$, dppm), 134.3 (t, J_{CP} = 3 Hz, C$_o$, dppm), 135.4 (quin., J_{CP} = 11 Hz, C$_i$, dppm), 135.9 (quin., J_{CP} = 11 Hz, C$_i$, dppm). MALDI (+)-MS (*m*/*z*): 1102 [RuCl(C≡CC$_6$H$_4$-4-C≡CSiMe$_3$)(dppm)$_2$]$^+$, 933 [RuCl(dppm)$_2$ + C$_2$H$_4$]$^+$. Anal. Found: C, 68.51; H, 5.35. Calc. for C$_{63}$H$_{57}$ClP$_4$RuSi: C, 68.59; H, 5.21.

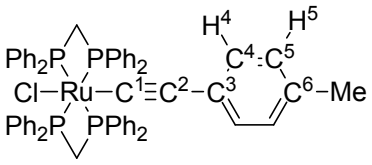
S2.4 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_5$)(dppm)$_2$] [2d]



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.049 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.05 mmol) and HC≡CC$_6$H$_5$ (6 µL, 0.06 mmol) in CH_2Cl_2 (5 ml) was stirred under N_2 for one hour. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The solution was then transferred, via cannula filtration (– TlCl), into a separate dry degassed flask containing 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.041 g, 0.19 mmol) in CH_2Cl_2 (2 ml), where solution colour immediately changed from orange to yellow. The solution was stirred for a further ten minutes, then filtered through celite to remove reaction salts. The yellow filtrate is concentrated to *ca.* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a yellow solid. The solid is collected by filtration, washed with hexanes (3 × 20 ml) and dried in air (0.047 g, 90 %). Crystals suitable for single crystal X-ray diffraction were grown from CH_2Cl_2 / hexanes layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 2081 ν(C≡C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ / ppm: 4.89 – 4.93 (m, 4H, CH_2, dppm), 6.11 (d, J_{HH} = 7 Hz, 2H, H^4), 6.83 (t, J_{HH} = 7 Hz, 1H, H^6), 6.89 (t, J_{HH} = 7 Hz, 2H, H^5), 7.07 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.17 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.23 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.28 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.43 – 7.54 (m, 16H, H$_o$, dppm). ^{31}P{^{1}H} NMR ($CDCl_3$, 300 MHz) δ / ppm: – 5.2 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz) δ / ppm: 50.4 (t, J_{CP} = 10 Hz, CH_2, dppm), 112.5 (s, C^2), 122.4 (s, C^6), 123.0 (quin., J_{CP} = 15 Hz, C^1), 126.9 (s, C^5), 127.6 – 127.7 (m, C$_m$, dppm), 129.2 (s, C$_p$, dppm), 129.4 (s, C$_p$, dppm), 130.3 (s, C^4), 130.8 (s, C^3), 133.6 (t, J_{CP} = 3 Hz, C$_o$, dppm), 133.9 (t, J_{CP} = 3 Hz, C$_o$, dppm), 134.5 (quin., J_{CP} = 11 Hz, C$_i$, dppm), 135.3 (quin., J_{CP} = 11 Hz, C$_i$, dppm). ESI (+)-MS (*m/z*): 1032 [RuCl(C≡CC$_6$H$_5$)(dppm)$_2$ + MeOH]$^+$, 1007 [RuCl(C≡CC$_6$H$_5$)(dppm)$_2$ + H]$^+$, 933 [RuCl(dppm)$_2$ + C_2H_4]$^+$. A satisfactory elemental analysis was not obtained.

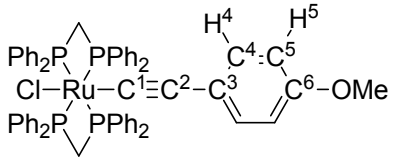
S2.5 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_4$-4-Me)(dppm)$_2$] [2e]



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.016 g, 0.05 mmol) and HC≡CC$_6$H$_4$-4-Me (7.5 μL, 0.06 mmol) in CH_2Cl_2 (7 ml) was stirred under N_2 for one hour. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The solution was then transferred, via cannula filtration (– TlCl), into a separate dry degassed flask containing 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.045 g, 0.21 mmol) in CH_2Cl_2 (2 ml), where solution colour immediately changed from orange to yellow. The solution was stirred for a further ten minutes, then filtered through celite to remove reaction salts. The yellow filtrate is concentrated to *ca.* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a bright yellow solid. The solid is collected by filtration, washed with hexanes (3 × 20 ml) and dried in air (0.050 g, 92 %). Crystals suitable for single crystal X-ray diffraction were grown from CH_2Cl_2 / pentane layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 2082 ν(C≡C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ / ppm: 2.20 (s, 3H, CH_3), 4.86 – 4.93 (m, 4H, CH_2, dppm), 6.03 (d, J_{HH} = 8 Hz, 2H, H^4), 6.71 (d, J_{HH} = 8 Hz, 2H, H^5), 7.07 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.17 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.23 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.27 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.42 – 7.54 (m, 16H, H$_o$, dppm). ^{31}P{^{1}H} NMR ($CDCl_3$, 400 MHz) δ / ppm: – 6.6 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 500 MHz) δ / ppm: 21.1 (s, CH_3), 50.2 (t, J_{CP} = 10 Hz, CH_2, dppm), 111.9 (s, C^2), 120.4 (quin., J_{CP} = 15 Hz, C^1), 127.2 – 127.7 (m, C$_m$, dppm), 127.6 (s, C^5), 128.8 (s, C^3), 129.1 (s, C$_p$, dppm), 129.3 (s, C$_p$, dppm), 130.0 (s, C^4), 131.5 (s, C^6), 133.6 (s, C$_o$, dppm), 133.9 (s, C$_o$, dppm), 134.6 (quin., J_{CP} = 10 Hz, C$_i$, dppm), 135.4 (quin., J_{CP} = 10 Hz, C$_i$, dppm). MALDI (+)-MS (*m/z*): 1020 [RuCl(C≡CC$_6$H$_4$-4-Me)(dppm)$_2$]$^+$, 933 [RuCl(dppm)$_2$ + C_2H_4]$^+$, 905 [RuCl(dppm)$_2$]$^+$, 870 [Ru(dppm)$_2$]$^+$. Anal. Found: C, 67.87; H, 4.78. Calc. for $C_{59}H_{51}ClP_4Ru$ × 0.5 CH_2Cl_2: C, 67.22; H, 4.93.

S2.6 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_4$-4-OMe)(dppm)$_2$] [2f]

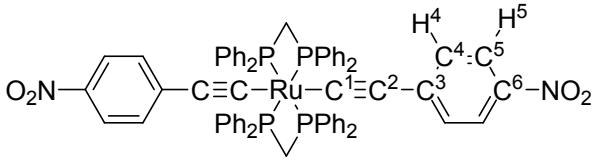


A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.050 g, 0.05 mmol), TlBF$_4$ (0.017 g, 0.06 mmol) and HC≡CC$_6$H$_4$-4-OMe (7 μL, 0.05 mmol) in CH_2Cl_2 (5 ml) was stirred under N_2 for one hour. The solution colour changed from yellow to orange and a white solid (TlCl) precipitated. The solution was then transferred, via cannula filtration (– TlCl), into a separate dry degassed flask containing 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.045 g, 0.21 mmol) in CH_2Cl_2 (2 ml), where solution colour immediately changed from orange to yellow. The solution was stirred for a further ten minutes, then filtered through celite to remove reaction salts. The yellow filtrate is concentrated to *ca.* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a yellow solid. The solid is collected by filtration, washed with hexanes (3 × 20 ml) and dried in air (0.041 g, 74 %). Crystals suitable for single crystal X-ray diffraction were grown from CH_2Cl_2 / diisopropylether layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 2083 ν(C≡C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ / ppm: 3.72 (s, 3H, CH_3), 4.85 – 4.96 (m, 4H, CH_2, dppm), 6.04 (d, J_{HH} = 8 Hz, 2H, H^4), 6.40 (d, J_{HH} = 8 Hz, 2H, H^5), 7.06 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.16 (t, J_{HH} = 8 Hz, 8H, H$_m$, dppm), 7.23 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.27 (t, J_{HH} = 8 Hz, 4H, H$_p$, dppm), 7.42 – 7.52 (m, 16H, H$_o$, dppm). ^{31}P{^{1}H} NMR ($CDCl_3$, 400 MHz) δ / ppm: – 6.6 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz) δ / ppm: 55.3 (s, CH_3), 50.5 (t, J_{CP} = 11 Hz, CH_2, dppm), 111.4 (s, C^2), 112.6 (s, C^5), 118.2 (quin., J = 15 Hz, C^1), 123.8 (s, C^3), 127.6 (s, C$_m$, dppm), 127.8 (s, C$_m$, dppm), 129.1 (s, C$_p$, dppm), 129.4 (s, C$_p$, dppm), 131.1 (s, C^4), 133.6 – 133.7 (m, C$_o$, dppm), 133.8 – 133.9 (m, C$_o$, dppm), 134.6 (quin., J_{CP} = 10 Hz, C$_i$, dppm), 135.4 (quin., J_{CP} = 10 Hz, C$_i$, dppm), 155.5 (s, C^6). MALDI (+)-MS *(m/z)*: 1036 [RuCl(C≡CC$_6$H$_4$-4-OMe)(dppm)$_2$]$^+$, 933 [RuCl(dppm)$_2$ + C_2H_4]$^+$, 905 [RuCl(dppm)$_2$]$^+$, 870 [Ru(dppm)$_2$]$^+$. Anal. Found: C, 64.53; H, 4.22. Calc. for $C_{59}H_{51}ClOP_4Ru \times CH_2Cl_2$: C, 64.28; H, 4.77.

S3. Synthesis of Ruthenium *bis*-Alkynyl Complexes

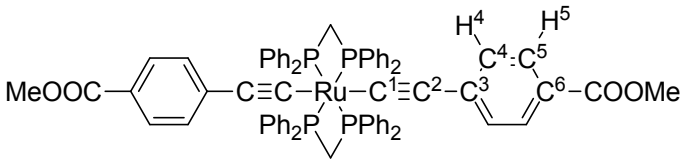
S3.1 Synthesis of *trans*-[Ru(C≡CC$_6$H$_4$NO$_2$)$_2$(dppm)$_2$] [3a]



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.049 g, 0.05 mmol), TlBF$_4$ (0.032 g, 0.10 mmol), HC≡CC$_6$H$_4$-4-NO$_2$ (0.016 g, 0.11 mmol) and 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.068 g, 0.32 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for 3.5 days. The red solution colour darkened over the reaction period and a white solid (TlCl) precipitated. The solution is then carefully concentrated to *ca.* 3 ml under high vacuum and then filtered through celite to remove TlCl and reaction salts. The red filtrate is then concentrated to dryness by rotary evaporation and purified by column chromatography on alumina (basic, oven-dried; 30 : 70 40 – 60 petroleum ether : CH$_2$Cl$_2$). The first red band was collected, concentrated to *ca.* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a dark red solid. The solid is collected by filtration, washed with hexanes (3 × 10 ml) then dried in air (0.048 g, 80 %).

IR (CH$_2$Cl$_2$, cm^{-1}): 2053 ν(C≡C), 1581 ν(N=O), 1322 ν(N-O). ^{1}H NMR (CDCl$_3$, 400 MHz) δ / ppm: 4.83 – 4.90 (m, 4H, CH$_2$, dppm), 6.16 (d, J_{HH} = 8 Hz, 4H, H^4), 7.12 (t, J_{HH} = 8 Hz, 16H H$_m$, dppm), 7.30 (t, J_{HH} = 8 Hz, 8H, H$_p$, dppm), 7.35 – 7.45 (m, 16H, H$_o$, dppm), 7.83 (d, J_{HH} = 8 Hz, 4H, H^5). ^{31}P{^{1}H} NMR (CDCl$_3$, 400 MHz) δ / ppm: – 4.1 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ / ppm: 52.3 (t, J_{CP} = 11 Hz, CH$_2$, dppm), 119.0 (s, C^2), 123.2 (s, C^5), 127.8 (s, C$_m$, dppm), 129.6 (s, C$_p$, dppm), 130.0 (s, C^4), 133.4 (s, C$_o$, dppm), 135.2 (quin., J_{CP} = 11 Hz, C$_i$, dppm), 137.7 (s, C^6), 142.7 (s, C^3), 150.1 (quin., J_{CP} = 15 Hz, C^1). MALDI (+)-MS (*m/z*): 1162 [Ru(C≡CC$_6$H$_4$NO$_2$)$_2$(dppm)$_2$]$^+$, 870 [Ru(dppm)$_2$]$^+$. Anal. Found: C, 68.27; H, 4.50; N, 2.37. Calc. for C$_{66}$H$_{52}$N$_2$O$_4$P$_4$Ru: C, 68.15; H, 4.51; N, 2.41.

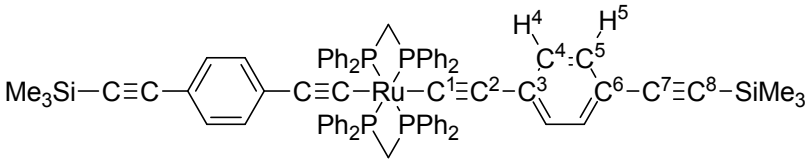
S3.2 Synthesis of *trans*-[Ru(C≡CC$_6$H$_4$-4-COOMe)$_2$(dppm)$_2$] [3b]



A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.051 g, 0.05 mmol), TlBF$_4$ (0.032 g, 0.10 mmol), HC≡CC$_6$H$_4$-4-COOMe (0.019 g, 0.12 mmol) and 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.069 g, 0.32 mmol) in CH_2Cl_2 (5 ml) was stirred under N_2 for 36 hours. The yellow solution colour darkened over the reaction period and a white solid (TlCl) precipitated. The solution is then carefully concentrated to *ca.* 1 ml under high vacuum and then filtered through a short pad of alumina (basic, oven-dried) to remove TlCl and reaction salts. The first yellow fraction is collected, concentrated to *ca* 0.5 ml by rotary evaporation then excess hexanes added; resulting in the instantaneous precipitation of a bright yellow solid. The solid is collected by filtration, washed with hexanes (3 × 10 ml) and diethyl ether (3 × 5 ml) then dried in air (0.038 g, 60 %). Crystals suitable for single crystal X-ray diffraction were grown from $CDCl_3$ / 40 – 60 petroleum ether layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 2062 ν(C≡C), 1705 ν(C=O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ / ppm: 3.79 (s, 6H, CH_3), 4.74 – 4.80 (m, 4H, CH_2, dppm), 6.15 (d, J_{HH} = 8 Hz, 4H, H^4), 7.02 (t, J_{HH} = 8 Hz, 16H H$_m$, dppm), 7.18 (t, J_{HH} = 8 Hz, 8H, H$_p$, dppm), 7.34 – 7.48 (m, 16H, H$_o$, dppm), 7.55 (d, J_{HH} = 8 Hz, 4H, H^5). ^{31}P{^{1}H} NMR ($CDCl_3$, 400 MHz) δ / ppm: – 4.0 (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ / ppm: 51.8 (s, CH_3), 52.4 (t, J_{CP} = 10 Hz, CH_2, dppm), 117.3 (s, C^2), 123.5 (s, C^3), 127.7 (s, C$_m$, dppm), 128.7 (s, C^5), 129.3 (s, C$_p$, dppm), 129.8 (s, C^4), 133.5 (s, C$_o$, dppm), 135.6 (quin., J_{CP} = 11 Hz, C$_i$, dppm), 135.8 (s, C^6), 141.1 (quin., J_{CP} = 15 Hz, C^1), 167.8 (s, C=O). MALDI (+)-MS (*m/z*): 1189 [Ru(C≡CC$_6$H$_4$-4-COOMe)$_2$(dppm)$_2$ + H]$^+$, 870 [Ru(dppm)$_2$]$^+$. Anal. Found: C, 70.62; H, 5.05. Calc. for C$_{70}$H$_{58}$O$_4$P$_4$Ru: C, 70.69; H, 4.92.

S3.3 Synthesis of *trans*-[Ru(C≡CC$_6$H$_4$C≡CSiMe$_3$)$_2$(dppm)$_2$] [3c]

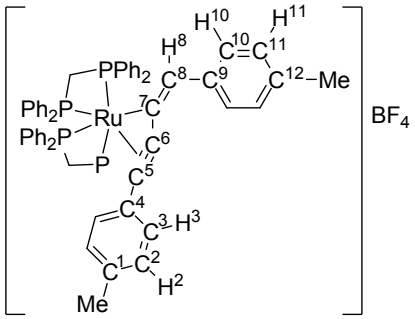


A mixture of *cis*-[RuCl$_2$(dppm)$_2$] (0.051 g, 0.05 mmol), TlBF$_4$ (0.032 g, 0.10 mmol), HC≡CC$_6$H$_4$-4-C≡CSiMe$_3$ (0.022 g, 0.11 mmol) and 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.073 g, 0.34 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred under N$_2$ for 16 hours. The yellow solution colour darkened over the reaction period and a white solid (TlCl) precipitated. The solution is then carefully concentrated to *ca.* 3 ml under high vacuum and then filtered through celite to remove TlCl and reaction salts. The yellow filtrate is concentrated again to *ca.* 1 ml by rotary evaporation then excess diethyl ether added (*ca.* 10 ml); resulting in the instantaneous precipitation of a yellow solid. The mixture is left in the fridge to aid precipitation for several hours before filtering. The collected yellow solid is washed with cold diethyl ether (1 × 5 ml) and hexanes (3 × 15 ml) then dried in air (0.033 g, 48 %).

IR (CH$_2$Cl$_2$, cm^{-1}): 2149 ν(C≡CSiMe$_3$), 2058 ν(C≡C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ / ppm: 0.26 (s, 18H, SiMe$_3$), 4.80 – 4.89 (m, 4H, CH$_2$, dppm), 6.15 (d, J_{HH} = 8 Hz, 4H, H^4), 7.07 (d, J_{HH} = 8 Hz, 4H, H^5), 7.09 (t, J_{HH} = 8 Hz, 16H, H$_m$, dppm), 7.25 (t, J_{HH} = 8 Hz, 8H, H$_p$, dppm) 7.41 – 7.55 (m, 16H, H$_o$, dppm). ^{31}P{^{1}H} NMR (CDCl$_3$, 400 MHz) δ / ppm: – 3.8 ppm (s, Ru(dppm)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 600 MHz) δ / ppm: 0.3 (s, SiMe$_3$), 52.4 (t, J_{CP} = 11 Hz, CH$_2$, dppm), 93.3 (s, C^8), 106.9 (s, C^7), 116.2 (s, C^2), 129.4 (s, C^3), 127.6 (s, C$_m$, dppm), 129.2 (s, C$_p$, dppm), 129.9 (s, C^4), 131.0 (s, C^5), 131.5 (s, C^6), 133.4 – 133.6 (m, C$_o$, dppm), 135.8 (quin., J_{CP} = 10 Hz, C$_i$, dppm), 136.7 – 137.0 (m, C^1). ASAP (+)-MS (*m*/*z*): 1265 [Ru(C≡CC$_6$H$_4$C≡CSiMe$_3$)$_2$(dppm)$_2$ + H]$^+$, 1264 [Ru(C≡CC$_6$H$_4$C≡CSiMe$_3$)$_2$(dppm)$_2$]$^+$, 1067 [Ru(C≡CC$_6$H$_4$C≡CSiMe$_3$)(dppm)$_2$]$^+$, 870 [Ru(dppm)$_2$]$^+$. A satisfactory elemental analysis was not obtained.

S4. Synthesis of Ruthenium η^3-Butenynyl Complexes

S4.1 Synthesis of *trans*-[RuCl(η^3-{HC(C_6H_4-4-Me)=CC≡CC_6H_4-4-Me})$(dppm)_2$]BF_4 [4e]BF_4

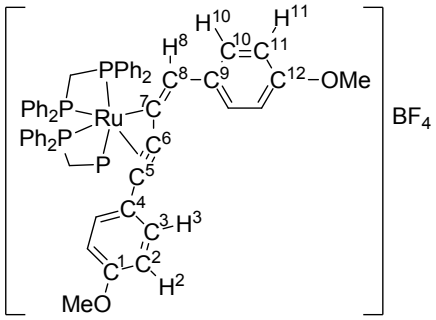


A mixture of *cis*-[$RuCl_2(dppm)_2$] (0.049 g, 0.05 mmol), $TlBF_4$ (0.032 g, 0.11 mmol), HC≡CC_6H_4-4-Me (14.5 µL, 0.11 mmol) and 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.066 g, 0.31 mmol) in CH_2Cl_2 (8 ml) was stirred under N_2 for 40 hours. A white solid (TlCl) precipitated from the yellow solution over the reaction period. The yellow solution is concentrated carefully to half volume under high vacuum then filtered through a HPLC Teflon filter (20 µm pores) to remove TlCl and reaction salts. To the yellow filtrate, CH_2Cl_2 (*ca.* 5 ml) and diethyl ether (*ca.* 30 ml) are then added and left to crystallise overnight, where large yellow crystals formed round the flask. The solvent is decanted, crystals washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml) then dried in air before collection (0.042 g, 56 %). Crystals suitable for single crystal X-ray diffraction were grown from acetone / pentane layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 1967 ν(C≡C), 1606 ν(C=C). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ / ppm: 2.34 (s, 6H, CH_3), 4.20 (dt, J_{HP} = 15 Hz, J_{HH} 11 Hz, 1H, CH_2, dppm), 4.50 (dt, J_{HP} = 15, J_{HH} = 11 Hz, 1H, CH_2, dppm), 4.93 – 5.07 (m, 2H, CH_2, dppm), 5.55 (d, J_{HP} = 5 Hz, 1H, H^8), 6.18 (d_{HH}, J = 8 Hz, 2H, H^3), 6.36 – 7.76 (m, 40H, Ph, dppm), 6.85 (d, J_{HH} = 8 Hz, 2H, H^2), 7.14 (d, J_{HH} = 8 Hz, 2H, H^{11}), 7.29 (d, J_{HH} = 8 Hz, 2H, H^{10}). ^{11}B NMR (CD_2Cl_2, 400 MHz) δ / ppm: – 2.1 (s, BF_4). ^{19}F NMR (CD_2Cl_2, 400 MHz) δ / ppm: – 149.9 (s, BF_4). ^{31}P{^{1}H} NMR ($CDCl_3$, 400 MHz) δ / ppm: – 27.2 (ddd, J_{PP} = 318, 49, 27 Hz, dppm), – 16.9 (ddd, J_{PP} = 321, 42, 26 Hz, dppm), – 14.0 (ddd, J_{PP} = 36, 27, 10 Hz, dppm), – 0.2 (ddd, J_{PP} = 46, 26, 9 Hz, dppm). ^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz) δ / ppm: 21.7 (s, CH_3), 22.0 (s, CH_3), 42.0 (t, J_{CP} = 24 Hz, CH_2, dppm), 45.2 (t, J_{CP} = 24 Hz, CH_2, dppm), 108.7 (d, J_{CP} = 22 Hz, C^5), 126.7 (s, C^9), 128.9 – 139.9 (m, Ph, dppm), 129.7 (s, C^2), 130.2 (s, C^1 or C^{12}), 130.4 (s, C^8),

131.0 (s, C^3), 138.9 (s, C^1 or C^{12}), 139.8 (s, C^4). The resonances from quaternary C^6 and C^7 atoms were not unambiguously resolved. ESI (+)-MS (*m/z*): 1101 [RuCl(η^3-{HC(C_6H_4-4-Me)=CC≡CC_6H_4-4-Me})$(dppm)_2]^+$. Anal. Found: C, 68.59; H, 4.68. Calc. for $C_{68}H_{59}BF_4P_4Ru$: C, 68.67; H, 5.00.

S4.2 Synthesis of *trans*-[RuCl(η³-{HC(C_6H_4-4-OMe)=CC≡CC_6H_4-4-OMe})(dppm)$_2$]BF_4 [4f]BF_4



A mixture of *cis*-[$RuCl_2$(dppm)$_2$] (0.10 g, 0.11 mmol), $TlBF_4$ (0.065 g, 0.22 mmol), HC≡CC_6H_4-4-OMe (30 μL, 0.23 mmol) and 1,8-*bis*-dimethylaminonapthalene (Proton Sponge) (0.078 g, 0.43 mmol) in CH_2Cl_2 (20 ml) was stirred under N_2 overnight. A white solid (TlCl) precipitated from the yellow solution over the reaction period. The solution was then filtered through celite to remove TlCl and reaction salts and the yellow filtrate concentrated to half volume. To the yellow solution, diethyl ether (*ca.* 30 ml) is then added and left to crystallise for several days, where large yellow crystals formed round the flask. The solvent is then decanted, crystals collected by filtration and washed with diethyl ether (3 × 10 ml) and hexanes (3 × 10 ml) then dried in air (0.066 g, 50 %).

IR (CH_2Cl_2, cm^{-1}): 1870 ν(C≡C), 1602 ν(C=C). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ / ppm: 3.81 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 4.21 (dt, J_{HP} = 15 Hz, J_{HH} = 11 Hz, 1H, CH_2, dppm), 4.49 (dt, J_{HP} = 15 Hz, J_{HH} = 11 Hz, 1H, CH_2, dppm), 4.93 – 5.03 (m, 2H, CH_2, dppm), 5.53 (d, J_{HP} = 5 Hz, 1H, H^8), 6.23 (d, J_{HH} = 8 Hz, 2H, H^3), 6.36 – 7.74 (m, 40H, Ph, dppm), 6.56 (d, J_{HH} = 8 Hz, 2H, H^2), 6.87 (d, J_{HH} = 8 Hz, 2H, H^{11}), 7.29 (d, J_{HH} = 8 Hz, 2H, H^{10}). ^{11}B NMR (CD_2Cl_2, 400 MHz) δ / ppm: – 2.1 (s, BF_4). ^{19}F NMR (CD_2Cl_2, 400 MHz) δ / ppm: – 153.1 (s, BF_4). ^{31}P{^{1}H} NMR (CD_2Cl_2, 400 MHz) δ / ppm: – 25.4 (ddd, J_{PP} = 322, 48, 28 Hz, dppm), – 16.4 (ddd, J_{PP} = 323, 32, 26 Hz, dppm), – 13.2 (ddd, J_{PP} = 37, 23, 9 Hz, dppm), 0.69 (ddd, J_{PP} = 48, 27, 9 Hz, dppm). ^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz) δ / ppm: 42.2 (t, J_{CP} = 26 Hz, CH_2, dppm), 45.4 (t, J_{CP} = 26 Hz, CH_2, dppm), 56.1 (s, CH_3), 56.3 (s, CH_3), 108.5 (d, J_{CP} = 22 Hz, C^5), 114.8 (s, C^2 or C^{11}), 114.9 (s, C^2 or C^{11}), 127.7 – 133.2 (m, Ph), 130.3 (s, C^8), 132.8 (s, C^3), 159.8 (s, C^{12}), 160.8 (s, C^1). The resonances from quaternary C^6 and C^7 atoms were not unambiguously resolved. ESI (+)-MS (*m/z*): 1133 [RuCl(η³-{HC(C_6H_4-4-OMe)=CC≡CC_6H_4-4-OMe})(dppm)$_2$]$^+$.

S5. Crystal Structure Analysis

The X-ray single crystal data have been collected using on a Bruker SMART CCD 6000 (fine-focused sealed tube, graphite monochromated λMoKα radiation, λ =0.71073Å) and Oxford Diffraction Gemini -Ultra (compounds **2c** and **2d**: fine-focus sealed tube and Enchance MoX-ray source, λMoKα- and λCuKα-radiations, graphite monochromator and focusing mirrors, λ = 0.71073 and 1.54178Å respectively) diffractometers. The data were collected at the temperatures 100K (**2c** and **2d**), 150K (**2e**) and 120K for the rest of the samples. The temperature was maintained by the Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats. All structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using Olex2[8] and SHELXTL[7] software. All non-disordered non-hydrogen atoms were refined anisotropically, the hydrogen atoms were placed in the calculated positions and refined in riding mode. Disordered atoms in structures **2b**, **2e** and **2f** were refined isotropically with fixed SOF= 0.5, 0.9:0.1 and 0.75:0.25 respectively. The structures **2b** and **2e** contain severely disordered solvent molecules which could not be modeled properly and were taken into account by MASK procedure of Olex2 program package. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1426045-1426051.

S5.1 Structure of [2b]

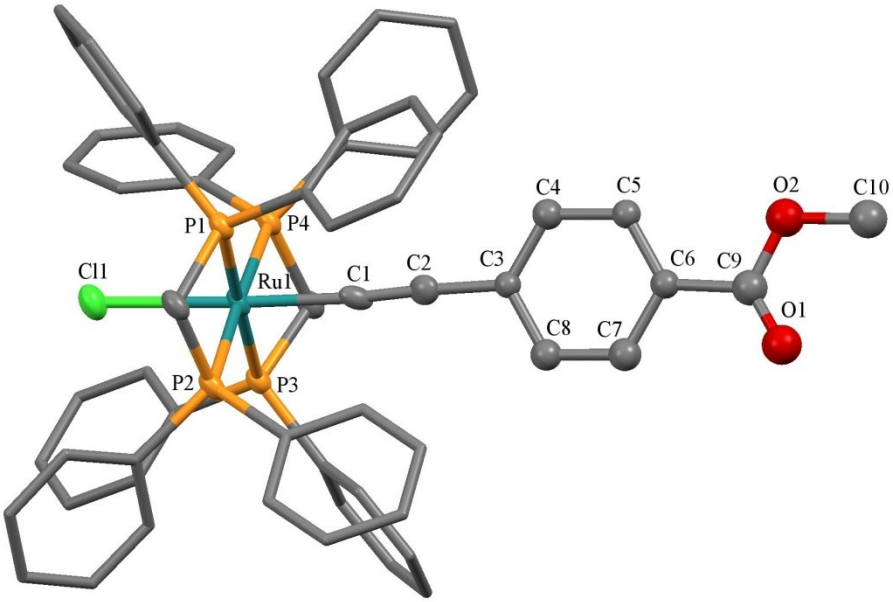


Figure S1: A plot of a molecule of [**2b**]. One set of the disordered atoms, the solvent of crystallisation and hydrogen atoms have been removed for clarity.

Table S1: Crystal data and structure refinement for [**2b]**

Empirical formula	$C_{60}H_{51}ClO_2P_4Ru.CH_2Cl_2$
Formula weight	1149.33
Temperature/K	120
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.8804(4)
b/Å	11.4875(4)
c/Å	24.2218(9)
α/°	103.3270(10)
β/°	91.8920(10)
γ/°	104.7960(10)
Volume/Å^3	2834.62(18)
Z	2
ρ_{calc} mg/mm^3	1.347
μ/mm^{-1}	0.572
Crystal size/mm^3	0.31 × 0.3 × 0.24
2θ range for data collection	3.48 to 62.04°
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-35 \leq l \leq 35$
Reflections collected	53960
Independent reflections	15073[*R*(int) = 0.0345]
Data/restraints/parameters	15073/0/608
Goodness-of-fit on F^2	1.093
Final *R* indexes [$I>=2\sigma(I)$]	$R_1 = 0.0490$, $wR_2 = 0.1298$
Final *R* indexes [all data]	$R_1 = 0.0609$, $wR_2 = 0.1379$
Largest diff. peak and hole	2.062 and -0.819 e.Å^{-3}

S5.2 Structure of [2c]

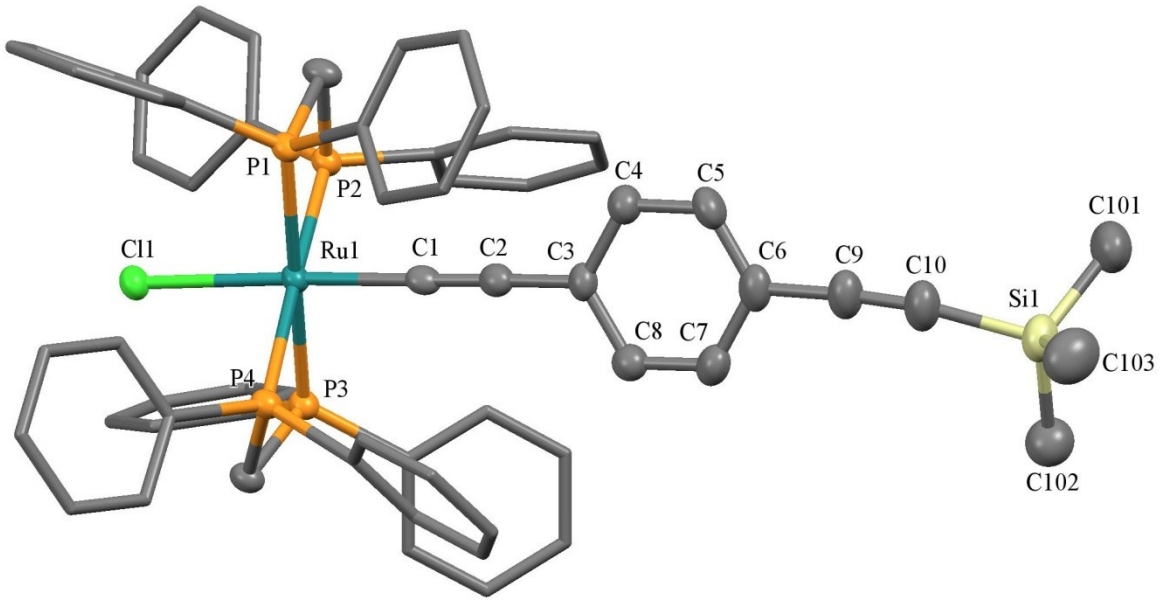


Figure S2: A plot of a molecule of [**2c**]. Solvent of crystallisation and hydrogen atoms have been removed for clarity.

Table S2: Crystal data and structure refinement for [**2c]**

Empirical formula	$C_{63}H_{57}ClP_4RuSi.CH_2Cl_2$
Formula weight	1187.50
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.24630(10)
b/Å	31.3382(3)
c/Å	18.1430(2)
β/°	94.3440(10)
Volume/Å^3	5808.99(10)
Z	4
ρ_{calc} mg/mm^3	1.358
μ/mm^{-1}	4.992
Crystal size/mm^3	0.39 x 0.070 x 0.035
2θ range for data collection	5.64 to 134.616°.
Index ranges	-12≤h≤7, -37≤k≤35, -20≤l≤21
Reflections collected	33175
Independent reflections	10331 [*R*(int) = 0.0410]
Data / restraints / parameters	10331 / 0 / 661
Goodness-of-fit on F^2	1.044
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0399, wR_2 = 0.0986
R indices (all data)	R_1 = 0.0503, wR_2 = 0.1059
Largest diff. peak and hole	0.815 and -0.783 e.Å^{-3}

S5.3 Structure of [2d]

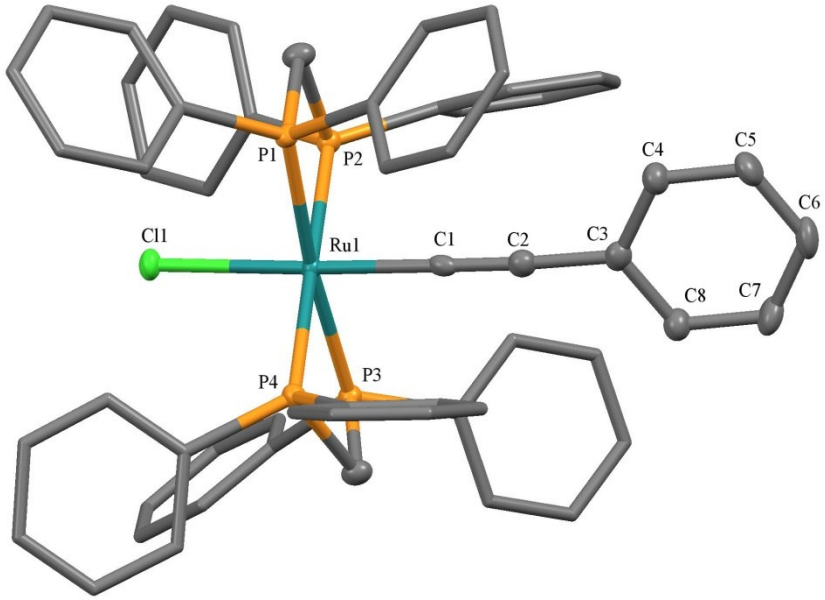


Figure S3: A plot of a molecule of [**2d**] with hydrogen atoms removed for clarity.

Table S3: Crystal data and structure refinement for [**2d**]

Empirical formula	$C_{58}H_{49}ClP_4Ru$
Formula weight	1006.37
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P***Error!**
a/Å	13.5448(4)
b/Å	13.5845(4)
c/Å	13.8574(3)
α/°	93.781(2)
β/°	109.044(2)
γ/°	94.896(2)
Volume/Å^3	2389.47(12)
Z	2
ρ_{calc} mg/mm^3	1.399
μ/mm^{-1}	0.557
Crystal size/mm^3	0.45 x 0.27 x 0.17
2θ range for data collection	4.126 to 65.242°.
Index ranges	-20≤h≤19, -19≤k≤20, -20≤l≤21
Reflections collected	35385
Independent reflections	15874 [*R*(int) = 0.0359]
Data / restraints / parameters	15874 / 0 / 577
Goodness-of-fit on F^2	1.049
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0400, wR_2 = 0.0912
R indices (all data)	R_1 = 0.0551, wR_2 = 0.101
Largest diff. peak and hole	1.385 and -0.902 e.Å^{-3}

S5.4 Structure of [2e]

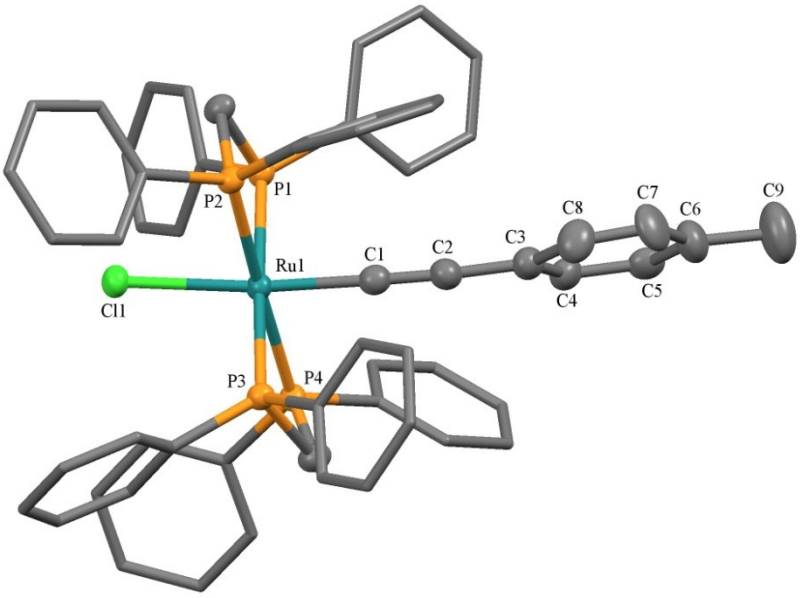


Figure S4: A plot of a molecule of [**2e**]. The solvent of crystallisation and hydrogen atoms have been removed for clarity.

Table S4: Crystal data and structure refinement for [**2e]**

Empirical formula	$C_{59}H_{51}ClP_4Ru.CH_2Cl_2$
Formula weight	1105.32
Temperature/K	150
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.9313(5)
b/Å	11.6259(6)
c/Å	21.9491(10)
α/°	78.5220(10)
β/°	88.2700(10)
γ/°	75.2510(10)
Volume/Å^3	2643.0(2)
Z	2
ρ_{calc} mg/mm^3	1.389
μ/mm^{-1}	0.608
Crystal size/mm^3	0.18 × 0.1 × 0.09
2θ range for data collection	3.7 to 62°
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-31 \leq l \leq 31$
Reflections collected	37618
Independent reflections	13993[*R*(int) = 0.0457]
Data/restraints/parameters	13993/12/618
Goodness-of-fit on F^2	1.086
Final *R* indexes [$I>=2\sigma(I)$]	$R_1 = 0.0528$, $wR_2 = 0.1413$
Final *R* indexes [all data]	$R_1 = 0.0803$, $wR_2 = 0.1564$
Largest diff. peak/hole / e Å^{-3}	1.49/-1.11

S5.5 Structure of [2f]

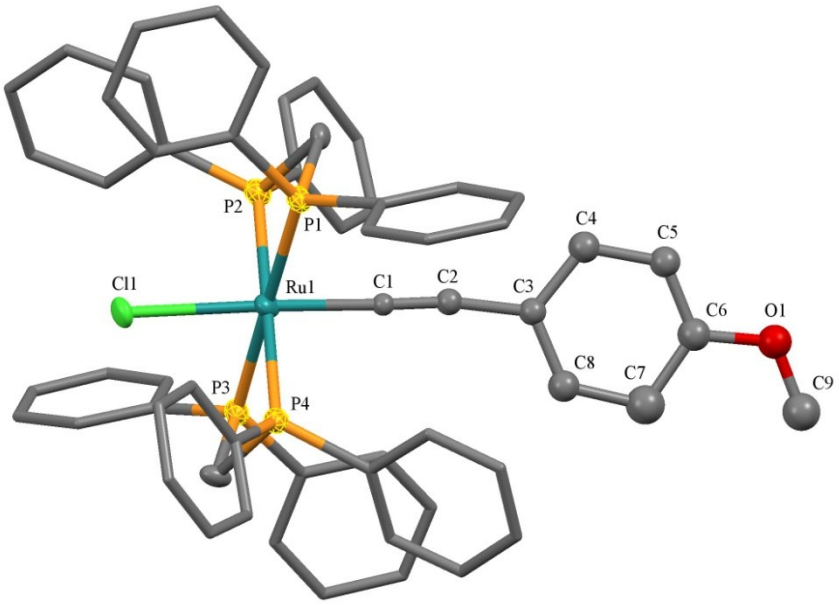


Figure S5: A plot of a molecule of [**2f**]. The solvent of crystallisation and hydrogen atoms have been removed for clarity.

Table S5: Crystal data and structure refinement for [**2f**]

Empirical formula	$C_{59}H_{52}ClOP_4Ru.CH_2Cl_2$
Formula weight	1122.33
Temperature/K	120
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	9.5876(3)
b/Å	22.2227(7)
c/Å	12.7177(4)
α/°	90.00
β/°	107.6030(10)
γ/°	90.00
Volume/Å^3	2582.78(14)
Z	2
ρ_{calc} mg/mm^3	1.443
μ/mm^{-1}	0.625
Crystal size/mm^3	0.33 × 0.18 × 0.08
2θ range for data collection	3.36 to 58°
Index ranges	$-12 \leq h \leq 13$, $-30 \leq k \leq 30$, $-17 \leq l \leq 17$
Reflections collected	31889
Independent reflections	13673[*R*(int) = 0.0400]
Data/restraints/parameters	13673/3/623
Goodness-of-fit on F^2	1.171
Final *R* indexes [$I>=2\sigma(I)$]	$R_1 = 0.0735$, $wR_2 = 0.1574$
Final *R* indexes [all data]	$R_1 = 0.0848$, $wR_2 = 0.1626$
Largest diff. peak/hole / e Å^{-3}	1.82/-1.97

S5.6 Structure of [3b]

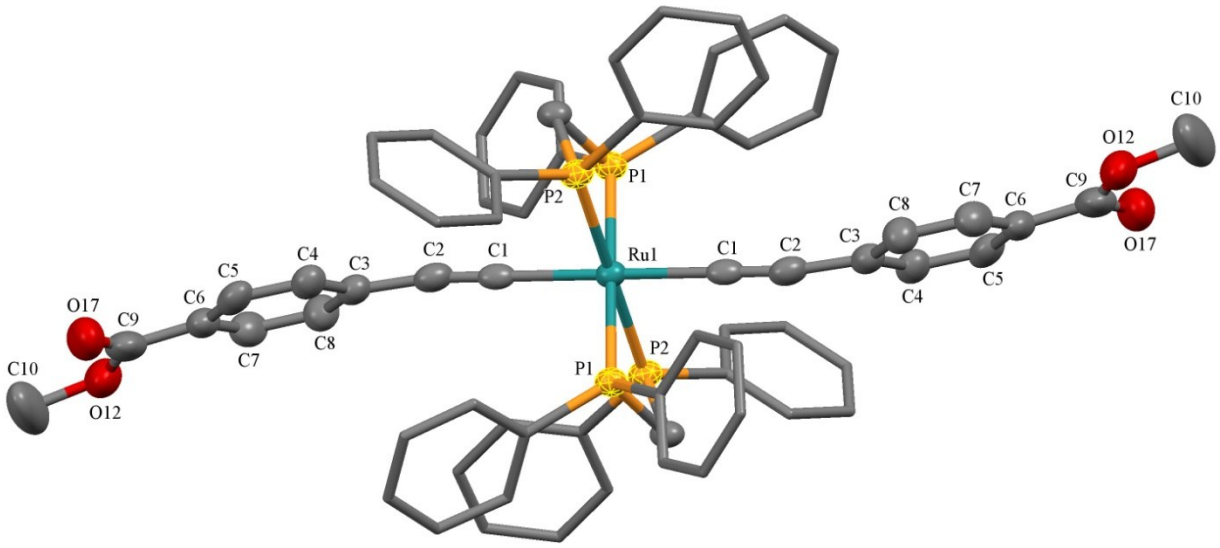


Figure S6: A plot of a molecule of [**3b**]. The solvent of crystallisation and hydrogen atoms have been removed for clarity.

Table S6: Crystal data and structure refinement for [**3b**]

Empirical formula	$C_{70}H_{58}O_4P_4Ru.CHCl_3$
Formula weight	1307.48
Temperature/K	120
Crystal system	Monoclinic
Space group	*C*2/c
a/Å	17.7726(15)
b/Å	13.9939(12)
c/Å	25.218(2)
α/°	90.00
β/°	104.388(3)
γ/°	90.00
Volume/Å^3	6075.1(9)
Z	4
ρ_{calc} mg/mm^3	1.430
μ/mm^{-1}	0.546
Crystal size/mm^3	0.16 × 0.15 × 0.08
2θ range for data collection	3.34 to 56°
Index ranges	$-23 \leq h \leq 23$, $-18 \leq k \leq 18$, $-33 \leq l \leq 33$
Reflections collected	34789
Independent reflections	7324[*R*(int) = 0.2025]
Data/restraints/parameters	7324/10/383
Goodness-of-fit on F^2	0.914
Final *R* indexes [$I>=2\sigma(I)$]	$R_1 = 0.0680$, $wR_2 = 0.1614$
Final *R* indexes [all data]	$R_1 = 0.1402$, $wR_2 = 0.1935$
Largest diff. peak/hole / e Å^{-3}	0.97/-1.04

S5.7 Structure of $[4e]^+$

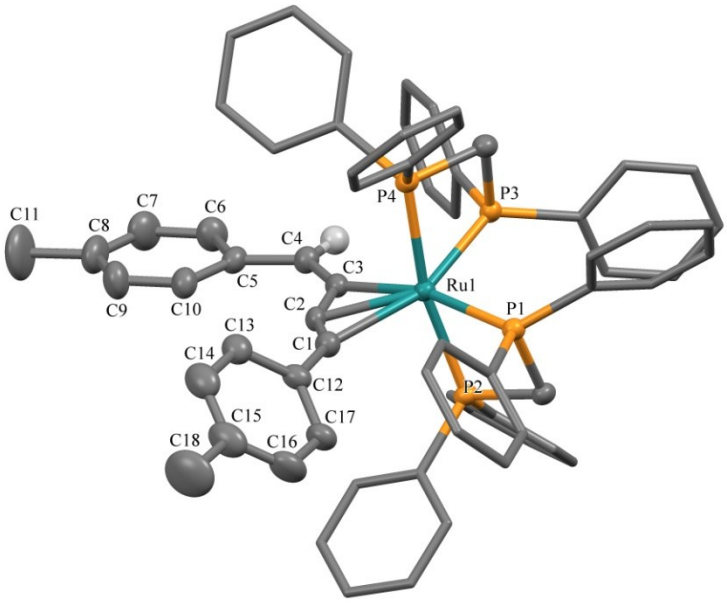


Figure S7: A plot of the cation [**4e**]$^+$. The counter anions, solvent of crystallisation and selected hydrogen atoms have been removed for clarity.

Table S7: Crystal data and structure refinement for [**4e**]

Empirical formula	$C_{68}H_{59}P_4Ru.BF_4.0.5C_3H_6O$
Formula weight	1216.95
Temperature/K	120
Crystal system	Orthorhombic
Space group	$Pca2_1$
a/Å	13.5079(7)
b/Å	22.8614(11)
c/Å	20.0977(10)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	6206.4(5)
Z	4
ρ_{calc} mg/mm^3	1.302
μ/mm^{-1}	0.409
Crystal size/mm^3	0.28 × 0.24 × 0.04
2θ range for data collection	3.56 to 59°
Index ranges	$-18 \leq h \leq 18$, $-31 \leq k \leq 31$, $-27 \leq l \leq 27$
Reflections collected	77460
Independent reflections	17276[*R*(int) = 0.0633]
Data/restraints/parameters	17276/1/723
Goodness-of-fit on F^2	1.046
Final *R* indexes [$I>=2\sigma(I)$]	$R_1 = 0.0443$, $wR_2 = 0.1098$
Final *R* indexes [all data]	$R_1 = 0.0705$, $wR_2 = 0.1271$
Largest diff. peak/hole / e Å^{-3}	0.99/-0.55
Flack parameter	-0.04(2)

S6. Electrochemistry

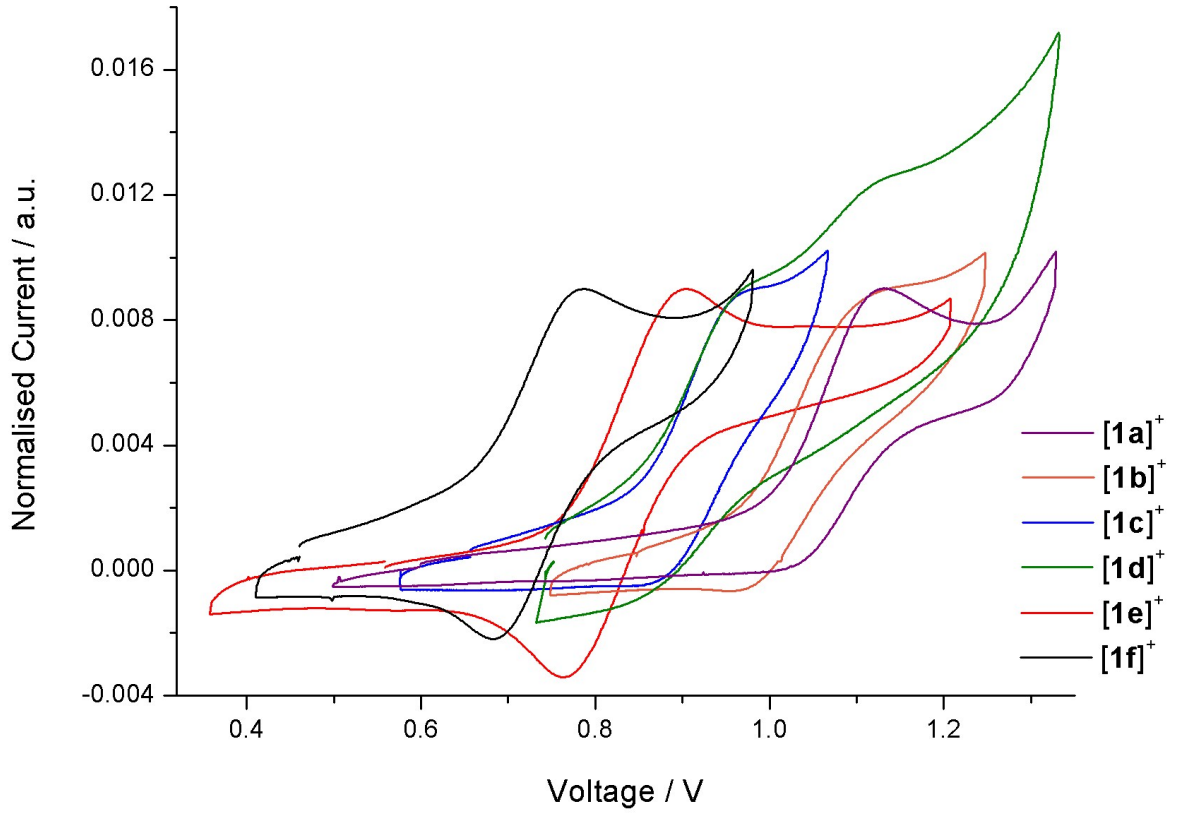


Figure S8: Cyclic voltammograms of *trans*-[RuCl(=C=CHC$_6$H$_4$-4-R)(dppm)$_2$]$^+$, [**1**]$^+$, where R = NO$_2$, [**1a**]$^+$; COOMe, [**1b**]$^+$; C≡CSiMe$_3$, [**1c**]$^+$; H, [**1d**]$^+$; Me, [**1e**]$^+$ and OMe, [**1f**]$^+$, showing the first oxidation potentials. Scans were recorded at -40 °C in CH_2Cl_2 0.1M [N^{n}Bu$_4$]PF$_6$ solutions at scan rates of 100 mVs^{-1} and have been normalised to equal the maximum current of [**1a**]$^+$.

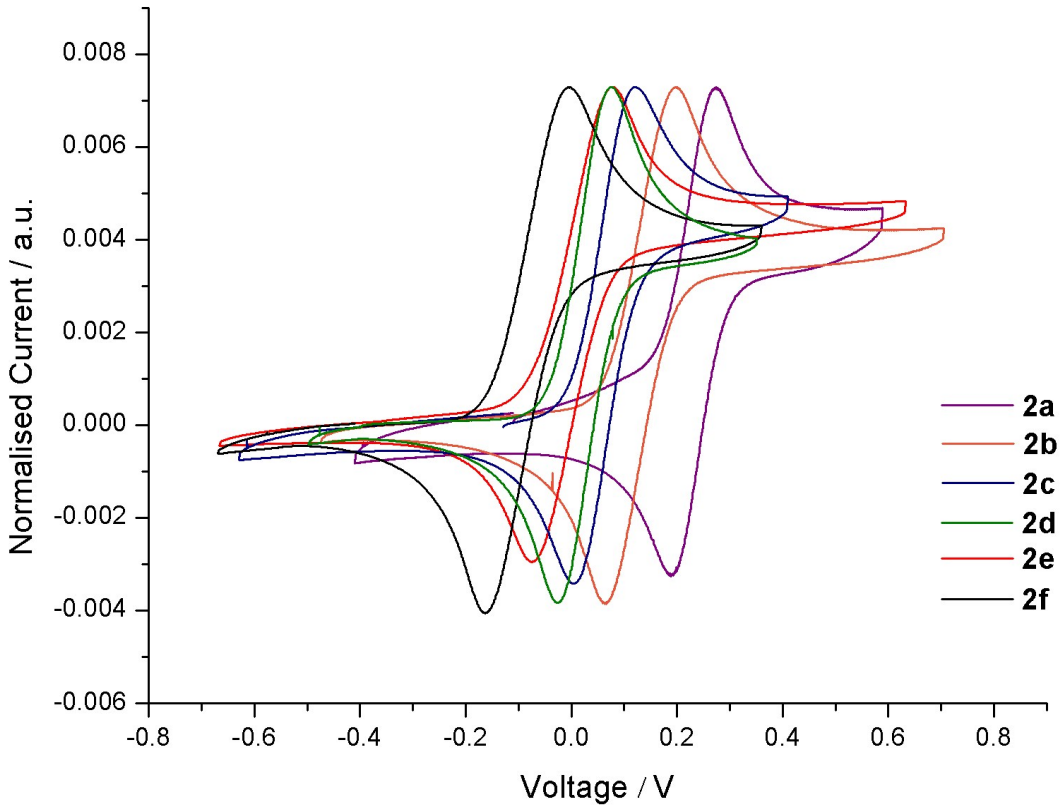


Figure S9: Cyclic voltammograms of *trans*-[RuCl(C≡CC_6H_4-4-R)(dppm)$_2$], [**2**], where R = NO_2, [**2a**]; COOMe, [**2b**]; C≡C$SiMe_3$, [**2c**]; H, [**2d**]; Me, [**2e**] and OMe, [**2f**], showing the perturbations in first oxidation potentials, caused as a result of the varying the R group. Scans were recorded at -40 °C in CH_2Cl_2 0.1M [N^nBu_4]PF_6 solutions at scan rates of 100 mVs^{-1} and have been normalised to equal the maximum current of [**2b**].

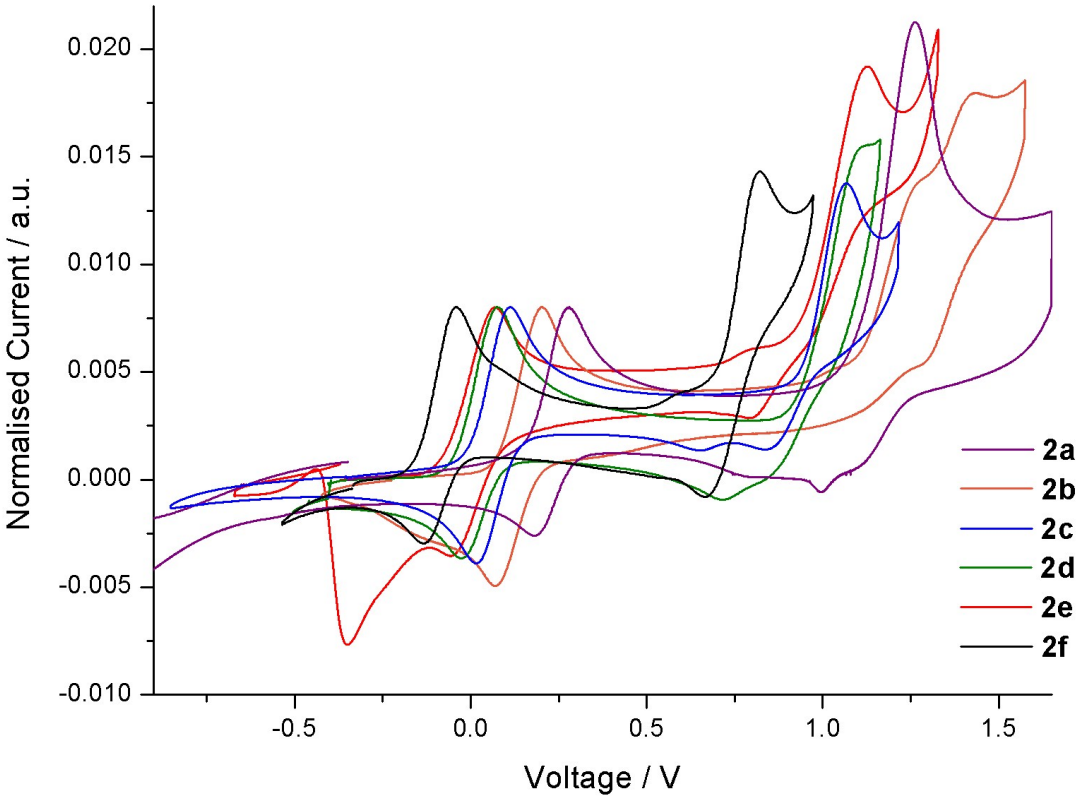


Figure S10: Cyclic voltammograms of *trans*-[RuCl(C≡CC_6H_4-4-R)$(dppm)_2$], [**2**], where R = NO_2, [**2a**]; COOMe, [**2b**]; C≡C$SiMe_3$, [**2c**]; H, [**2d**]; Me, [**2e**] and OMe, [**2f**], showing the first and second oxidations. Scans were recorded at r.t. ([**2d, f**]) and -40 °C ([**2a – c, e**]) in CH_2Cl_2 0.1M [N^nBu_4]PF_6 solutions at scan rates of 100 mVs^{-1} and have been normalised to equal the maximum current of $E_{1/2}(1)$ of [**2a**].

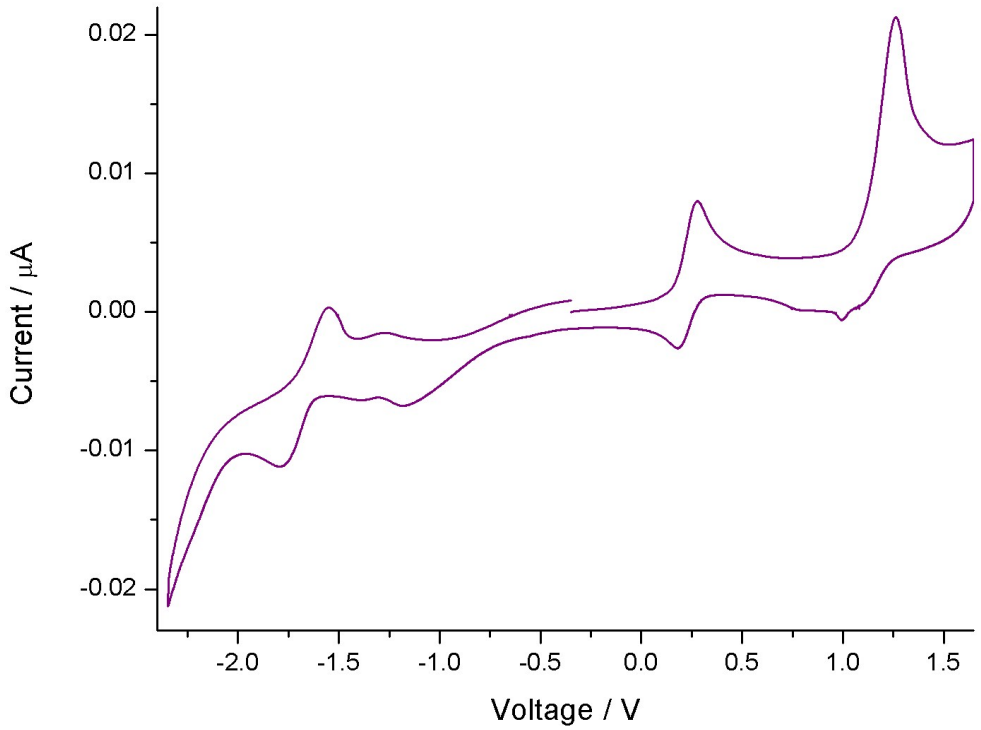


Figure S11: Cyclic voltammogram of *trans*-[RuCl(C≡CC_6H_4-4-NO_2)(dppm)$_2$], [**2a**], showing two oxidations and a reduction. The scan was recorded at -40 °C ([**2a – c, e**]) in CH_2Cl_2 0.1M [N^nBu_4]PF_6 solution at scan rates of 100 mVs^{-1}.

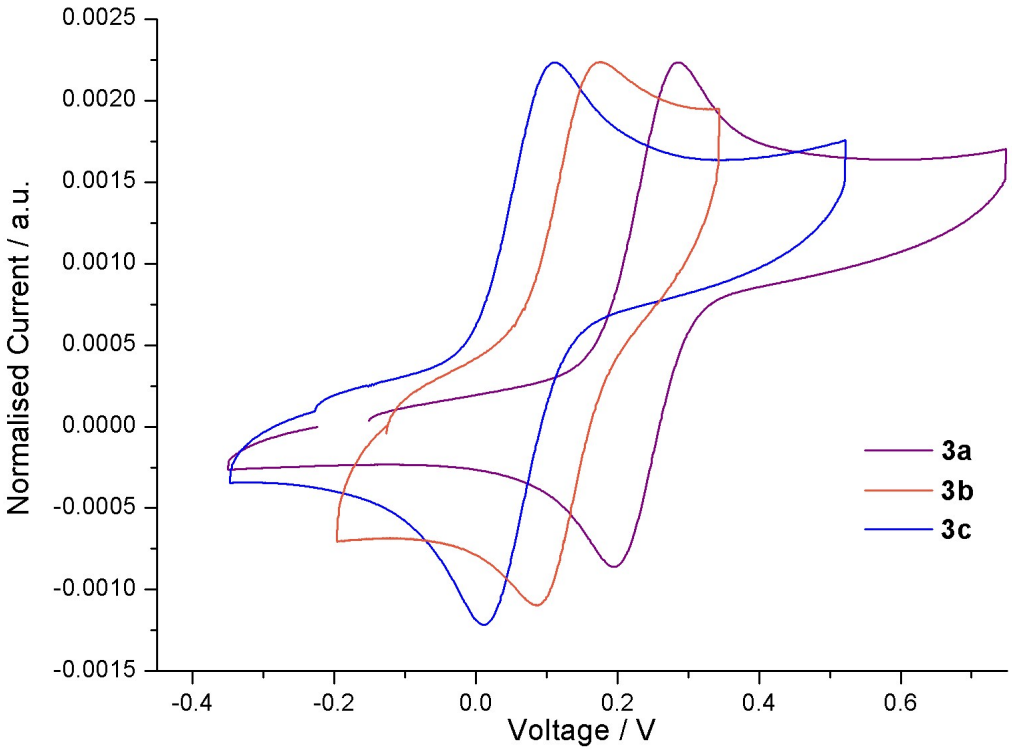


Figure S12: Cyclic voltammograms of *trans*-[Ru(C≡CC_6H_4-4-R)$_2$(dppm)$_2$], [**3**], where R = NO_2, [**3a**]; COOMe, [**3b**] and C≡C$SiMe_3$, [**3c**] showing the first oxidation only. Scans were recorded at -40 °C in CH_2Cl_2 0.1M [N^nBu_4]PF_6 solutions at scan rates of 100 mVs^{-1} and have been normalised to equal the maximum current of $E_{1/2}(1)$ of [**3a**].

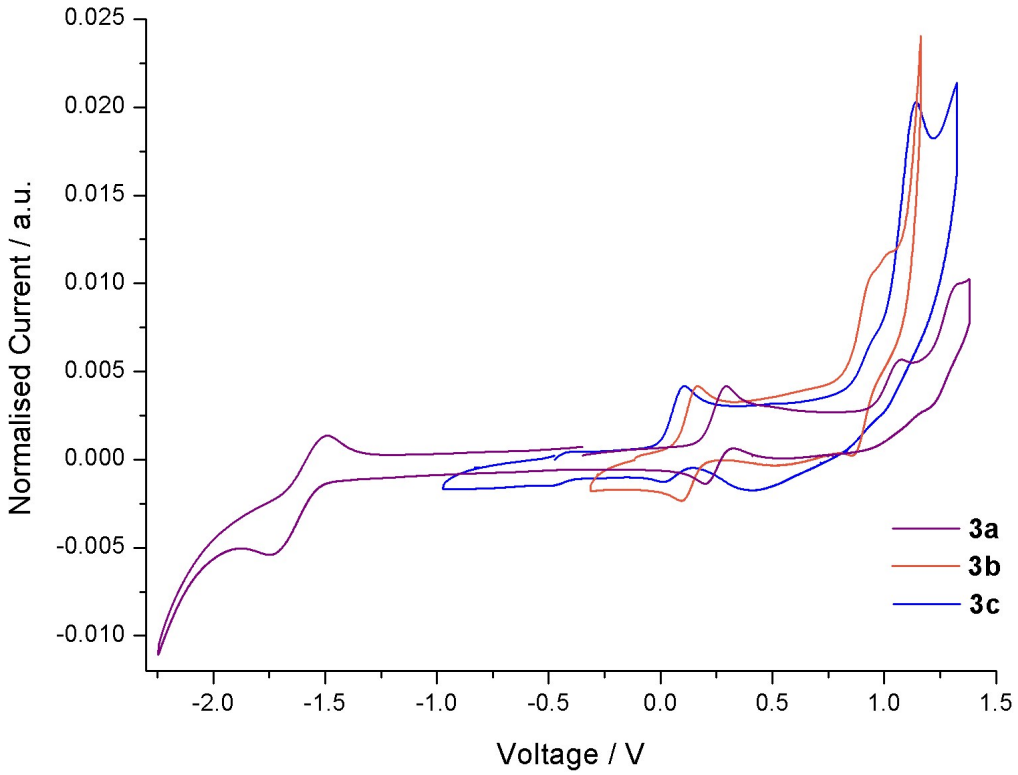


Figure S13: Cyclic voltammograms of *trans*-[Ru(C≡CC_6H_4-4-R)$_2$(dppm)$_2$], [**3**], where R = NO_2, [**3a**]; COOMe, [**3b**] and C≡C$SiMe_3$, [**3c**] showing two oxidations ([**3a – c**]) and a reduction ([**3a**]). Scans were recorded at -40 °C in CH_2Cl_2 0.1M [N^nBu_4]PF_6 solutions at scan rates of 100 mVs^{-1} and have been normalised to equal the maximum current of $E_{1/2}(1)$ of [**3a**].

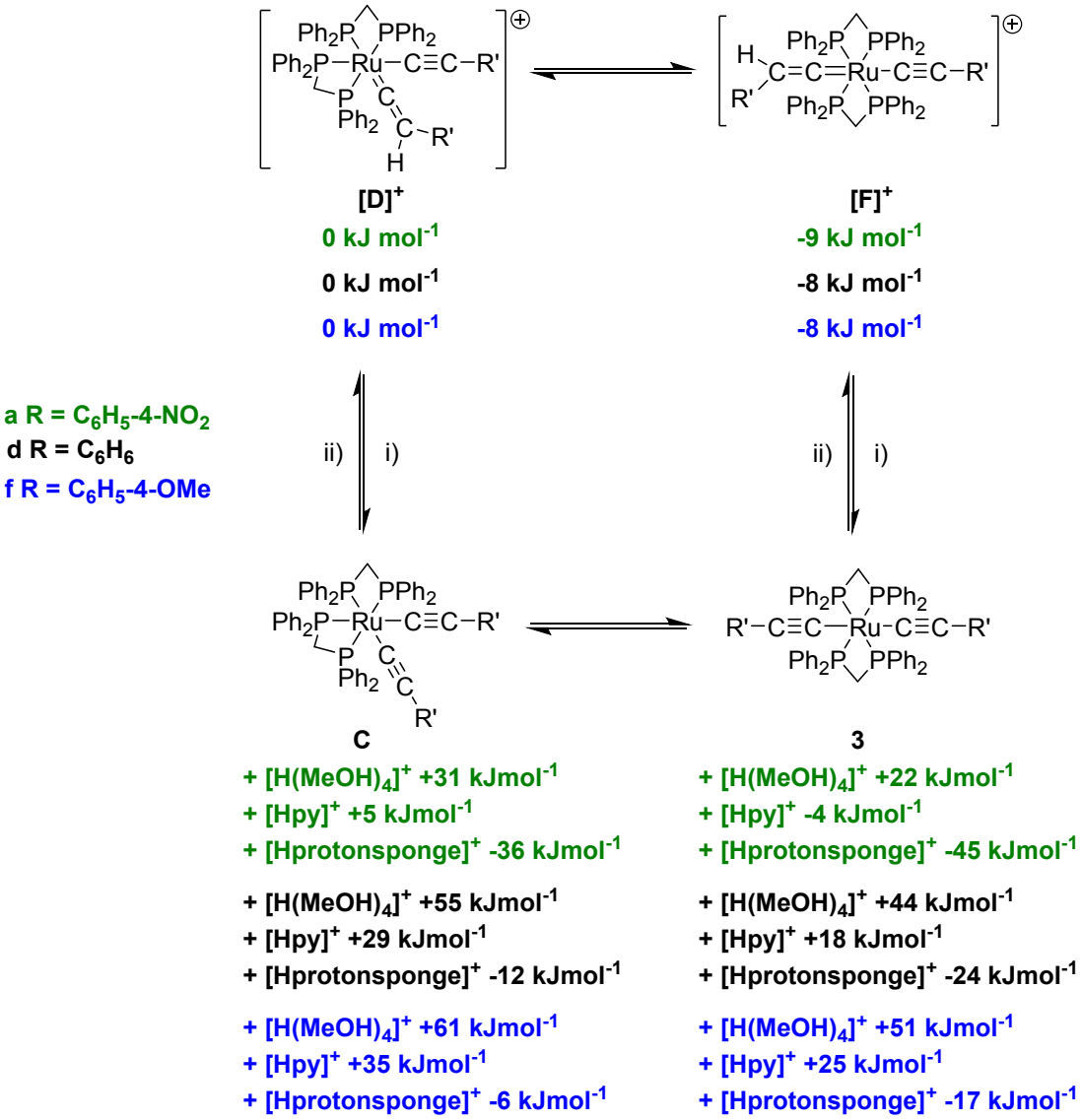
S7. DFT Calculations

Initial optimisations were performed at the (RI-)BP86/SV(P) level, followed by frequency calculations at the same level. Transition states were located by initially performing a constrained minimisation (by freezing internal coordinates that change most during the reaction) of a structure close to the anticipated transition state. This was followed by a frequency calculation to identify the transition vector to follow during a subsequent transition state optimisation. A final frequency calculation was then performed on the optimised transition-state structure. All minima were confirmed as such by the absence of imaginary frequencies and all transition states were identified by the presence of only one imaginary frequency. Energies, coordinates and first 50 vibrational modes are given.

Single-point calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the flexible def2-TZVPP basis set. The (RI-)PBE0/def2-TZVPP SCF energies were corrected for their zero point energies, thermal energies and entropies (obtained from the (RI-)BP86/SV(P)-level frequency calculations). In all calculations, a 28 electron quasi-relativistic ECP replaced the core electrons of Ru and Rh. No symmetry constraints were applied during optimisations. Sovlent corrections were applied with the COSMO dielectric continuum model[9] and dispersion effects modelled with Grimme's D3 method.[10, 11] All calculations were performed using the TURBOMOLE V6.4 package using the resolution of identity (RI) approximation.[12-20]

S7.1 Modelling Deprotonation Reactions

The differences in energy between the protonation and deprotonated complexes reported in this study was modelled by comparing the sum of the energies of the cationic vinylidene complexes (e.g. $[\mathbf{D}]^+$ and $[\mathbf{F}]^+$) and the bases $(MeOH)_4$, pyridine and proton sponge (1,8-*bis*(dimethylamino)naphthalene) with the sum of the energies of the (neutral) *bis*-alkynyl complexes and the appropriate conguate acids (Scheme 1). The data indicate that the NO_2-containing complexes are the most readily deprotonated and that the in case of both the cationic and neuctral complexes the *trans*-isomers are more stable (typically by *ca.* 10 kJ mol^{-1}) than their *cis* forms.



Scheme S1: (i) + $(MeOH)_4$, pyridine or proton sponge; (ii) - $(MeOH)_4$, pyridine or proton sponge.

S7.2 Complex [Ca]

SCF Energy (au) (RI)BP86/SV(P) -4414.6823114170
SCF Energy (au) PBE0/def2-TZVPP -4414.014671791
SCF Energy (au) PBE0/def2-TZVPP -4414.0552660812 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9702508
Chemical potential (kJ mol^{-1}) 2231.50
Dispersion correction (au) PBE0/def2-TZVPP -0.24714811

xyz coordinates

129

Ru	0.19241	-0.18671	0.03963
C	-1.39799	0.03242	-1.15567
C	-0.27124	1.60655	0.79802
P	-1.11067	-1.35142	1.63466
P	1.57971	-0.58317	2.02089
P	0.99520	-1.93779	-1.47589
P	1.67471	0.80334	-1.51625
C	0.26723	-1.64313	2.87484
C	2.21764	-0.78881	-2.34809
C	-1.85450	-3.01244	1.29402
C	-2.44690	-3.22745	0.03064
C	-3.07106	-4.45397	-0.25595
C	-3.10010	-5.47669	0.70755
C	-2.50565	-5.27033	1.96512
C	-1.88921	-4.04267	2.26005
C	-2.47660	-0.51045	2.55959
C	-3.24566	0.46356	1.88775
C	-4.33197	1.07366	2.53989
C	-4.65004	0.72837	3.86442
C	-3.88185	-0.23688	4.54004
C	-2.80278	-0.85744	3.88942
C	1.91790	0.75013	3.26812
C	0.84152	1.40016	3.91310
C	1.08457	2.42709	4.84015
C	2.40074	2.82818	5.12582
C	3.47529	2.19541	4.47879
C	3.23739	1.16359	3.55440
C	3.13464	-1.58544	2.15121
C	3.39417	-2.40167	3.27478
C	4.59342	-3.12611	3.36678
C	5.55453	-3.03319	2.34414
C	5.31161	-2.21183	1.23112
C	4.10611	-1.49511	1.13415
C	-0.04389	-2.58175	-2.87343
C	-0.53863	-1.68982	-3.85163
C	-1.34600	-2.16166	-4.89978
C	-1.68150	-3.52400	-4.97887
C	-1.20396	-4.41445	-4.00277
C	-0.39124	-3.94799	-2.95507
C	1.99580	-3.44338	-1.06192
C	1.68715	-4.18493	0.09620

C	2.40306	-5.35373	0.40878
C	3.44135	-5.78889	-0.43092
C	3.75377	-5.05847	-1.59155
C	3.03141	-3.89706	-1.90911
C	1.05558	1.91190	-2.86395
C	1.68268	1.97247	-4.12821
C	1.22001	2.86691	-5.10729
C	0.13334	3.71519	-4.82822
C	-0.49114	3.66129	-3.57049
C	-0.03905	2.75954	-2.59061
C	3.22809	1.66951	-1.00158
C	3.16933	2.52508	0.12000
C	4.30902	3.24532	0.51793
C	5.51561	3.11059	-0.19001
C	5.58148	2.25487	-1.30392
C	4.44246	1.54040	-1.71178
H	0.05028	-1.34633	3.92278
H	0.58428	-2.70727	2.86024
H	2.15081	-0.80624	-3.45650
H	3.25310	-1.05219	-2.04551
H	-2.41663	-2.42646	-0.72809
H	-3.53231	-4.60918	-1.24487
H	-3.58729	-6.43921	0.47924
H	-2.52622	-6.06878	2.72558
H	-1.43963	-3.89295	3.25642
H	-2.98581	0.74376	0.85409
H	-4.92862	1.83148	2.00621
H	-5.49941	1.21275	4.37426
H	-4.12665	-0.51307	5.57917
H	-2.22025	-1.62277	4.42984
H	-0.19896	1.11591	3.68961
H	0.23381	2.92389	5.33415
H	2.58782	3.63624	5.85221
H	4.51223	2.50051	4.69767
H	4.09159	0.67328	3.06139
H	2.66114	-2.46589	4.09640
H	4.78229	-3.76210	4.24768
H	6.49712	-3.60037	2.41847
H	6.06333	-2.12862	0.42926
H	3.92397	-0.84395	0.26405
H	-0.30502	-0.61467	-3.79822
H	-1.72370	-1.45269	-5.65432
H	-2.31754	-3.89056	-5.80147
H	-1.45887	-5.48606	-4.05702
H	-0.01935	-4.66080	-2.20226
H	0.86658	-3.85270	0.75236
H	2.14805	-5.92500	1.31630
H	4.00731	-6.70228	-0.18374
H	4.56183	-5.40012	-2.25972
H	3.27227	-3.34869	-2.83531
H	2.54540	1.32485	-4.35933
H	1.71490	2.90464	-6.09199
H	-0.22698	4.42035	-5.59563
H	-1.34511	4.32156	-3.34706
H	-0.53657	2.70587	-1.60872
H	2.22356	2.62387	0.68032

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H          6.40935        3.67367        0.12634
H          6.52517        2.14605       -1.86415
H          4.50834        0.88403       -2.59619
C         -2.43303        0.17365       -1.84059
C         -3.60148        0.33050       -2.63355
C         -0.55399        2.75360        1.20392
C         -0.87679        4.05165        1.68294
C         -5.92125        0.62642       -4.22212
C         -6.00041       -0.08048       -3.00819
C         -4.85366       -0.22424       -2.22618
C         -3.56575        1.04671       -3.86954
C         -4.70926        1.19393       -4.65609
N         -7.12669        0.77336       -5.05316
H         -6.96731       -0.50586       -2.70280
H         -4.90553       -0.77481       -1.27366
H         -2.61288        1.49378       -4.19386
H         -4.69140        1.74408       -5.60802
C         -1.50701        6.63233        2.65025
C         -2.13710        5.50901        3.21633
C         -1.82485        4.23631        2.73607
C         -0.26427        5.21905        1.13187
C         -0.57291        6.49423        1.60719
N         -1.82984        7.97489        3.15878
H         -2.86525        5.66066        4.02623
H         -2.31889        3.34979        3.16378
H          0.46538        5.10043        0.31537
H         -0.10509        7.39743        1.18947
O         -2.65075        8.05941        4.08137
O         -1.26039        8.94151        2.63603
O         -7.02071        1.39832       -6.11633
O         -8.17603        0.26175       -4.64201

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1                        0.00        0.00000         -       -
     2                        0.00        0.00000         -       -
     3                        0.00        0.00000         -       -
     4                        0.00        0.00000         -       -
     5                        0.00        0.00000         -       -
     6                        0.00        0.00000         -       -
     7        a              10.04        0.42845       YES     YES
     8        a              11.43        0.17708       YES     YES
     9        a              13.46        0.23869       YES     YES
    10        a              14.43        0.52047       YES     YES
    11        a              16.37        0.03087       YES     YES
    12        a              19.80        0.02050       YES     YES
    13        a              22.34        0.02532       YES     YES
    14        a              22.97        0.05430       YES     YES
    15        a              25.19        0.00723       YES     YES
    16        a              27.24        0.01730       YES     YES
    17        a              29.73        0.07713       YES     YES
    18        a              32.50        0.01958       YES     YES
```

19	a	37.38	0.03034	YES	YES
20	a	39.10	0.07349	YES	YES
21	a	43.48	0.01417	YES	YES
22	a	45.09	0.04523	YES	YES
23	a	46.43	0.13855	YES	YES
24	a	47.58	0.00217	YES	YES
25	a	48.61	0.01779	YES	YES
26	a	49.36	0.08584	YES	YES
27	a	51.35	0.82291	YES	YES
28	a	51.76	0.02029	YES	YES
29	a	52.34	0.11620	YES	YES
30	a	57.68	0.13265	YES	YES
31	a	59.42	0.09273	YES	YES
32	a	60.08	0.54840	YES	YES
33	a	64.19	0.00797	YES	YES
34	a	68.50	0.00543	YES	YES
35	a	69.71	0.06438	YES	YES
36	a	72.51	0.00416	YES	YES
37	a	73.13	0.05297	YES	YES
38	a	79.41	0.16472	YES	YES
39	a	81.70	2.72302	YES	YES
40	a	83.70	0.39169	YES	YES
41	a	84.00	0.30339	YES	YES
42	a	94.68	0.14482	YES	YES
43	a	97.81	0.69016	YES	YES
44	a	105.36	0.27777	YES	YES
45	a	112.01	1.53000	YES	YES
46	a	136.69	0.06325	YES	YES
47	a	138.45	0.17775	YES	YES
48	a	159.31	0.01361	YES	YES
49	a	161.53	0.06187	YES	YES
50	a	161.95	0.45158	YES	YES

S7.3 Complex $[Da]^+$

SCF Energy (au) (RI)BP86/SV(P) -4415.0913828010
SCF Energy (au) PBE0/def2-TZVPP -4414.422351381
SCF Energy (au) PBE0/def2-TZVPP -4414.4933755759 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9823432
Chemical potential (kJ mol^{-1}) 2264.27
Dispersion correction (au) PBE0/def2-TZVPP -0.25061338

xyz coordinates

130

Ru	0.30395	0.03053	0.29869
C	-1.23788	0.10689	-1.01526
C	-0.14059	1.66013	1.02505
P	-0.97732	-1.26031	1.87637
P	1.75078	-0.53865	2.21989
P	1.19639	-1.85414	-1.23499
P	1.84161	0.95655	-1.30813
C	0.48580	-1.70781	2.96730
C	2.46452	-0.67996	-1.97457
C	-1.76927	-2.86683	1.43227
C	-2.27576	-3.06378	0.13041
C	-2.92886	-4.26702	-0.19260
C	-3.07483	-5.27605	0.77356
C	-2.56832	-5.08344	2.07224
C	-1.92132	-3.88274	2.40429
C	-2.24232	-0.44276	2.93614
C	-3.14209	0.44615	2.30897
C	-4.18196	1.03426	3.04744
C	-4.32817	0.74519	4.41486
C	-3.43430	-0.13870	5.04457
C	-2.39630	-0.73537	4.30962
C	2.01879	0.74560	3.53005
C	0.91521	1.25583	4.25165
C	1.10863	2.22303	5.25241
C	2.39912	2.70318	5.53493
C	3.49745	2.20851	4.81238
C	3.31259	1.23350	3.81681
C	3.36255	-1.43183	2.19765
C	3.62587	-2.49670	3.08664
C	4.89148	-3.10535	3.10516
C	5.90828	-2.65112	2.24759
C	5.65616	-1.58476	1.36832
C	4.38811	-0.97982	1.33856
C	0.24232	-2.45966	-2.69910
C	-0.15838	-1.55181	-3.70539
C	-0.87495	-2.00722	-4.82388
C	-1.21184	-3.36600	-4.94605
C	-0.82456	-4.27095	-3.94410
C	-0.10128	-3.82381	-2.82523
C	2.13187	-3.35922	-0.71704
C	1.54754	-4.22563	0.23353

C	2.18627	-5.42589	0.58964
C	3.41868	-5.76770	0.00839
C	4.00573	-4.91065	-0.93862
C	3.36474	-3.71587	-1.30532
C	1.22642	1.94425	-2.73987
C	1.79512	1.83669	-4.02847
C	1.35782	2.67628	-5.06640
C	0.36001	3.63684	-4.82448
C	-0.20412	3.75224	-3.54231
C	0.22151	2.90659	-2.50439
C	3.35635	1.89439	-0.81422
C	3.29016	2.79281	0.27167
C	4.41211	3.56401	0.62145
C	5.60877	3.43990	-0.10405
C	5.68167	2.54554	-1.18719
C	4.56079	1.77894	-1.54540
H	0.35068	-1.60055	4.06404
H	0.78649	-2.75287	2.74150
H	2.56210	-0.75821	-3.07765
H	3.45078	-0.89084	-1.51004
H	-2.16176	-2.27176	-0.62825
H	-3.32377	-4.41268	-1.21097
H	-3.58798	-6.21738	0.51738
H	-2.68477	-5.87066	2.83502
H	-1.54402	-3.74123	3.43125
H	-3.02998	0.67362	1.23628
H	-4.87824	1.72789	2.54942
H	-5.14279	1.21006	4.99371
H	-3.54699	-0.37099	6.11617
H	-1.71425	-1.43391	4.82214
H	-0.10921	0.90568	4.04365
H	0.23956	2.60012	5.81581
H	2.54869	3.45936	6.32268
H	4.51443	2.57286	5.03142
H	4.18915	0.84319	3.27702
H	2.85024	-2.85378	3.78343
H	5.08561	-3.93663	3.80232
H	6.90199	-3.12737	2.26919
H	6.45182	-1.21667	0.70035
H	4.20742	-0.13092	0.65862
H	0.08102	-0.47976	-3.62633
H	-1.17583	-1.28918	-5.60351
H	-1.77456	-3.71961	-5.82527
H	-1.07618	-5.34031	-4.03502
H	0.20767	-4.55173	-2.05930
H	0.56905	-3.97852	0.67835
H	1.71371	-6.09883	1.32365
H	3.92084	-6.70814	0.28807
H	4.96737	-5.17847	-1.40601
H	3.83042	-3.07254	-2.06958
H	2.59026	1.10248	-4.23889
H	1.80587	2.58245	-6.06906
H	0.02327	4.29919	-5.63863
H	-0.98586	4.50350	-3.34533
H	-0.23127	2.99843	-1.50519
H	2.35373	2.89540	0.84186

H	4.34808	4.26690	1.46778
H	6.48793	4.04507	0.17104
H	6.61596	2.44986	-1.76432
H	4.63197	1.09558	-2.40828
C	-2.22617	0.19189	-1.76488
C	-3.34840	0.28256	-2.64507
C	-0.41933	2.86509	1.53441
H	0.30068	3.20669	2.30848
C	-1.53663	3.76685	1.22866
C	-5.54973	0.45485	-4.38600
C	-5.67234	-0.28661	-3.20049
C	-4.57646	-0.36928	-2.33652
C	-3.26603	1.03064	-3.85438
C	-4.35912	1.11818	-4.72167
N	-6.70874	0.53778	-5.31025
H	-6.62721	-0.78440	-2.97802
H	-4.65869	-0.94547	-1.40158
H	-2.32565	1.54909	-4.09877
H	-4.31403	1.69159	-5.65885
C	-3.64244	5.54874	0.69161
C	-2.70372	5.87768	1.68100
C	-1.65713	4.98778	1.94333
C	-2.50453	3.46622	0.23034
C	-3.55259	4.35144	-0.03786
N	-4.75482	6.48803	0.40758
H	-2.81053	6.82638	2.22659
H	-0.91426	5.23902	2.71820
H	-2.42498	2.52749	-0.34316
H	-4.30881	4.13604	-0.80654
O	-5.55589	6.16550	-0.47318
O	-4.80280	7.52580	1.07171
O	-7.73838	-0.05513	-4.98111
O	-6.56068	1.19115	-6.34557

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	9.99	0.00135	YES	YES
8	a	12.24	0.24883	YES	YES
9	a	13.48	0.37674	YES	YES
10	a	14.18	0.32991	YES	YES
11	a	15.28	0.22434	YES	YES
12	a	18.62	0.17165	YES	YES
13	a	21.73	0.08450	YES	YES
14	a	27.67	0.06945	YES	YES
15	a	30.92	0.01382	YES	YES
16	a	33.58	0.06358	YES	YES
17	a	34.16	0.00904	YES	YES

18	a	34.84	0.11441	YES	YES
19	a	36.95	0.06057	YES	YES
20	a	39.56	0.03326	YES	YES
21	a	41.14	0.11863	YES	YES
22	a	42.36	0.14752	YES	YES
23	a	43.57	0.17822	YES	YES
24	a	45.93	0.07770	YES	YES
25	a	46.33	0.08650	YES	YES
26	a	50.70	0.02171	YES	YES
27	a	51.27	0.07976	YES	YES
28	a	53.09	0.05899	YES	YES
29	a	56.03	0.05111	YES	YES
30	a	57.75	0.01382	YES	YES
31	a	61.17	0.26560	YES	YES
32	a	63.01	0.08898	YES	YES
33	a	63.12	0.03156	YES	YES
34	a	63.50	0.11697	YES	YES
35	a	67.90	0.09807	YES	YES
36	a	70.54	0.25852	YES	YES
37	a	72.95	0.12209	YES	YES
38	a	78.89	0.96687	YES	YES
39	a	80.78	0.55347	YES	YES
40	a	82.52	0.73700	YES	YES
41	a	89.48	0.05010	YES	YES
42	a	96.03	0.13928	YES	YES
43	a	97.73	0.92025	YES	YES
44	a	105.51	1.20953	YES	YES
45	a	113.09	1.45449	YES	YES
46	a	138.06	0.25197	YES	YES
47	a	139.13	0.13672	YES	YES
48	a	152.89	0.17519	YES	YES
49	a	155.34	0.30586	YES	YES
50	a	160.21	0.49621	YES	YES

S7.4 Complex $[Fa]^+$

SCF Energy (au) (RI)BP86/SV(P) -4415.0965565700
SCF Energy (au) PBE0/def2-TZVPP -4414.429150638
SCF Energy (au) PBE0/def2-TZVPP -4414.4971860093 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9826514
Chemical potential (kJ mol^{-1}) 2267.18
Dispersion correction (au) PBE0/def2-TZVPP -0.25143364

xyz coordinates

130

C	0.35866	-1.86408	0.26310
C	-1.66027	-0.19065	-2.77317
C	1.03148	0.74472	-3.66484
C	0.62222	-2.05572	-3.09839
C	1.61826	0.28141	2.60644
C	-0.94481	1.74857	3.11844
C	-0.93321	-1.10418	3.33873
C	3.59358	-0.72166	0.62072
P	-2.22157	-0.23044	-0.97870
C	-0.06013	1.96564	-0.63113
P	2.20186	0.46293	0.82514
P	0.18387	-0.37705	-2.47680
P	-0.22981	0.25855	2.30220
Ru	-0.00063	0.14605	-0.11783
C	0.64503	-3.05857	0.47173
C	-3.11748	-1.82542	-0.76601
C	-3.57484	1.02090	-0.82073
C	3.02413	2.11378	0.76568
H	-1.84804	0.82134	-3.19148
H	-2.11745	-0.94989	-3.44244
H	1.96592	1.09209	3.28025
H	1.96276	-0.69077	3.01542
C	-2.06405	-3.16452	4.91179
C	-0.77081	-3.30887	4.38145
C	-0.20914	-2.29013	3.59384
C	-2.23570	-0.96731	3.87293
C	-2.79550	-1.99299	4.65200
H	-2.49991	-3.96387	5.53306
H	-0.18809	-4.22305	4.57875
H	0.79687	-2.43880	3.17413
H	-2.81767	-0.04880	3.69751
H	-3.80806	-1.86689	5.06877
C	-2.24374	3.86175	4.46543
C	-1.06173	3.31063	4.99226
C	-0.42074	2.25051	4.33096
C	-2.12700	2.31069	2.58996
C	-2.77860	3.35646	3.26866
H	-2.75019	4.68643	4.99286
H	-0.64042	3.70083	5.93301
H	0.48335	1.80813	4.78093
H	-2.54659	1.92618	1.64535

H	-3.70640	3.78081	2.85228
C	5.77720	-2.47330	0.28736
C	4.75879	-2.42537	-0.67940
C	3.66578	-1.55702	-0.51209
C	4.62158	-0.77147	1.59085
C	5.70566	-1.64809	1.42497
H	6.63089	-3.15837	0.15708
H	4.80460	-3.07736	-1.56645
H	2.85474	-1.54962	-1.25667
H	4.58712	-0.11629	2.47782
H	6.50231	-1.68251	2.18595
C	4.22957	4.66544	0.61909
C	4.84603	3.55872	0.01206
C	4.24908	2.28791	0.08319
C	2.40197	3.23514	1.35967
C	3.00675	4.50022	1.29290
H	4.70315	5.65940	0.56937
H	5.80858	3.67897	-0.51169
H	4.75506	1.42520	-0.37931
H	1.43553	3.13273	1.88096
H	2.51447	5.36386	1.76827
C	1.28717	-4.62618	-4.05758
C	0.12262	-4.43668	-3.29336
C	-0.20698	-3.16199	-2.80656
C	1.79335	-2.25085	-3.86467
C	2.12219	-3.53234	-4.33886
H	1.54207	-5.62904	-4.43697
H	-0.53673	-5.29059	-3.06955
H	-1.11574	-3.03784	-2.19681
H	2.44737	-1.39967	-4.11201
H	3.03248	-3.67062	-4.94489
C	2.40352	2.38371	-5.50627
C	1.19083	1.77324	-5.87387
C	0.50884	0.95236	-4.96109
C	2.24800	1.36097	-3.30118
C	2.93260	2.17449	-4.22123
H	2.93810	3.02484	-6.22596
H	0.77406	1.93264	-6.88167
H	-0.43110	0.46594	-5.27103
H	2.66020	1.21594	-2.28864
H	3.88151	2.65164	-3.92748
C	-4.60031	-4.19380	-0.38326
C	-3.67668	-3.77582	0.58897
C	-2.93025	-2.59819	0.39875
C	-4.05755	-2.24455	-1.73713
C	-4.78888	-3.42721	-1.54837
H	-5.18056	-5.11906	-0.23350
H	-3.52919	-4.36888	1.50582
H	-2.19382	-2.28721	1.15464
H	-4.23710	-1.64087	-2.64276
H	-5.51703	-3.74747	-2.31131
C	-5.61663	2.94991	-0.49751
C	-4.46857	3.25552	-1.24950
C	-3.44955	2.30177	-1.40563
C	-4.72821	0.72275	-0.05894
C	-5.74060	1.68446	0.10062

H	-6.41656	3.69906	-0.38032
H	-4.36107	4.24602	-1.72006
H	-2.54943	2.57222	-1.98027
H	-4.84739	-0.26958	0.40410
H	-6.63861	1.43507	0.68927
C	0.96087	-4.42673	0.72539
C	1.58027	-7.12207	1.24047
C	2.55263	-6.13867	1.48183
C	2.24215	-4.79998	1.22510
C	0.00184	-5.45471	0.49404
C	0.30645	-6.79483	0.74900
N	1.90683	-8.54416	1.51195
H	3.53661	-6.44407	1.86600
H	2.99667	-4.01770	1.40101
H	-0.99417	-5.17901	0.11408
H	-0.42174	-7.60071	0.57725
C	0.12811	3.15664	-1.21720
C	-0.36262	4.50654	-0.92757
H	0.80807	3.08240	-2.09496
C	-1.25989	7.13029	-0.44734
C	-1.55491	6.11951	0.48263
C	-1.10690	4.81904	0.24039
C	-0.07619	5.55630	-1.84204
C	-0.52078	6.86174	-1.60989
N	-1.73592	8.51001	-0.19099
H	-2.12879	6.37621	1.38463
H	-1.32326	4.02684	0.97234
H	0.50645	5.33684	-2.75190
H	-0.30709	7.68204	-2.31028
O	1.02837	-9.37969	1.28561
O	3.03420	-8.79325	1.94528
O	-2.38784	8.70151	0.83949
O	-1.45003	9.37267	-1.02445

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	10.07	1.25799	YES	YES
8	a	11.08	1.01111	YES	YES
9	a	13.12	0.60105	YES	YES
10	a	16.88	0.05467	YES	YES
11	a	17.08	0.13715	YES	YES
12	a	21.84	0.01633	YES	YES
13	a	23.87	0.16237	YES	YES
14	a	26.11	0.01403	YES	YES
15	a	26.92	0.03881	YES	YES
16	a	30.21	0.03654	YES	YES
17	a	32.32	0.37058	YES	YES

18	a	33.90	0.02360	YES	YES
19	a	36.38	0.19615	YES	YES
20	a	39.09	0.02565	YES	YES
21	a	41.79	0.24397	YES	YES
22	a	44.65	0.00717	YES	YES
23	a	46.12	0.13299	YES	YES
24	a	47.64	0.03392	YES	YES
25	a	50.71	0.01981	YES	YES
26	a	51.87	0.03382	YES	YES
27	a	53.33	0.02482	YES	YES
28	a	56.54	0.08476	YES	YES
29	a	57.16	0.22462	YES	YES
30	a	59.15	0.38226	YES	YES
31	a	61.18	0.27714	YES	YES
32	a	63.77	0.11814	YES	YES
33	a	64.66	0.01654	YES	YES
34	a	65.83	0.05464	YES	YES
35	a	68.06	0.10114	YES	YES
36	a	71.16	0.30568	YES	YES
37	a	76.17	0.09982	YES	YES
38	a	77.67	0.25172	YES	YES
39	a	80.58	0.14780	YES	YES
40	a	84.67	0.09820	YES	YES
41	a	88.09	0.06611	YES	YES
42	a	96.08	4.16955	YES	YES
43	a	99.87	1.26133	YES	YES
44	a	104.41	0.10112	YES	YES
45	a	122.78	2.17684	YES	YES
46	a	142.60	0.30901	YES	YES
47	a	147.66	0.04182	YES	YES
48	a	149.50	0.55996	YES	YES
49	a	156.99	0.67706	YES	YES
50	a	161.08	1.07876	YES	YES

S7.5 Complex [3a]

SCF Energy (au) (RI)BP86/SV(P) -4414.6858956400
SCF Energy (au) PBE0/def2-TZVPP -4414.020956248
SCF Energy (au) PBE0/def2-TZVPP -4414.0578065813 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9704468
Chemical potential (kJ mol^{-1}) 2227.92
Dispersion correction (au) PBE0/def2-TZVPP -0.24667993

xyz coordinates

129

C	0.17892	-2.01128	0.56127
C	-1.55003	0.13533	-2.78245
C	1.35654	0.72349	-3.41109
C	0.39921	-1.97941	-3.30323
C	1.49079	-0.07309	2.64601
C	-0.69560	1.88167	3.08124
C	-1.31268	-0.88561	3.35307
C	3.56834	-0.79540	0.61667
P	-2.20745	-0.30937	-1.07445
C	-0.14828	1.89744	-0.57635
P	2.08994	0.28241	0.89927
P	0.23013	-0.35506	-2.41872
P	-0.32341	0.25245	2.28183
Ru	-0.04955	-0.07194	-0.06359
C	0.37104	-3.14315	1.06416
C	-3.03040	-1.95042	-1.30164
C	-3.66538	0.79524	-0.74857
C	2.84785	1.96564	0.93386
H	-1.60231	1.24001	-2.87354
H	-2.02583	-0.34759	-3.66216
H	1.96699	0.46659	3.49148
H	1.61711	-1.16872	2.77899
C	-2.95550	-2.50893	4.98020
C	-1.57060	-2.45268	5.20895
C	-0.75162	-1.64499	4.39987
C	-2.70509	-0.94889	3.12608
C	-3.52088	-1.75455	3.93624
H	-3.59607	-3.14231	5.61591
H	-1.11834	-3.04487	6.02153
H	0.33289	-1.61848	4.59312
H	-3.15834	-0.36004	2.31022
H	-4.60689	-1.79351	3.74997
C	-1.35506	4.32717	4.32481
C	-0.63763	3.34730	5.03612
C	-0.31381	2.12867	4.42001
C	-1.41974	2.86346	2.37633
C	-1.74805	4.08129	2.99951
H	-1.61019	5.28426	4.80949
H	-0.33470	3.53066	6.08054
H	0.22715	1.35946	4.99762
H	-1.71111	2.67813	1.33124

H	-2.31072	4.84433	2.43750
C	5.81292	-2.44492	0.16581
C	4.61037	-2.68854	-0.51903
C	3.48909	-1.87056	-0.29193
C	4.78226	-0.54991	1.29690
C	5.89617	-1.37572	1.07600
H	6.69068	-3.08840	-0.01144
H	4.54068	-3.52276	-1.23675
H	2.53747	-2.07141	-0.80868
H	4.86374	0.29882	1.99641
H	6.83851	-1.17795	1.61340
C	4.08684	4.50582	0.83767
C	4.02504	3.70518	-0.31743
C	3.40639	2.44746	-0.27234
C	2.89425	2.78210	2.08223
C	3.51361	4.04493	2.03337
H	4.57302	5.49467	0.80086
H	4.45474	4.06608	-1.26600
H	3.35371	1.83620	-1.18859
H	2.44045	2.45194	3.02915
H	3.54429	4.66972	2.94133
C	0.53612	-4.45044	-4.66475
C	0.36434	-4.42076	-3.27160
C	0.29475	-3.19152	-2.59064
C	0.57143	-2.01479	-4.70741
C	0.63777	-3.24401	-5.38173
H	0.59215	-5.41506	-5.19636
H	0.28247	-5.36073	-2.70153
H	0.15937	-3.16919	-1.49684
H	0.65996	-1.07676	-5.28000
H	0.77281	-3.25922	-6.47619
C	3.21514	2.32449	-4.82111
C	1.86757	2.71072	-4.73916
C	0.94350	1.91669	-4.03684
C	2.71647	0.34336	-3.49492
C	3.63781	1.13723	-4.19607
H	3.93749	2.94843	-5.37292
H	1.52692	3.64192	-5.22058
H	-0.10608	2.24217	-3.98226
H	3.06180	-0.58630	-3.01218
H	4.69321	0.82354	-4.25528
C	-4.34881	-4.43267	-1.57269
C	-3.55695	-4.17482	-0.44202
C	-2.89780	-2.93950	-0.30513
C	-3.83806	-2.21240	-2.43199
C	-4.48906	-3.44821	-2.56814
H	-4.85897	-5.40423	-1.68177
H	-3.43899	-4.94328	0.33949
H	-2.25416	-2.74800	0.56782
H	-3.97331	-1.44505	-3.21247
H	-5.11171	-3.64333	-3.45706
C	-5.85681	2.48804	-0.15268
C	-4.67317	3.02384	-0.68912
C	-3.58206	2.18777	-0.97806
C	-4.85819	0.26500	-0.20504
C	-5.94317	1.10761	0.09248

```
H         -6.71146        3.14663        0.07418
H         -4.59148        4.10614       -0.88315
H         -2.64845        2.62718       -1.36342
H         -4.94941       -0.81760       -0.02278
H         -6.86700        0.67584        0.51225
C          0.55131       -4.44607        1.60262
C          0.89690       -7.04544        2.66184
C          1.87489       -6.51383        1.80128
C          1.70193       -5.23053        1.28111
C         -0.41491       -5.02103        2.48586
C         -0.24758       -6.30419        3.00857
N          1.07525       -8.39886        3.21122
H          2.75726       -7.12354        1.55878
H          2.46459       -4.80185        0.61248
H         -1.30187       -4.42830        2.75889
H         -0.98627       -6.75441        3.68733
C         -0.15582        3.10522       -0.91015
C         -0.16479        4.49091       -1.21217
C         -0.19220        7.26379       -1.78690
C          0.52660        6.79236       -0.67156
C          0.53912        5.42658       -0.39013
C         -0.88247        5.01239       -2.33469
C         -0.89874        6.37794       -2.62113
N         -0.20531        8.70209       -2.08560
H          1.06595        7.51668       -0.04420
H          1.10112        5.04651        0.47646
H         -1.43632        4.31610       -2.98513
H         -1.44941        6.78433       -3.48182
O          0.19697       -8.83363        3.96743
O          2.09274       -9.02339        2.88498
O          0.42721        9.45362       -1.33134
O         -0.84799        9.08038       -3.07464

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1                        0.00        0.00000         -       -
     2                        0.00        0.00000         -       -
     3                        0.00        0.00000         -       -
     4                        0.00        0.00000         -       -
     5                        0.00        0.00000         -       -
     6                        0.00        0.00000         -       -
     7        a               7.97        0.93724       YES     YES
     8        a               9.61        0.90920       YES     YES
     9        a              12.50        0.74822       YES     YES
    10        a              14.03        0.45632       YES     YES
    11        a              15.03        0.26518       YES     YES
    12        a              16.93        0.11791       YES     YES
    13        a              18.54        0.11897       YES     YES
    14        a              23.76        0.00600       YES     YES
    15        a              24.97        0.09444       YES     YES
    16        a              25.70        0.04708       YES     YES
    17        a              29.46        0.04086       YES     YES
    18        a              30.64        0.11069       YES     YES
```

19	a	32.36	0.11539	YES	YES
20	a	34.07	0.04354	YES	YES
21	a	36.77	0.06864	YES	YES
22	a	37.23	0.13466	YES	YES
23	a	39.31	0.05882	YES	YES
24	a	43.72	0.00857	YES	YES
25	a	45.28	0.13094	YES	YES
26	a	47.45	0.11721	YES	YES
27	a	49.22	0.17009	YES	YES
28	a	50.32	0.06909	YES	YES
29	a	53.27	0.12928	YES	YES
30	a	55.40	0.14373	YES	YES
31	a	57.96	0.48882	YES	YES
32	a	59.25	0.14563	YES	YES
33	a	63.88	0.02511	YES	YES
34	a	68.20	0.23011	YES	YES
35	a	71.87	0.12358	YES	YES
36	a	73.10	0.03531	YES	YES
37	a	74.53	0.28821	YES	YES
38	a	76.00	0.02188	YES	YES
39	a	80.88	0.48807	YES	YES
40	a	86.95	0.16394	YES	YES
41	a	88.60	0.12583	YES	YES
42	a	96.27	0.79911	YES	YES
43	a	100.22	2.02203	YES	YES
44	a	106.67	0.30281	YES	YES
45	a	124.95	1.68536	YES	YES
46	a	125.93	0.02343	YES	YES
47	a	146.39	0.27583	YES	YES
48	a	149.01	0.00738	YES	YES
49	a	158.95	0.47087	YES	YES
50	a	163.13	0.62718	YES	YES

S7.6 Complex $[4a]^+$

SCF Energy (au) (RI)BP86/SV(P) -4415.1264505100
SCF Energy (au) PBE0/def2-TZVPP -4414.460118520
SCF Energy (au) PBE0/def2-TZVPP -4414.5281117027 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9847536
Chemical potential (kJ mol^{-1}) 2280.76
Dispersion correction (au) PBE0/def2-TZVPP -0.25513376

xyz coordinates

130

C	1.71823	-1.97370	2.69977
C	2.10892	-2.07960	4.05573
H	2.20761	-1.17702	4.68255
C	2.39329	-3.33393	4.61626
H	2.69532	-3.40401	5.67413
C	2.30619	-4.49611	3.82684
H	2.53553	-5.48032	4.26692
C	1.93533	-4.39627	2.47687
H	1.87201	-5.30162	1.85165
C	1.64064	-3.14112	1.91317
H	1.34971	-3.07283	0.85516
C	3.05171	0.46709	2.26154
C	4.10506	0.08284	1.39927
H	3.90726	-0.60263	0.55798
C	5.40751	0.56190	1.61308
H	6.22190	0.24653	0.94041
C	5.67383	1.43267	2.68536
H	6.69702	1.80561	2.85469
C	4.63301	1.81703	3.54691
H	4.83801	2.48958	4.39596
C	3.32752	1.33494	3.34021
H	2.53041	1.63321	4.04094
C	-2.41124	1.80757	2.49713
C	-3.42874	2.21431	1.60677
H	-3.54378	1.71478	0.63107
C	-4.32282	3.23839	1.96565
H	-5.12099	3.53529	1.26566
C	-4.20240	3.87451	3.21218
H	-4.90392	4.67615	3.49542
C	-3.18795	3.47865	4.10132
H	-3.09011	3.96989	5.08314
C	-2.30191	2.44694	3.75106
H	-1.52980	2.13759	4.47385
C	-2.32902	-0.99952	2.87474
C	-1.71549	-1.99911	3.66220
H	-0.62542	-2.01327	3.81219
C	-2.48764	-3.01163	4.25798
H	-1.99017	-3.77869	4.87335
C	-3.87962	-3.04563	4.07325
H	-4.48358	-3.83731	4.54568
C	-4.49745	-2.05755	3.28693

H	-5.59016	-2.06866	3.14193
C	-3.73074	-1.04139	2.69336
H	-4.24053	-0.26637	2.09967
C	0.18750	0.52064	3.14662
H	0.12422	0.11709	4.17972
H	0.42509	1.60632	3.18905
C	-1.08268	0.46250	-3.43327
C	-0.04054	1.16365	-4.07974
H	0.51511	1.95787	-3.55518
C	0.30500	0.85316	-5.40510
H	1.11242	1.41470	-5.90238
C	-0.37143	-0.16887	-6.09290
H	-0.09794	-0.41006	-7.13295
C	-1.39773	-0.88138	-5.44999
H	-1.93451	-1.68265	-5.98361
C	-1.75386	-0.56971	-4.12739
H	-2.57178	-1.12631	-3.64207
C	-3.35062	0.56805	-1.67232
C	-3.91734	-0.54709	-1.02119
H	-3.26915	-1.25600	-0.48156
C	-5.30749	-0.75861	-1.06364
H	-5.74080	-1.63932	-0.56251
C	-6.13818	0.14746	-1.74343
H	-7.22751	-0.01792	-1.77431
C	-5.57803	1.26383	-2.39246
H	-6.22658	1.97258	-2.93297
C	-4.18988	1.47067	-2.36610
H	-3.76051	2.33526	-2.90017
C	1.69248	3.18587	-1.14418
C	2.99644	2.83933	-0.72944
H	3.14400	2.06652	0.04187
C	4.11710	3.47357	-1.29305
H	5.12726	3.19639	-0.95007
C	3.95050	4.45199	-2.28740
H	4.82891	4.94702	-2.73245
C	2.65566	4.80281	-2.70640
H	2.51368	5.57610	-3.47896
C	1.53301	4.18209	-2.13276
H	0.53054	4.50558	-2.45604
C	0.06002	3.78248	1.04851
C	1.08621	3.90566	2.01353
H	1.94426	3.21302	2.00540
C	1.05180	4.93464	2.96809
H	1.86669	5.02151	3.70548
C	-0.00588	5.86041	2.97068
H	-0.03003	6.67352	3.71428
C	-1.02435	5.75030	2.01076
H	-1.85291	6.47674	1.99611
C	-0.99358	4.71933	1.05536
H	-1.80342	4.66938	0.31189
C	-1.23058	2.63582	-1.39322
H	-2.09763	3.03153	-0.82461
H	-1.09142	3.25550	-2.30330
C	-0.40011	-2.11421	-0.63932
C	0.63087	-1.58425	-1.21487
C	1.46305	-0.51885	-1.41093

C	2.55891	-0.19116	-2.14844
H	2.94209	0.83936	-2.07028
C	3.30296	-1.06159	-3.06232
C	3.00087	-2.43564	-3.26069
H	2.16679	-2.89515	-2.70658
C	3.74793	-3.21912	-4.14271
H	3.52824	-4.28404	-4.30567
C	4.81476	-2.62986	-4.84247
N	5.60942	-3.46071	-5.78263
C	5.14832	-1.27788	-4.67441
H	5.99163	-0.85899	-5.24208
C	4.39320	-0.50534	-3.78640
H	4.64381	0.55915	-3.64500
C	-1.21135	-3.30378	-0.63900
C	-1.09584	-4.22197	-1.72709
H	-0.39774	-3.99546	-2.54837
C	-1.86255	-5.38741	-1.76848
H	-1.78668	-6.10307	-2.59998
C	-2.75842	-5.64934	-0.71758
C	-2.89688	-4.77247	0.36772
H	-3.60495	-5.02126	1.17063
C	-2.12757	-3.60446	0.40312
H	-2.21908	-2.91600	1.25399
P	1.39196	-0.29690	1.96863
P	-1.33926	0.35691	2.06961
P	0.24203	2.45275	-0.24351
P	-1.52239	0.80938	-1.67595
Ru	-0.02983	0.09764	0.03875
O	6.53905	-2.90986	-6.37585
O	5.28331	-4.64342	-5.90495
N	-3.58140	-6.88509	-0.75866
O	-3.42641	-7.63412	-1.72491
O	-4.36284	-7.07394	0.17651

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	11.24	0.04966	YES	YES
8	a	14.23	0.58100	YES	YES
9	a	16.84	0.51049	YES	YES
10	a	20.04	0.16311	YES	YES
11	a	22.48	0.19931	YES	YES
12	a	24.09	0.10877	YES	YES
13	a	27.25	0.00640	YES	YES
14	a	30.53	0.06394	YES	YES
15	a	30.96	0.11481	YES	YES
16	a	35.88	0.00857	YES	YES
17	a	38.25	0.02175	YES	YES

18	a	39.41	0.13811	YES	YES
19	a	41.11	0.07873	YES	YES
20	a	43.20	0.18312	YES	YES
21	a	43.57	0.13303	YES	YES
22	a	45.62	0.05928	YES	YES
23	a	47.98	0.11543	YES	YES
24	a	49.64	0.05758	YES	YES
25	a	50.42	0.05554	YES	YES
26	a	51.36	0.01825	YES	YES
27	a	53.13	0.07725	YES	YES
28	a	57.30	0.05413	YES	YES
29	a	59.58	0.03909	YES	YES
30	a	60.19	0.27577	YES	YES
31	a	62.85	0.04280	YES	YES
32	a	64.26	0.30615	YES	YES
33	a	67.70	0.37652	YES	YES
34	a	68.35	0.02852	YES	YES
35	a	74.76	0.17936	YES	YES
36	a	75.82	0.13189	YES	YES
37	a	79.66	0.21202	YES	YES
38	a	81.70	0.41244	YES	YES
39	a	85.20	0.30745	YES	YES
40	a	90.55	0.08056	YES	YES
41	a	95.64	0.46826	YES	YES
42	a	100.64	0.44060	YES	YES
43	a	106.19	0.48920	YES	YES
44	a	110.39	0.21825	YES	YES
45	a	132.02	1.21286	YES	YES
46	a	141.59	0.89693	YES	YES
47	a	149.76	0.48134	YES	YES
48	a	159.62	0.38742	YES	YES
49	a	162.68	0.05242	YES	YES
50	a	164.90	0.77574	YES	YES

S7.7 Complex $[4'a]^+$

S7.8 Complex $TS_{[Da]+-[4'a]}$

SCF Energy (au) (RI)BP86/SV(P) -4415.0822987510
SCF Energy (au) PBE0/def2-TZVPP -4414.415216112
SCF Energy (au) PBE0/def2-TZVPP -4414.4830294445 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9817220
Chemical potential (kJ mol^{-1}) 2264.65
Dispersion correction (au) PBE0/def2-TZVPP -0.25228148

xyz coordinates

130

C	-1.32138	0.33367	-0.78259
C	-0.42178	1.56762	0.67832
Ru	0.37552	-0.08339	0.27804
P	-0.85173	-1.42555	1.85305
P	1.83745	-0.64259	2.14511
P	1.37738	-1.89991	-1.15572
P	1.92939	0.88700	-1.25722
C	0.67100	-1.95868	2.81018
C	2.72439	-0.73003	-1.76256
C	-1.72869	-2.96722	1.34850
C	-2.21523	-3.09052	0.03033
C	-2.91202	-4.24963	-0.35557
C	-3.12100	-5.28811	0.56698
C	-2.63829	-5.16728	1.88366
C	-1.94918	-4.00953	2.27746
C	-2.02688	-0.65672	3.04815
C	-3.01140	0.21270	2.52597
C	-3.97908	0.77458	3.37524
C	-3.97120	0.47919	4.74949
C	-2.99153	-0.38120	5.27458
C	-2.02274	-0.94854	4.42972
C	1.98004	0.59315	3.52654
C	0.84143	1.34094	3.90192
C	0.90591	2.24865	4.97159
C	2.11283	2.43800	5.66766
C	3.25061	1.70485	5.29443
C	3.18742	0.78301	4.23427
C	3.51855	-1.40736	2.12237
C	3.80343	-2.60460	2.81323
C	5.11125	-3.11858	2.83356
C	6.14903	-2.44197	2.17081
C	5.87528	-1.24509	1.48605
C	4.56834	-0.72994	1.45986
C	0.57330	-2.53194	-2.70408
C	-0.52055	-1.83620	-3.26307
C	-1.10994	-2.28505	-4.45801
C	-0.61824	-3.43151	-5.10391
C	0.46931	-4.12993	-4.55078
C	1.06283	-3.68722	-3.35740
C	2.24480	-3.41533	-0.54617
C	1.46069	-4.40900	0.08609

C	2.04632	-5.61144	0.51487
C	3.42001	-5.83813	0.31804
C	4.20390	-4.85733	-0.31169
C	3.62161	-3.65223	-0.74265
C	1.34275	1.72096	-2.79351
C	1.23372	1.06405	-4.03733
C	0.77654	1.76325	-5.16888
C	0.41811	3.11769	-5.06864
C	0.51704	3.77610	-3.82884
C	0.97632	3.08423	-2.69750
C	3.28374	2.00889	-0.70331
C	3.18228	2.68454	0.53066
C	4.20504	3.55813	0.94256
C	5.33458	3.75260	0.13062
C	5.44032	3.08022	-1.10169
C	4.41661	2.21787	-1.52365
H	0.59997	-2.02044	3.91638
H	0.98321	-2.94636	2.40507
H	3.02675	-0.84314	-2.82503
H	3.62101	-0.85467	-1.11771
H	-2.05062	-2.27543	-0.69236
H	-3.29087	-4.33906	-1.38647
H	-3.66629	-6.19630	0.26226
H	-2.80658	-5.97779	2.61162
H	-1.59017	-3.92078	3.31677
H	-3.01680	0.45136	1.44989
H	-4.74238	1.45153	2.95842
H	-4.73096	0.92116	5.41459
H	-2.97979	-0.61627	6.35139
H	-1.26609	-1.62061	4.86586
H	-0.11104	1.20718	3.36531
H	0.00431	2.81253	5.26170
H	2.16470	3.15596	6.50232
H	4.20109	1.84296	5.83537
H	4.08833	0.21063	3.96680
H	3.01075	-3.14608	3.35310
H	5.31923	-4.05317	3.37937
H	7.17506	-2.84407	2.19438
H	6.68558	-0.70097	0.97383
H	4.37380	0.22537	0.94494
H	-0.91610	-0.94144	-2.75820
H	-1.96587	-1.73409	-4.88076
H	-1.08553	-3.78541	-6.03749
H	0.85895	-5.03297	-5.04863
H	1.90738	-4.25347	-2.93436
H	0.37674	-4.25635	0.22141
H	1.42042	-6.38011	0.99700
H	3.87814	-6.78450	0.64888
H	5.27935	-5.03084	-0.47875
H	4.25681	-2.90670	-1.24633
H	1.50191	0.00203	-4.14375
H	0.70833	1.24173	-6.13715
H	0.06767	3.66502	-5.95888
H	0.24078	4.83902	-3.74206
H	1.06096	3.61559	-1.73551
H	2.29921	2.52554	1.17019

```
H          4.11611        4.08746        1.90494
H          6.13660        4.43577        0.45484
H          6.32273        3.23696       -1.74351
H          4.49855        1.71406       -2.50165
C         -2.40746        0.56432       -1.35464
C         -3.61693        0.78004       -2.07776
C         -0.90878        2.76547        1.02233
H         -0.43456        3.07779        1.98093
C         -1.90995        3.70376        0.49732
C         -5.99195        1.19624       -3.51841
C         -6.06607        0.68125       -2.21482
C         -4.88246        0.47245       -1.50099
C         -3.58346        1.30316       -3.40357
C         -4.76440        1.50918       -4.12302
N         -7.24938        1.41505       -4.28184
H         -7.05229        0.45341       -1.78552
H         -4.92316        0.06334       -0.47962
H         -2.61074        1.54611       -3.85972
H         -4.76079        1.91213       -5.14595
C         -3.85055        5.53276       -0.38870
C         -3.49495        5.52026        0.96840
C         -2.52320        4.61271        1.40118
C         -2.27667        3.76276       -0.87135
C         -3.24504        4.66975       -1.31470
N         -4.88669        6.48702       -0.85781
H         -3.98750        6.21977        1.65900
H         -2.23890        4.59295        2.46619
H         -1.78120        3.09767       -1.59292
H         -3.54241        4.72800       -2.37134
O         -8.30798        1.14305       -3.71329
O         -7.14248        1.84997       -5.42979
O         -5.15739        6.48060       -2.06075
O         -5.40626        7.21800       -0.01200

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1        a            -167.54         0.00000       YES     YES
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7                        0.00         0.00000        -       -
     8        a               7.31         0.06810       YES     YES
     9        a               9.07         0.20773       YES     YES
    10        a              12.50         0.34022       YES     YES
    11        a              14.27         0.34359       YES     YES
    12        a              16.94         0.09446       YES     YES
    13        a              21.26         0.22390       YES     YES
    14        a              24.68         0.06506       YES     YES
    15        a              25.91         0.09234       YES     YES
    16        a              27.33         0.05194       YES     YES
    17        a              31.58         0.11584       YES     YES
```

18	a	33.18	0.02877	YES	YES
19	a	34.30	0.08693	YES	YES
20	a	37.91	0.15189	YES	YES
21	a	40.41	0.09302	YES	YES
22	a	41.55	0.10566	YES	YES
23	a	42.42	0.17594	YES	YES
24	a	43.97	0.00965	YES	YES
25	a	46.18	0.04070	YES	YES
26	a	48.25	0.17003	YES	YES
27	a	51.81	0.02402	YES	YES
28	a	52.32	0.27070	YES	YES
29	a	54.99	0.26180	YES	YES
30	a	58.66	0.45749	YES	YES
31	a	60.92	0.10825	YES	YES
32	a	62.00	0.03849	YES	YES
33	a	62.98	0.03195	YES	YES
34	a	65.15	0.18977	YES	YES
35	a	66.52	0.59513	YES	YES
36	a	70.12	0.11553	YES	YES
37	a	73.77	0.05614	YES	YES
38	a	78.99	0.39562	YES	YES
39	a	81.24	0.17375	YES	YES
40	a	87.35	4.27660	YES	YES
41	a	95.38	3.34393	YES	YES
42	a	98.01	3.11575	YES	YES
43	a	98.94	0.77228	YES	YES
44	a	103.81	2.09470	YES	YES
45	a	111.20	4.30521	YES	YES
46	a	114.17	4.29656	YES	YES
47	a	134.90	0.90579	YES	YES
48	a	141.67	1.78940	YES	YES
49	a	151.27	1.45347	YES	YES
50	a	158.36	1.31688	YES	YES

S7.9 Complex [Cd]

SCF Energy (au) (RI)BP86/SV(P) -4005.8897602980
SCF Energy (au) PBE0/def2-TZVPP -4005.234579914
SCF Energy (au) PBE0/def2-TZVPP -4005.2659683361 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9650456
Chemical potential (kJ mol^{-1}) 2240.46
Dispersion correction (au) PBE0/def2-TZVPP -0.24089199

xyz coordinates

125

Ru	0.04707	-0.04531	0.00888
C	-1.55517	0.18093	-1.18761
C	-0.42487	1.75912	0.76419
P	-1.26110	-1.20076	1.59560
P	1.42347	-0.43221	1.98640
P	0.83978	-1.78455	-1.50880
P	1.51823	0.95214	-1.54144
C	0.10423	-1.47713	2.85385
C	2.04922	-0.63121	-2.39854
C	-1.99667	-2.86658	1.25527
C	-2.58540	-3.07936	-0.01038
C	-3.19980	-4.30904	-0.30414
C	-3.22278	-5.33726	0.65389
C	-2.63222	-5.13293	1.91359
C	-2.02563	-3.90192	2.21576
C	-2.64216	-0.36568	2.50533
C	-3.39830	0.61507	1.82896
C	-4.49134	1.22415	2.47096
C	-4.82908	0.87087	3.78839
C	-4.07319	-0.10104	4.46852
C	-2.98708	-0.72014	3.82835
C	1.77901	0.90102	3.23114
C	0.70801	1.58726	3.84739
C	0.96013	2.62112	4.76435
C	2.28050	2.99201	5.07029
C	3.35047	2.32248	4.45310
C	3.10294	1.28524	3.53725
C	2.97001	-1.45025	2.12790
C	3.22622	-2.25551	3.26009
C	4.41706	-2.99353	3.35565
C	5.37381	-2.92578	2.32693
C	5.13467	-2.11567	1.20481
C	3.93724	-1.38596	1.10501
C	-0.20055	-2.44500	-2.89959
C	-0.73662	-1.55445	-3.85731
C	-1.55363	-2.03377	-4.89462
C	-1.85615	-3.40306	-4.98460
C	-1.33661	-4.29313	-4.02965
C	-0.51610	-3.81834	-2.99172
C	1.85925	-3.28320	-1.10538
C	1.57761	-4.01779	0.06382

C	2.30784	-5.17842	0.37368
C	3.33533	-5.61237	-0.47992
C	3.62151	-4.88914	-1.65180
C	2.88401	-3.73620	-1.96602
C	0.90280	2.08117	-2.87525
C	1.54136	2.16803	-4.13214
C	1.07874	3.07252	-5.10193
C	-0.02004	3.90426	-4.81996
C	-0.65610	3.82338	-3.56962
C	-0.20377	2.91180	-2.59877
C	3.07658	1.80894	-1.02281
C	3.01354	2.66387	0.09931
C	4.15443	3.37612	0.50772
C	5.36652	3.23438	-0.18971
C	5.43662	2.37924	-1.30374
C	4.29627	1.67260	-1.72212
H	-0.12206	-1.15557	3.89261
H	0.41896	-2.54211	2.86639
H	1.95484	-0.63699	-3.50520
H	3.09155	-0.89854	-2.12395
H	-2.55924	-2.27293	-0.76424
H	-3.65713	-4.46232	-1.29523
H	-3.70169	-6.30265	0.41947
H	-2.64749	-5.93572	2.66983
H	-1.57832	-3.75368	3.21344
H	-3.12186	0.90085	0.80084
H	-5.07630	1.98880	1.93411
H	-5.68387	1.35481	4.29003
H	-4.33263	-0.38301	5.50273
H	-2.41313	-1.49049	4.37109
H	-0.33452	1.32766	3.60601
H	0.11252	3.14913	5.23060
H	2.47481	3.80640	5.78796
H	4.39093	2.60387	4.68738
H	3.95327	0.76834	3.06520
H	2.49628	-2.30008	4.08586
H	4.60284	-3.62046	4.24386
H	6.30958	-3.50410	2.40324
H	5.88266	-2.05229	0.39760
H	3.75596	-0.74623	0.22631
H	-0.53035	-0.47468	-3.79336
H	-1.96778	-1.32392	-5.62892
H	-2.50076	-3.77547	-5.79813
H	-1.56577	-5.37028	-4.09186
H	-0.11408	-4.53017	-2.25364
H	0.76776	-3.68396	0.73236
H	2.07331	-5.74373	1.29048
H	3.91363	-6.51859	-0.23441
H	4.42081	-5.22983	-2.33115
H	3.10387	-3.19325	-2.90068
H	2.41318	1.53269	-4.36390
H	1.58264	3.13083	-6.08126
H	-0.38089	4.61733	-5.58010
H	-1.52063	4.46898	-3.34398
H	-0.70964	2.83583	-1.62235
H	2.06250	2.76734	0.65085

H	4.09202	4.04119	1.38444
H	6.26141	3.79096	0.13535
H	6.38474	2.26408	-1.85546
H	4.36547	1.01573	-2.60599
C	-2.59142	0.32540	-1.86608
C	-3.77156	0.49154	-2.65482
C	-0.71033	2.90577	1.16254
C	-1.04174	4.21408	1.63259
C	-6.12725	0.82094	-4.23151
C	-6.17429	0.10320	-3.02204
C	-5.01906	-0.06080	-2.24533
C	-3.74540	1.21644	-3.88089
C	-4.90483	1.37576	-4.65304
H	-7.03794	0.94917	-4.84011
H	-7.12692	-0.33521	-2.67825
H	-5.06469	-0.62274	-1.29837
H	-2.79294	1.66208	-4.21061
H	-4.85492	1.94495	-5.59730
C	-1.70131	6.82605	2.57414
C	-2.31268	5.69065	3.13707
C	-1.99159	4.40573	2.67686
C	-0.43573	5.37638	1.07506
C	-0.76220	6.65785	1.53975
H	-1.95692	7.83554	2.93714
H	-3.05453	5.80858	3.94569
H	-2.48171	3.52076	3.11389
H	0.29948	5.25328	0.26331
H	-0.27704	7.53978	1.08727

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	15.25	0.00944	YES	YES
8	a	16.55	0.02340	YES	YES
9	a	17.80	0.01367	YES	YES
10	a	19.30	0.01641	YES	YES
11	a	20.04	0.00792	YES	YES
12	a	22.93	0.02213	YES	YES
13	a	23.30	0.02157	YES	YES
14	a	26.80	0.00288	YES	YES
15	a	26.87	0.01374	YES	YES
16	a	30.38	0.19010	YES	YES
17	a	30.70	0.15127	YES	YES
18	a	34.26	0.08204	YES	YES
19	a	37.96	0.03428	YES	YES
20	a	40.66	0.07730	YES	YES
21	a	43.70	0.00790	YES	YES
22	a	46.31	0.08035	YES	YES

23	a	47.40	0.10623	YES	YES
24	a	50.35	0.02872	YES	YES
25	a	50.68	0.06873	YES	YES
26	a	51.51	0.01286	YES	YES
27	a	52.60	0.45237	YES	YES
28	a	53.10	0.01133	YES	YES
29	a	57.10	0.00825	YES	YES
30	a	60.09	0.03975	YES	YES
31	a	60.57	0.22618	YES	YES
32	a	66.10	0.21308	YES	YES
33	a	67.91	0.19854	YES	YES
34	a	80.48	2.16842	YES	YES
35	a	80.90	0.42823	YES	YES
36	a	89.58	1.08432	YES	YES
37	a	95.30	0.53537	YES	YES
38	a	102.76	0.70443	YES	YES
39	a	104.00	1.73217	YES	YES
40	a	108.92	1.45955	YES	YES
41	a	112.64	1.28138	YES	YES
42	a	117.31	0.10068	YES	YES
43	a	122.38	1.66180	YES	YES
44	a	147.21	0.88898	YES	YES
45	a	150.04	1.93862	YES	YES
46	a	161.15	0.00536	YES	YES
47	a	161.59	0.88328	YES	YES
48	a	162.04	0.29980	YES	YES
49	a	166.79	0.08763	YES	YES
50	a	169.88	0.03545	YES	YES

S7.10 Complex $[Dd]^+$

SCF Energy (au) (RI)BP86/SV(P) -4006.3163698720
SCF Energy (au) PBE0/def2-TZVPP -4005.659314730
SCF Energy (au) PBE0/def2-TZVPP -4005.7137581801 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9775050
Chemical potential (kJ mol^{-1}) 2273.10
Dispersion correction (au) PBE0/def2-TZVPP -0.24387311

xyz coordinates

126

Ru	0.11676	0.13636	0.20484
C	-1.42861	0.21323	-1.10937
C	-0.33778	1.77626	0.92059
P	-1.17323	-1.14464	1.77437
P	1.54623	-0.41845	2.13572
P	1.00668	-1.74233	-1.32901
P	1.64800	1.06666	-1.39814
C	0.27764	-1.58380	2.88551
C	2.26496	-0.56488	-2.08310
C	-1.95535	-2.75655	1.32892
C	-2.47230	-2.94477	0.02980
C	-3.11607	-4.15115	-0.29990
C	-3.24245	-5.17223	0.65641
C	-2.72556	-4.98842	1.95218
C	-2.08747	-3.78463	2.29083
C	-2.44874	-0.32818	2.82372
C	-3.31552	0.59491	2.20050
C	-4.35265	1.19386	2.93442
C	-4.53004	0.87922	4.29223
C	-3.66992	-0.04075	4.91779
C	-2.63381	-0.64622	4.18782
C	1.80545	0.87252	3.44171
C	0.69638	1.39057	4.14900
C	0.88243	2.36630	5.14283
C	2.17096	2.84723	5.43258
C	3.27496	2.34522	4.72374
C	3.09718	1.36190	3.73512
C	3.15830	-1.31432	2.14284
C	3.42003	-2.35002	3.06624
C	4.68311	-2.96290	3.10261
C	5.69981	-2.54124	2.22824
C	5.44967	-1.50367	1.31475
C	4.18364	-0.89538	1.26756
C	0.04694	-2.35555	-2.78629
C	-0.38383	-1.44648	-3.77895
C	-1.11227	-1.90452	-4.88862
C	-1.42918	-3.26749	-5.01625
C	-1.01075	-4.17420	-4.02848
C	-0.27724	-3.72387	-2.91760
C	1.95835	-3.24316	-0.82368
C	1.39688	-4.10465	0.14462

C	2.04742	-5.29946	0.49780
C	3.26966	-5.64096	-0.10464
C	3.83413	-4.78926	-1.07009
C	3.18072	-3.60019	-1.43332
C	1.03654	2.06821	-2.82261
C	1.62022	1.98358	-4.10616
C	1.18305	2.82954	-5.13872
C	0.16970	3.77358	-4.89577
C	-0.40977	3.86539	-3.61881
C	0.01588	3.01324	-2.58615
C	3.16917	1.99606	-0.90315
C	3.09972	2.90162	0.17677
C	4.22444	3.66519	0.53403
C	5.42781	3.52675	-0.17780
C	5.50414	2.62573	-1.25500
C	4.38029	1.86663	-1.62047
H	0.12976	-1.46322	3.97926
H	0.58392	-2.63047	2.67538
H	2.34150	-0.63577	-3.18836
H	3.25945	-0.77918	-1.63835
H	-2.37260	-2.14285	-0.72106
H	-3.51841	-4.28930	-1.31642
H	-3.74760	-6.11645	0.39466
H	-2.82595	-5.78527	2.70732
H	-1.70032	-3.65085	3.31519
H	-3.17844	0.84343	1.13557
H	-5.01884	1.91839	2.43937
H	-5.34176	1.35321	4.86799
H	-3.80697	-0.29292	5.98212
H	-1.97669	-1.37143	4.69603
H	-0.32660	1.04104	3.93329
H	0.00858	2.75059	5.69384
H	2.31457	3.61051	6.21466
H	4.29043	2.71098	4.94773
H	3.97734	0.96666	3.20466
H	2.64374	-2.68012	3.77570
H	4.87563	-3.77170	3.82627
H	6.69163	-3.02076	2.26305
H	6.24508	-1.16131	0.63291
H	4.00343	-0.06949	0.55979
H	-0.16169	-0.37138	-3.69372
H	-1.44099	-1.18414	-5.65465
H	-2.00215	-3.62297	-5.88817
H	-1.24723	-5.24675	-4.12345
H	0.05357	-4.45188	-2.16090
H	0.42661	-3.85687	0.60686
H	1.59251	-5.96801	1.24687
H	3.78169	-6.57663	0.17338
H	4.78772	-5.05682	-1.55400
H	3.62793	-2.96070	-2.21181
H	2.42748	1.26231	-4.31570
H	1.64292	2.75367	-6.13765
H	-0.16742	4.44083	-5.70591
H	-1.20494	4.60185	-3.41999
H	-0.45048	3.08587	-1.59181
H	2.15778	3.01515	0.73589

H	4.15728	4.37301	1.37607
H	6.30940	4.12559	0.10352
H	6.44368	2.51839	-1.82159
H	4.45478	1.17743	-2.47843
C	-2.42396	0.30742	-1.84766
C	-3.56211	0.41358	-2.71172
C	-0.62414	2.98370	1.41067
H	0.10211	3.34047	2.17280
C	-1.75151	3.88416	1.10818
C	-5.81987	0.63306	-4.42280
C	-5.90550	-0.10540	-3.22862
C	-4.79401	-0.21491	-2.38141
C	-3.49280	1.15763	-3.92160
C	-4.60952	1.26393	-4.76292
H	-6.69609	0.71886	-5.08616
H	-6.85161	-0.60048	-2.95322
H	-4.86705	-0.79068	-1.44470
H	-2.54734	1.65806	-4.18571
H	-4.53592	1.84791	-5.69559
C	-3.88728	5.67601	0.57625
C	-2.93195	5.98550	1.55985
C	-1.87515	5.10110	1.82325
C	-2.71984	3.58291	0.11466
C	-3.77353	4.47171	-0.14355
H	-4.71623	6.37205	0.36841
H	-3.00821	6.92719	2.12832
H	-1.12983	5.35366	2.59636
H	-2.63827	2.64611	-0.46229
H	-4.51439	4.21935	-0.92023

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	11.81	0.03356	YES	YES
8	a	14.41	0.01212	YES	YES
9	a	17.13	0.02411	YES	YES
10	a	19.33	0.02770	YES	YES
11	a	22.33	0.01069	YES	YES
12	a	22.66	0.02580	YES	YES
13	a	25.97	0.03545	YES	YES
14	a	28.83	0.01417	YES	YES
15	a	30.87	0.00881	YES	YES
16	a	32.87	0.00058	YES	YES
17	a	33.95	0.02518	YES	YES
18	a	38.16	0.09023	YES	YES
19	a	39.06	0.06645	YES	YES
20	a	40.25	0.02522	YES	YES
21	a	42.69	0.06671	YES	YES

22	a	42.84	0.12992	YES	YES
23	a	45.89	0.07015	YES	YES
24	a	46.77	0.01759	YES	YES
25	a	48.68	0.17605	YES	YES
26	a	52.71	0.01235	YES	YES
27	a	54.71	0.01624	YES	YES
28	a	58.91	0.05827	YES	YES
29	a	59.04	0.03245	YES	YES
30	a	60.14	0.35697	YES	YES
31	a	62.15	0.03997	YES	YES
32	a	67.26	0.30118	YES	YES
33	a	68.14	0.08979	YES	YES
34	a	76.21	0.83817	YES	YES
35	a	80.49	1.08663	YES	YES
36	a	83.74	0.27596	YES	YES
37	a	90.71	0.15417	YES	YES
38	a	95.75	1.01832	YES	YES
39	a	103.57	0.45290	YES	YES
40	a	109.26	1.80749	YES	YES
41	a	115.04	1.76053	YES	YES
42	a	117.42	0.46659	YES	YES
43	a	122.92	0.62742	YES	YES
44	a	142.93	1.21886	YES	YES
45	a	148.88	0.23540	YES	YES
46	a	156.96	0.20793	YES	YES
47	a	161.10	0.65991	YES	YES
48	a	163.64	0.16685	YES	YES
49	a	168.23	1.03451	YES	YES
50	a	170.68	1.23554	YES	YES

S7.11 Complex $[Fd]^+$

SCF Energy (au) (RI)BP86/SV(P) -4006.3208473510
SCF Energy (au) PBE0/def2-TZVPP -4005.665619968
SCF Energy (au) PBE0/def2-TZVPP -4005.7168549260 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9777822
Chemical potential (kJ mol^{-1}) 2276.11
Dispersion correction (au) PBE0/def2-TZVPP -0.24495152

xyz coordinates

126

C	0.36510	-1.87027	0.29365
C	-1.66002	-0.16722	-2.74572
C	1.03384	0.76232	-3.63289
C	0.61762	-2.03899	-3.08413
C	1.62275	0.23323	2.62828
C	-0.91722	1.72554	3.15986
C	-0.95301	-1.12329	3.34944
C	3.59523	-0.73398	0.62277
P	-2.21615	-0.22817	-0.94951
C	-0.06846	1.97074	-0.59836
P	2.19921	0.44329	0.84667
P	0.18426	-0.36337	-2.44832
P	-0.22571	0.23453	2.32209
Ru	0.00013	0.13860	-0.09116
C	0.65870	-3.06134	0.51065
C	-3.11439	-1.82587	-0.75937
C	-3.57287	1.01858	-0.77147
C	3.01804	2.09729	0.80846
H	-1.84352	0.85192	-3.14852
H	-2.12054	-0.91638	-3.42410
H	1.98007	1.02586	3.31849
H	1.95698	-0.75280	3.01187
C	-2.12954	-3.18064	4.89257
C	-0.83601	-3.34188	4.36803
C	-0.25141	-2.32426	3.59562
C	-2.25587	-0.96923	3.87804
C	-2.83851	-1.99326	4.64235
H	-2.58409	-3.97974	5.50084
H	-0.27097	-4.26928	4.55459
H	0.75272	-2.48739	3.17734
H	-2.82088	-0.03922	3.70745
H	-3.85176	-1.85432	5.05357
C	-2.18694	3.83812	4.53472
C	-1.03314	3.23976	5.07284
C	-0.40725	2.18023	4.39685
C	-2.06933	2.33589	2.62016
C	-2.70686	3.38161	3.31234
H	-2.68295	4.66158	5.07410
H	-0.62330	3.59205	6.03351
H	0.47398	1.69965	4.85319
H	-2.47541	1.98912	1.65538

H	-3.61163	3.84360	2.88549
C	5.77869	-2.48020	0.26124
C	4.74765	-2.43494	-0.69194
C	3.65493	-1.56923	-0.51062
C	4.63512	-0.78238	1.57999
C	5.71960	-1.65571	1.39998
H	6.63216	-3.16348	0.11995
H	4.78206	-3.08798	-1.57870
H	2.83295	-1.56526	-1.24295
H	4.60879	-0.12833	2.46811
H	6.52583	-1.68839	2.15102
C	4.20235	4.66037	0.68206
C	4.83888	3.55955	0.08529
C	4.25211	2.28340	0.14596
C	2.37631	3.21303	1.39198
C	2.97000	4.48367	1.33511
H	4.66661	5.65909	0.63847
H	5.80810	3.68881	-0.42400
H	4.77170	1.42613	-0.31137
H	1.40105	3.10148	1.89430
H	2.45905	5.34295	1.79839
C	1.27838	-4.60946	-4.04681
C	0.13705	-4.42632	-3.24706
C	-0.19021	-3.15167	-2.75891
C	1.76619	-2.22810	-3.88517
C	2.09278	-3.50937	-4.36172
H	1.53255	-5.61276	-4.42574
H	-0.50388	-5.28551	-2.99247
H	-1.07857	-3.03234	-2.11937
H	2.40548	-1.37279	-4.15525
H	2.98584	-3.64268	-4.99409
C	2.40982	2.40991	-5.46438
C	1.19657	1.80310	-5.83625
C	0.51283	0.97836	-4.92828
C	2.25065	1.37526	-3.26523
C	2.93722	2.19297	-4.18002
H	2.94570	3.05471	-6.17992
H	0.78057	1.96896	-6.84341
H	-0.42825	0.49562	-5.24056
H	2.66075	1.22478	-2.25267
H	3.88576	2.66819	-3.88193
C	-4.59293	-4.20211	-0.41030
C	-3.65850	-3.80462	0.55997
C	-2.91444	-2.62280	0.38670
C	-4.06418	-2.22549	-1.72916
C	-4.79392	-3.41160	-1.55728
H	-5.17129	-5.13069	-0.27384
H	-3.49868	-4.41758	1.46149
H	-2.16665	-2.32885	1.13824
H	-4.25180	-1.60321	-2.62050
H	-5.52994	-3.71627	-2.31916
C	-5.61099	2.94518	-0.40990
C	-4.45583	3.26786	-1.14359
C	-3.43914	2.31494	-1.31921
C	-4.73287	0.70387	-0.02663
C	-5.74357	1.66398	0.15172

H	-6.40946	3.69348	-0.27714
H	-4.33776	4.27163	-1.58240
H	-2.53193	2.59929	-1.87542
H	-4.85751	-0.29969	0.40982
H	-6.64631	1.40145	0.72746
C	0.98249	-4.42839	0.78287
C	1.62063	-7.14012	1.34761
C	2.56689	-6.12609	1.58249
C	2.25622	-4.78732	1.30518
C	0.03810	-5.46651	0.55115
C	0.35628	-6.80281	0.83095
H	1.86813	-8.19176	1.56661
H	3.56074	-6.38277	1.98560
H	3.00256	-3.99665	1.48232
H	-0.95436	-5.20336	0.15174
H	-0.39093	-7.59242	0.64514
C	0.11201	3.15961	-1.18339
C	-0.37452	4.52357	-0.92130
H	0.79239	3.07415	-2.06096
C	-1.26561	7.19061	-0.50563
C	-1.51156	6.19766	0.46085
C	-1.07261	4.88172	0.25842
C	-0.12622	5.53619	-1.88301
C	-0.56843	6.85154	-1.67848
H	-1.61010	8.22476	-0.34220
H	-2.04757	6.45350	1.39012
H	-1.25846	4.11856	1.02923
H	0.42282	5.28108	-2.80523
H	-0.36327	7.62044	-2.44166

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	11.62	0.01362	YES	YES
8	a	17.05	0.07188	YES	YES
9	a	17.78	0.00109	YES	YES
10	a	19.86	0.05157	YES	YES
11	a	22.26	0.03034	YES	YES
12	a	24.90	0.00370	YES	YES
13	a	27.41	0.04637	YES	YES
14	a	28.29	0.05288	YES	YES
15	a	29.30	0.04856	YES	YES
16	a	31.86	0.15108	YES	YES
17	a	33.95	0.05342	YES	YES
18	a	34.52	0.09691	YES	YES
19	a	37.22	0.06735	YES	YES
20	a	41.14	0.10546	YES	YES
21	a	43.88	0.02819	YES	YES

22	a	46.52	0.05524	YES	YES
23	a	47.34	0.03431	YES	YES
24	a	49.77	0.10881	YES	YES
25	a	53.03	0.09675	YES	YES
26	a	53.88	0.11859	YES	YES
27	a	54.54	0.02808	YES	YES
28	a	57.53	0.13203	YES	YES
29	a	59.18	0.41566	YES	YES
30	a	60.68	0.51487	YES	YES
31	a	63.52	0.17132	YES	YES
32	a	66.31	0.02627	YES	YES
33	a	68.16	0.01977	YES	YES
34	a	77.77	0.04936	YES	YES
35	a	85.61	0.01358	YES	YES
36	a	88.35	0.03362	YES	YES
37	a	96.63	0.15911	YES	YES
38	a	102.86	2.00384	YES	YES
39	a	105.40	0.55473	YES	YES
40	a	109.11	1.49956	YES	YES
41	a	109.70	4.63037	YES	YES
42	a	119.77	2.33180	YES	YES
43	a	128.66	0.64664	YES	YES
44	a	147.83	0.04790	YES	YES
45	a	150.01	0.76571	YES	YES
46	a	161.21	0.50737	YES	YES
47	a	166.61	0.24600	YES	YES
48	a	176.48	1.24310	YES	YES
49	a	183.63	1.67869	YES	YES
50	a	185.19	0.55041	YES	YES

S7.12 Complex [3d]

SCF Energy (au) (RI)BP86/SV(P) -4005.8933626370
SCF Energy (au) PBE0/def2-TZVPP -4005.241867445
SCF Energy (au) PBE0/def2-TZVPP -4005.2682441185 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9651649
Chemical potential (kJ mol^{-1}) 2232.87
Dispersion correction (au) PBE0/def2-TZVPP -0.24012730

xyz coordinates

125

C	0.19447	-2.01065	0.59673
C	-1.53269	0.16522	-2.75363
C	1.38699	0.71938	-3.37859
C	0.39504	-1.96700	-3.27196
C	1.49721	-0.09645	2.67367
C	-0.65547	1.86630	3.14419
C	-1.33152	-0.88672	3.35425
C	3.58334	-0.78815	0.64095
P	-2.18703	-0.28412	-1.04357
C	-0.13166	1.91803	-0.57589
P	2.09573	0.27949	0.92997
P	0.24294	-0.34098	-2.38427
P	-0.31390	0.24717	2.30412
Ru	-0.03449	-0.06024	-0.03753
C	0.39241	-3.13913	1.09974
C	-3.02413	-1.91700	-1.29342
C	-3.64255	0.82093	-0.70193
C	2.85287	1.96353	0.98076
H	-1.57493	1.27065	-2.84038
H	-2.01198	-0.31437	-3.63349
H	1.96843	0.43191	3.52936
H	1.62028	-1.19439	2.78727
C	-3.02329	-2.51712	4.92455
C	-1.62879	-2.59791	5.07142
C	-0.78553	-1.78781	4.28988
C	-2.73485	-0.81386	3.20746
C	-3.57445	-1.62299	3.98887
H	-3.68270	-3.15331	5.53812
H	-1.18669	-3.30183	5.79568
H	0.30539	-1.87330	4.41505
H	-3.17783	-0.11523	2.47694
H	-4.66802	-1.55418	3.86511
C	-1.22338	4.30544	4.44471
C	-0.65568	3.23871	5.16704
C	-0.37730	2.02405	4.52198
C	-1.22849	2.93503	2.42751
C	-1.51087	4.15002	3.07941
H	-1.44378	5.25949	4.95247
H	-0.43561	3.35150	6.24199
H	0.04567	1.18673	5.10355
H	-1.42892	2.81908	1.35093

H	-1.95345	4.98150	2.50690
C	5.83600	-2.42331	0.17277
C	4.62541	-2.68352	-0.49173
C	3.50083	-1.87236	-0.25645
C	4.80467	-0.52727	1.30157
C	5.92291	-1.34513	1.07192
H	6.71698	-3.06061	-0.01188
H	4.55109	-3.52583	-1.19951
H	2.54289	-2.08554	-0.75610
H	4.88817	0.32828	1.99248
H	6.87134	-1.13383	1.59359
C	4.07953	4.50991	0.89913
C	3.99880	3.72649	-0.26661
C	3.38501	2.46626	-0.22885
C	2.91847	2.76261	2.14005
C	3.53106	4.02902	2.09848
H	4.56049	5.50172	0.86773
H	4.40674	4.10394	-1.21837
H	3.31437	1.86909	-1.15310
H	2.48450	2.41496	3.09015
H	3.57549	4.64070	3.01491
C	0.51947	-4.44078	-4.62960
C	0.39958	-4.40819	-3.23118
C	0.33560	-3.17743	-2.55177
C	0.51528	-2.00529	-4.68145
C	0.57516	-3.23558	-5.35424
H	0.57037	-5.40654	-5.16006
H	0.35362	-5.34667	-2.65450
H	0.23703	-3.15137	-1.45319
H	0.56874	-1.06745	-5.25917
H	0.66904	-3.25319	-6.45315
C	3.27826	2.30043	-4.76878
C	1.94666	2.73040	-4.65004
C	1.00678	1.94698	-3.95700
C	2.73135	0.29581	-3.49822
C	3.66900	1.07974	-4.18902
H	4.01354	2.91690	-5.31224
H	1.63066	3.68980	-5.09133
H	-0.02717	2.31088	-3.86620
H	3.05160	-0.65951	-3.04973
H	4.71199	0.73216	-4.27496
C	-4.35007	-4.39073	-1.60530
C	-3.52614	-4.16758	-0.49042
C	-2.86364	-2.93630	-0.33253
C	-3.86229	-2.14494	-2.40904
C	-4.51794	-3.37580	-2.56552
H	-4.86319	-5.35899	-1.73058
H	-3.38355	-4.96058	0.26206
H	-2.19117	-2.77162	0.52444
H	-4.01747	-1.35315	-3.16117
H	-5.16522	-3.54365	-3.44255
C	-5.82437	2.51467	-0.07182
C	-4.63972	3.05277	-0.60364
C	-3.55338	2.21648	-0.90941
C	-4.83560	0.28829	-0.16097
C	-5.91589	1.13099	0.15320

H	-6.67518	3.17366	0.16893
H	-4.55136	4.13777	-0.77914
H	-2.61643	2.65656	-1.28621
H	-4.92940	-0.79607	0.00884
H	-6.83978	0.69698	0.57105
C	0.58918	-4.44757	1.64246
C	0.97708	-7.06470	2.71548
C	2.01679	-6.41736	2.02250
C	1.83013	-5.13214	1.49495
C	-0.44834	-5.11819	2.35341
C	-0.25480	-6.40421	2.87725
H	1.12668	-8.07609	3.12877
H	2.98947	-6.92207	1.89205
H	2.65032	-4.62933	0.95774
H	-1.41188	-4.60275	2.49428
H	-1.07735	-6.89849	3.42227
C	-0.14614	3.11547	-0.93682
C	-0.17539	4.50138	-1.27830
C	-0.25008	7.28255	-1.93339
C	0.50617	6.82594	-0.83713
C	0.54654	5.46348	-0.51225
C	-0.93442	4.98583	-2.38425
C	-0.96955	6.35093	-2.70357
H	-0.27836	8.35573	-2.18525
H	1.07590	7.54583	-0.22459
H	1.14344	5.11272	0.34405
H	-1.50743	4.26773	-2.99469
H	-1.56827	6.69249	-3.56545

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	6.81	0.05101	YES	YES
8	a	9.99	0.04010	YES	YES
9	a	14.20	0.08817	YES	YES
10	a	16.28	0.15328	YES	YES
11	a	18.53	0.03270	YES	YES
12	a	19.57	0.14714	YES	YES
13	a	22.90	0.04275	YES	YES
14	a	24.95	0.07147	YES	YES
15	a	25.67	0.01497	YES	YES
16	a	27.61	0.02195	YES	YES
17	a	29.63	0.01211	YES	YES
18	a	31.05	0.17992	YES	YES
19	a	33.41	0.13450	YES	YES
20	a	36.08	0.06095	YES	YES
21	a	36.72	0.03605	YES	YES
22	a	37.95	0.02067	YES	YES

23	a	41.98	0.07891	YES	YES
24	a	43.21	0.01982	YES	YES
25	a	44.67	0.15931	YES	YES
26	a	47.75	0.17275	YES	YES
27	a	49.20	0.04202	YES	YES
28	a	51.85	0.06858	YES	YES
29	a	55.39	0.13007	YES	YES
30	a	57.55	0.19101	YES	YES
31	a	58.46	0.70862	YES	YES
32	a	60.82	0.04216	YES	YES
33	a	63.44	0.01731	YES	YES
34	a	74.17	0.13070	YES	YES
35	a	79.77	0.19633	YES	YES
36	a	95.81	0.37164	YES	YES
37	a	102.76	2.19500	YES	YES
38	a	105.39	1.47177	YES	YES
39	a	108.63	0.41643	YES	YES
40	a	110.17	2.93198	YES	YES
41	a	118.73	3.04167	YES	YES
42	a	120.65	2.95289	YES	YES
43	a	126.58	0.08185	YES	YES
44	a	146.18	0.17359	YES	YES
45	a	150.32	0.30922	YES	YES
46	a	159.81	0.46912	YES	YES
47	a	161.76	0.18764	YES	YES
48	a	164.39	0.07166	YES	YES
49	a	178.28	1.66992	YES	YES
50	a	189.82	0.27404	YES	YES

S7.13 Complex $[4d]^+$

SCF Energy (au) (RI)BP86/SV(P) -4006.3534482470
SCF Energy (au) PBE0/def2-TZVPP -4005.699037285
SCF Energy (au) PBE0/def2-TZVPP -4005.7515249004 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9801172
Chemical potential (kJ mol^{-1}) 2290.64
Dispersion correction (au) PBE0/def2-TZVPP -0.24846821

xyz coordinates

126

C	1.75127	-2.15532	2.58223
C	2.17441	-2.25872	3.92859
H	2.30392	-1.35323	4.54557
C	2.45113	-3.51381	4.49124
H	2.77841	-3.58184	5.54180
C	2.32369	-4.67964	3.71266
H	2.54729	-5.66468	4.15416
C	1.91919	-4.58247	2.37221
H	1.82199	-5.49042	1.75514
C	1.63181	-3.32644	1.80664
H	1.31099	-3.25952	0.75709
C	3.08513	0.28353	2.13751
C	4.13310	-0.09575	1.26648
H	3.92965	-0.77637	0.42261
C	5.43590	0.38588	1.47260
H	6.24547	0.07520	0.79194
C	5.70812	1.25438	2.54524
H	6.73154	1.62990	2.70786
C	4.67256	1.63433	3.41505
H	4.88173	2.30609	4.26381
C	3.36684	1.14943	3.21624
H	2.57337	1.44448	3.92254
C	-2.37495	1.62215	2.38842
C	-3.39212	2.03083	1.49874
H	-3.50791	1.53086	0.52337
C	-4.28387	3.05722	1.85694
H	-5.08139	3.35533	1.15663
C	-4.16124	3.69471	3.10252
H	-4.86026	4.49886	3.38509
C	-3.14691	3.29746	3.99116
H	-3.04682	3.78993	4.97221
C	-2.26366	2.26320	3.64123
H	-1.49124	1.95298	4.36336
C	-2.29423	-1.17922	2.77578
C	-1.67809	-2.18046	3.55877
H	-0.58619	-2.20159	3.69413
C	-2.44918	-3.18501	4.16881
H	-1.94859	-3.95289	4.78071
C	-3.84360	-3.20973	4.00269
H	-4.44710	-3.99401	4.48818
C	-4.46422	-2.22190	3.21850

H	-5.55874	-2.22573	3.08662
C	-3.69792	-1.21397	2.61075
H	-4.20946	-0.43908	2.01840
C	0.22379	0.33605	3.03526
H	0.16407	-0.07038	4.06761
H	0.45989	1.42192	3.07921
C	-1.05664	0.26610	-3.54075
C	-0.00388	0.95323	-4.18475
H	0.56221	1.73837	-3.65786
C	0.34154	0.63763	-5.50873
H	1.16019	1.18594	-6.00233
C	-0.34652	-0.37551	-6.19791
H	-0.07216	-0.62165	-7.23664
C	-1.38326	-1.07457	-5.55728
H	-1.92775	-1.87064	-6.09103
C	-1.73836	-0.75828	-4.23551
H	-2.56107	-1.30742	-3.75000
C	-3.32090	0.38287	-1.77714
C	-3.88677	-0.73637	-1.13240
H	-3.23732	-1.45394	-0.60564
C	-5.27791	-0.94271	-1.16751
H	-5.70946	-1.82710	-0.67132
C	-6.11064	-0.02788	-1.83292
H	-7.20097	-0.18854	-1.85674
C	-5.55115	1.09186	-2.47660
H	-6.20096	1.80756	-3.00652
C	-4.16204	1.29356	-2.45771
H	-3.73307	2.16138	-2.98686
C	1.71904	3.00970	-1.26048
C	3.02417	2.66869	-0.84544
H	3.17398	1.89587	-0.07475
C	4.14261	3.30679	-1.40884
H	5.15361	3.03224	-1.06623
C	3.97282	4.28368	-2.40400
H	4.84958	4.78147	-2.84935
C	2.67682	4.62863	-2.82420
H	2.53208	5.40000	-3.59826
C	1.55652	4.00386	-2.25049
H	0.55275	4.32199	-2.57510
C	0.08754	3.60204	0.92800
C	1.10960	3.72388	1.89753
H	1.96567	3.02870	1.89338
C	1.07371	4.75319	2.85170
H	1.88577	4.83814	3.59251
C	0.01775	5.68091	2.85032
H	-0.00813	6.49394	3.59402
C	-0.99716	5.57209	1.88651
H	-1.82486	6.29955	1.86891
C	-0.96412	4.54096	0.93127
H	-1.77113	4.49179	0.18458
C	-1.20022	2.44929	-1.51298
H	-2.06749	2.85071	-0.94873
H	-1.05777	3.06177	-2.42749
C	-0.37016	-2.29816	-0.76349
C	0.66519	-1.77048	-1.32984
C	1.50065	-0.70912	-1.52489

C	2.60108	-0.37717	-2.25061
H	2.98272	0.65355	-2.16494
C	3.35800	-1.24213	-3.16379
C	3.06233	-2.61379	-3.37277
H	2.22225	-3.07698	-2.82945
C	3.82775	-3.38756	-4.25355
H	3.58225	-4.45256	-4.39933
C	4.90898	-2.81476	-4.95144
H	5.50918	-3.42762	-5.64364
C	5.21804	-1.45738	-4.75668
H	6.06271	-0.99944	-5.29747
C	4.45330	-0.68243	-3.87316
H	4.69933	0.38276	-3.72341
C	-1.19615	-3.48142	-0.76770
C	-1.08374	-4.39313	-1.85869
H	-0.38236	-4.16286	-2.67681
C	-1.85799	-5.55765	-1.90078
H	-1.75612	-6.24825	-2.75421
C	-2.76434	-5.84712	-0.86203
H	-3.37316	-6.76523	-0.89777
C	-2.88572	-4.95755	0.21909
H	-3.58715	-5.17778	1.04014
C	-2.11427	-3.78643	0.26864
H	-2.20453	-3.10266	1.12395
P	1.42295	-0.47843	1.84887
P	-1.30330	0.17030	1.95634
P	0.27149	2.26681	-0.36039
P	-1.49072	0.61992	-1.78275
Ru	-0.00231	-0.08157	-0.06997

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	17.06	0.00852	YES	YES
8	a	18.60	0.02008	YES	YES
9	a	22.76	0.02039	YES	YES
10	a	23.02	0.07399	YES	YES
11	a	24.06	0.14242	YES	YES
12	a	28.08	0.00080	YES	YES
13	a	31.67	0.02961	YES	YES
14	a	33.87	0.01924	YES	YES
15	a	36.19	0.00942	YES	YES
16	a	37.59	0.01870	YES	YES
17	a	40.65	0.03511	YES	YES
18	a	41.78	0.07393	YES	YES
19	a	43.72	0.01304	YES	YES
20	a	45.03	0.12072	YES	YES
21	a	46.61	0.02429	YES	YES

22	a	48.59	0.07703	YES	YES
23	a	48.68	0.03776	YES	YES
24	a	51.97	0.11377	YES	YES
25	a	52.33	0.00513	YES	YES
26	a	52.43	0.14923	YES	YES
27	a	55.79	0.03483	YES	YES
28	a	58.92	0.08057	YES	YES
29	a	62.73	0.16306	YES	YES
30	a	66.82	0.07555	YES	YES
31	a	72.36	0.11605	YES	YES
32	a	75.24	0.08911	YES	YES
33	a	77.61	0.51006	YES	YES
34	a	80.80	0.39383	YES	YES
35	a	81.60	0.14914	YES	YES
36	a	96.17	0.37566	YES	YES
37	a	98.00	0.08072	YES	YES
38	a	100.06	0.01445	YES	YES
39	a	109.97	0.67138	YES	YES
40	a	111.01	0.06831	YES	YES
41	a	116.22	0.50218	YES	YES
42	a	136.23	0.81662	YES	YES
43	a	140.09	0.70986	YES	YES
44	a	144.75	0.02771	YES	YES
45	a	151.89	0.13599	YES	YES
46	a	163.64	0.13123	YES	YES
47	a	167.21	0.21007	YES	YES
48	a	171.87	1.00909	YES	YES
49	a	178.67	1.56802	YES	YES
50	a	181.78	0.03150	YES	YES

S7.14Complex [4'd]$^{+}$

SCF Energy (au) (RI)BP86/SV(P) -4006.3541499250
SCF Energy (au) PBE0/def2-TZVPP -4005.700378075
SCF Energy (au) PBE0/def2-TZVPP -4005.7519932882 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9798067
Chemical potential (kJ mol^{-1}) 2282.93
Dispersion correction (au) PBE0/def2-TZVPP -0.24852501

xyz coordinates

126

C	-2.22662	0.62415	-0.05873
C	-1.32455	1.67647	0.03194
Ru	-0.00154	0.04757	0.02351
P	0.10590	-0.28796	2.39319
P	1.89842	1.13650	0.80374
P	1.18899	-1.95711	-0.71732
P	0.26951	0.14532	-2.34242
C	1.88162	0.31759	2.49270
C	1.49786	-1.25861	-2.44181
C	0.08457	-1.96830	3.16899
C	-0.72092	-2.97256	2.59287
C	-0.78718	-4.25076	3.17495
C	-0.04449	-4.53713	4.33228
C	0.76452	-3.54118	4.91004
C	0.82713	-2.26163	4.33497
C	-0.84312	0.70554	3.64047
C	-2.19005	1.03613	3.37618
C	-2.95117	1.73395	4.33015
C	-2.37769	2.10954	5.55569
C	-1.03662	1.78467	5.82732
C	-0.27376	1.08638	4.87758
C	1.87542	2.95842	1.18001
C	1.06816	3.45039	2.23069
C	1.05314	4.82066	2.53837
C	1.82789	5.72379	1.79047
C	2.61943	5.24609	0.73273
C	2.64774	3.87353	0.43017
C	3.62735	0.93427	0.16584
C	4.69595	0.65477	1.04568
C	6.01419	0.58521	0.56551
C	6.28577	0.80390	-0.79581
C	5.23050	1.09271	-1.67718
C	3.90933	1.15464	-1.20076
C	0.36439	-3.58743	-1.06935
C	-1.04198	-3.65680	-1.07591
C	-1.69808	-4.85890	-1.39329
C	-0.94954	-6.00675	-1.70270
C	0.45577	-5.94646	-1.69681
C	1.11274	-4.74580	-1.38100
C	2.84222	-2.53501	-0.10420
C	2.90285	-3.09062	1.19548

C	4.11335	-3.58914	1.70391
C	5.28142	-3.54269	0.92289
C	5.22916	-2.99829	-0.37047
C	4.01857	-2.49812	-0.88212
C	-1.17901	-0.30785	-3.39886
C	-1.35067	-1.57846	-3.98741
C	-2.46460	-1.83460	-4.80759
C	-3.42031	-0.83147	-5.03887
C	-3.26581	0.43122	-4.43736
C	-2.15477	0.69260	-3.62106
C	0.99083	1.53704	-3.32335
C	0.93970	2.85540	-2.82579
C	1.45534	3.91834	-3.58941
C	2.03281	3.66970	-4.84539
C	2.08828	2.35505	-5.34532
C	1.56297	1.29281	-4.59307
H	2.16815	0.96183	3.35109
H	2.54626	-0.57311	2.45652
H	1.40614	-1.97896	-3.28201
H	2.50676	-0.79596	-2.47641
H	-1.28950	-2.75849	1.67392
H	-1.41793	-5.02736	2.71307
H	-0.09293	-5.54014	4.78687
H	1.34949	-3.76146	5.81816
H	1.46458	-1.49309	4.80268
H	-2.64780	0.75297	2.41614
H	-3.99922	1.99095	4.10642
H	-2.97475	2.65876	6.30192
H	-0.57921	2.07527	6.78733
H	0.77507	0.84359	5.11541
H	0.43242	2.76971	2.81792
H	0.42441	5.18152	3.36844
H	1.81718	6.79876	2.03409
H	3.23613	5.94395	0.14282
H	3.29706	3.52038	-0.38550
H	4.51349	0.49914	2.12071
H	6.83640	0.36543	1.26589
H	7.32220	0.75657	-1.16814
H	5.43316	1.27860	-2.74469
H	3.09676	1.40582	-1.90119
H	-1.62917	-2.75777	-0.83225
H	-2.79972	-4.89214	-1.39134
H	-1.46042	-6.95307	-1.94541
H	1.04910	-6.84454	-1.93546
H	2.21417	-4.71789	-1.37249
H	1.99125	-3.15756	1.81125
H	4.13904	-4.02567	2.71582
H	6.23061	-3.93834	1.31984
H	6.13655	-2.96569	-0.99524
H	4.00810	-2.08777	-1.90366
H	-0.62144	-2.38540	-3.81706
H	-2.57906	-2.82800	-5.27144
H	-4.28726	-1.03202	-5.68948
H	-4.01308	1.22301	-4.60922
H	-2.04133	1.68987	-3.16436
H	0.49028	3.04872	-1.83936

H	1.40336	4.94710	-3.19736
H	2.43816	4.50313	-5.44225
H	2.53514	2.15728	-6.33352
H	1.59151	0.26975	-5.00504
C	-2.77740	-0.50763	-0.09187
C	-3.74287	-1.56450	-0.11640
C	-1.45124	3.03328	0.04504
H	-0.52576	3.62522	0.15082
C	-2.67708	3.83933	-0.04181
C	-5.73369	-3.57910	-0.15126
C	-5.15899	-3.17695	1.06859
C	-4.17246	-2.18218	1.09116
C	-4.32922	-1.98179	-1.34323
C	-5.31532	-2.97782	-1.35285
H	-6.51317	-4.35834	-0.16449
H	-5.48899	-3.63833	2.01371
H	-3.73344	-1.85994	2.04842
H	-4.00614	-1.50677	-2.28238
H	-5.76939	-3.28317	-2.30985
C	-4.96700	5.51993	-0.19799
C	-3.68760	6.08218	-0.04692
C	-2.55979	5.25271	0.02956
C	-3.97731	3.29062	-0.19551
C	-5.10352	4.12038	-0.27202
H	-5.85612	6.16864	-0.25901
H	-3.56800	7.17672	0.01153
H	-1.55822	5.69969	0.15029
H	-4.10513	2.19816	-0.25972
H	-6.10350	3.67125	-0.39218

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	7.84	0.02175	YES	YES
8	a	15.58	0.00686	YES	YES
9	a	19.17	0.03198	YES	YES
10	a	23.57	0.06963	YES	YES
11	a	25.67	0.13203	YES	YES
12	a	26.80	0.05415	YES	YES
13	a	29.63	0.06839	YES	YES
14	a	30.96	0.06137	YES	YES
15	a	32.73	0.15180	YES	YES
16	a	35.74	0.03516	YES	YES
17	a	36.47	0.07104	YES	YES
18	a	38.43	0.05345	YES	YES
19	a	39.03	0.00449	YES	YES
20	a	41.46	0.01861	YES	YES
21	a	43.34	0.09612	YES	YES

22	a	43.76	0.12532	YES	YES
23	a	46.18	0.02348	YES	YES
24	a	50.12	0.03978	YES	YES
25	a	50.78	0.12244	YES	YES
26	a	51.84	0.04532	YES	YES
27	a	54.60	0.00577	YES	YES
28	a	57.07	0.17073	YES	YES
29	a	59.04	0.03440	YES	YES
30	a	63.32	0.04625	YES	YES
31	a	64.89	0.14128	YES	YES
32	a	66.33	0.24388	YES	YES
33	a	70.94	0.05829	YES	YES
34	a	76.75	0.19969	YES	YES
35	a	83.65	0.18650	YES	YES
36	a	91.51	1.46390	YES	YES
37	a	96.07	0.85310	YES	YES
38	a	97.54	1.64998	YES	YES
39	a	103.16	0.41863	YES	YES
40	a	109.68	1.10453	YES	YES
41	a	110.03	0.45663	YES	YES
42	a	118.72	1.08971	YES	YES
43	a	135.15	2.50482	YES	YES
44	a	141.31	0.42384	YES	YES
45	a	152.53	0.03285	YES	YES
46	a	162.89	0.17690	YES	YES
47	a	167.81	0.24520	YES	YES
48	a	171.23	0.32242	YES	YES
49	a	177.82	1.83780	YES	YES
50	a	182.89	0.92937	YES	YES

S7.15Complex $TS_{[Dd]+-[4'd]}$

SCF Energy (au) (RI)BP86/SV(P) -4006.3087965910
SCF Energy (au) PBE0/def2-TZVPP -4005.653424065
SCF Energy (au) PBE0/def2-TZVPP -4005.7055594810 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9768819
Chemical potential (kJ mol^{-1}) 2270.88
Dispersion correction (au) PBE0/def2-TZVPP -0.24518860

xyz coordinates

126

C	-1.51667	0.45516	-0.90214
C	-0.62031	1.69964	0.60983
Ru	0.16877	0.04222	0.18243
P	-1.07817	-1.26936	1.75181
P	1.61189	-0.50222	2.05423
P	1.13585	-1.77971	-1.25160
P	1.71914	0.99265	-1.36442
C	0.42443	-1.78441	2.75261
C	2.49319	-0.63177	-1.87715
C	-1.94230	-2.82053	1.24968
C	-2.42121	-2.94770	-0.07124
C	-3.10904	-4.11164	-0.45913
C	-3.31551	-5.15120	0.46295
C	-2.83984	-5.02663	1.78178
C	-2.16051	-3.86371	2.17793
C	-2.28640	-0.49402	2.91092
C	-3.24962	0.38113	2.35982
C	-4.23667	0.95095	3.18109
C	-4.27032	0.65683	4.55498
C	-3.31316	-0.21114	5.10876
C	-2.32475	-0.78579	4.29224
C	1.78577	0.75588	3.41255
C	0.63705	1.45322	3.85111
C	0.72711	2.38942	4.89423
C	1.96740	2.65908	5.49930
C	3.11422	1.97736	5.06198
C	3.02681	1.02671	4.02923
C	3.28018	-1.29772	2.03677
C	3.55346	-2.48381	2.75095
C	4.85036	-3.02505	2.76022
C	5.89026	-2.38558	2.06476
C	5.62923	-1.19884	1.35809
C	4.33225	-0.65852	1.34090
C	0.30912	-2.38410	-2.79910
C	-0.60757	-1.54159	-3.46597
C	-1.21130	-1.95991	-4.66396
C	-0.91452	-3.22186	-5.20551
C	-0.00691	-4.06602	-4.54438
C	0.60308	-3.65341	-3.34785
C	1.99527	-3.30328	-0.65062
C	1.22599	-4.26864	0.04029

C	1.81100	-5.47101	0.47077
C	3.17108	-5.72435	0.22073
C	3.94110	-4.77147	-0.46664
C	3.35792	-3.56890	-0.90272
C	1.11335	1.84432	-2.88445
C	1.34145	1.37554	-4.19483
C	0.88364	2.11460	-5.30051
C	0.19415	3.32284	-5.10788
C	-0.04440	3.79058	-3.80258
C	0.40849	3.05568	-2.69638
C	3.10453	2.09423	-0.83793
C	3.00521	2.81698	0.36900
C	4.04510	3.67797	0.76343
C	5.19042	3.81315	-0.03845
C	5.29430	3.09355	-1.24374
C	4.25325	2.24342	-1.64830
H	0.33566	-1.79999	3.85931
H	0.73445	-2.79020	2.39396
H	2.78073	-0.76298	-2.94133
H	3.39470	-0.76692	-1.24168
H	-2.25673	-2.13167	-0.79386
H	-3.48186	-4.20386	-1.49200
H	-3.85266	-6.06362	0.15608
H	-3.00548	-5.83819	2.50931
H	-1.80624	-3.77188	3.21867
H	-3.22377	0.61947	1.28399
H	-4.98003	1.63531	2.74132
H	-5.04442	1.10646	5.19821
H	-3.33439	-0.44579	6.18563
H	-1.58574	-1.46371	4.74957
H	-0.34290	1.26198	3.38537
H	-0.18191	2.91193	5.23449
H	2.03825	3.39877	6.31341
H	4.09117	2.17761	5.53182
H	3.93596	0.49370	3.71254
H	2.75956	-2.99496	3.31806
H	5.04845	-3.95157	3.32330
H	6.90783	-2.80913	2.07940
H	6.44122	-0.68337	0.81947
H	4.14737	0.28723	0.80483
H	-0.86524	-0.55927	-3.04070
H	-1.92749	-1.29169	-5.17030
H	-1.39397	-3.55026	-6.14238
H	0.23101	-5.05929	-4.96001
H	1.31001	-4.33103	-2.84300
H	0.15237	-4.09380	0.22124
H	1.19508	-6.21752	0.99853
H	3.62949	-6.66930	0.55543
H	5.00577	-4.96576	-0.67517
H	3.98008	-2.84693	-1.45474
H	1.87557	0.42951	-4.37527
H	1.07315	1.73999	-6.32005
H	-0.15694	3.90327	-5.97683
H	-0.58712	4.73592	-3.64098
H	0.21498	3.43221	-1.67852
H	2.10982	2.70366	1.00093

H	3.95771	4.24357	1.70518
H	6.00635	4.48592	0.27266
H	6.18924	3.20295	-1.87812
H	4.33551	1.70164	-2.60588
C	-2.58223	0.65019	-1.52215
C	-3.76652	0.82100	-2.30285
C	-1.05975	2.89844	0.99771
H	-0.45609	3.18384	1.89234
C	-2.08360	3.88795	0.62511
C	-6.10565	1.14306	-3.87593
C	-6.17492	0.49017	-2.63139
C	-5.02244	0.32907	-1.85107
C	-3.71290	1.48009	-3.56367
C	-4.87118	1.63615	-4.33730
H	-7.01471	1.26806	-4.48670
H	-7.13997	0.10232	-2.26568
H	-5.07817	-0.18448	-0.87811
H	-2.74583	1.86734	-3.92327
H	-4.81187	2.14866	-5.31182
C	-4.04464	5.85646	0.03869
C	-3.35878	5.88622	1.26563
C	-2.38834	4.91651	1.55397
C	-2.77075	3.87932	-0.61279
C	-3.74178	4.85097	-0.89691
H	-4.80879	6.61735	-0.18946
H	-3.58126	6.67246	2.00586
H	-1.85703	4.94687	2.52049
H	-2.53585	3.10407	-1.35545
H	-4.26817	4.82022	-1.86503

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1	a	-174.34	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	4.92	0.03875	YES	YES
9	a	11.11	0.13720	YES	YES
10	a	16.18	0.20371	YES	YES
11	a	17.24	0.01095	YES	YES
12	a	18.60	0.03796	YES	YES
13	a	24.60	0.02976	YES	YES
14	a	24.93	0.14766	YES	YES
15	a	29.81	0.01430	YES	YES
16	a	31.61	0.06495	YES	YES
17	a	34.62	0.06548	YES	YES
18	a	35.55	0.00181	YES	YES
19	a	37.81	0.05592	YES	YES
20	a	38.88	0.10671	YES	YES
21	a	40.20	0.15565	YES	YES

22	a	41.14	0.00498	YES	YES
23	a	44.24	0.02726	YES	YES
24	a	45.27	0.04766	YES	YES
25	a	46.40	0.12569	YES	YES
26	a	48.25	0.04825	YES	YES
27	a	51.93	0.03263	YES	YES
28	a	52.69	0.03762	YES	YES
29	a	56.59	0.33365	YES	YES
30	a	60.35	0.19022	YES	YES
31	a	61.54	0.16100	YES	YES
32	a	64.21	0.23639	YES	YES
33	a	68.01	0.05564	YES	YES
34	a	72.11	0.09385	YES	YES
35	a	79.83	0.31768	YES	YES
36	a	87.42	2.19924	YES	YES
37	a	93.59	1.30484	YES	YES
38	a	97.52	1.80758	YES	YES
39	a	101.50	1.36543	YES	YES
40	a	103.70	2.32070	YES	YES
41	a	109.33	0.89557	YES	YES
42	a	118.22	1.44617	YES	YES
43	a	128.16	0.62056	YES	YES
44	a	143.48	3.47245	YES	YES
45	a	151.25	0.18860	YES	YES
46	a	154.48	1.28932	YES	YES
47	a	162.63	1.21232	YES	YES
48	a	167.01	0.93027	YES	YES
49	a	171.80	1.22120	YES	YES
50	a	178.83	6.33442	YES	YES

S7.16Complex [Dd-*Z*]$^{+}$

SCF Energy (au) (RI)BP86/SV(P) -4006.3123824210
SCF Energy (au) PBE0/def2-TZVPP -4005.655152406
SCF Energy (au) PBE0/def2-TZVPP -4005.7100569776 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9773421
Chemical potential (kJ mol^{-1}) 2271.15
Dispersion correction (au) PBE0/def2-TZVPP -0.24337569

xyz coordinates

126

Ru	-0.07904	0.09859	0.09650
C	-1.64180	0.22175	-1.19608
C	-0.63017	1.73120	0.76958
P	-1.36392	-1.23920	1.61115
P	1.33032	-0.47491	2.02836
P	0.80832	-1.78988	-1.43011
P	1.44766	1.02016	-1.52865
C	0.08069	-1.70490	2.71349
C	2.08243	-0.62145	-2.16594
C	-2.14266	-2.83437	1.10390
C	-2.63417	-2.99571	-0.20826
C	-3.27545	-4.19368	-0.57259
C	-3.42436	-5.23140	0.36218
C	-2.93476	-5.07271	1.67204
C	-2.30032	-3.87756	2.04565
C	-2.68154	-0.47293	2.64716
C	-3.64219	0.31783	1.97750
C	-4.72401	0.86221	2.68838
C	-4.85180	0.63087	4.06911
C	-3.89765	-0.15383	4.73908
C	-2.81737	-0.70925	4.03210
C	1.53758	0.73480	3.41900
C	0.39199	1.24033	4.07479
C	0.52646	2.13173	5.15089
C	1.80182	2.54304	5.57541
C	2.94307	2.06042	4.91431
C	2.81578	1.15825	3.84303
C	2.96205	-1.33386	2.00120
C	3.23697	-2.44578	2.82625
C	4.51592	-3.02669	2.82811
C	5.53551	-2.49705	2.01845
C	5.27218	-1.38354	1.20298
C	3.99047	-0.80739	1.18881
C	-0.14085	-2.38904	-2.90069
C	-0.62457	-1.45546	-3.84551
C	-1.34085	-1.89508	-4.97052
C	-1.59191	-3.26430	-5.16203
C	-1.11873	-4.19584	-4.22325
C	-0.39758	-3.76399	-3.09700
C	1.74869	-3.29546	-0.91383
C	1.13829	-4.19447	-0.01025

C	1.78460	-5.38784	0.35451
C	3.05184	-5.69233	-0.17008
C	3.66530	-4.80393	-1.06977
C	3.01686	-3.61547	-1.44499
C	0.81489	1.97574	-2.97564
C	1.43399	1.90198	-4.24316
C	0.99197	2.72220	-5.29361
C	-0.05990	3.63166	-5.08311
C	-0.67378	3.71277	-3.82180
C	-0.24532	2.88394	-2.77060
C	2.96155	1.99047	-1.09418
C	2.84532	3.04456	-0.16450
C	3.95480	3.85205	0.13596
C	5.19238	3.61132	-0.48460
C	5.31531	2.56454	-1.41522
C	4.20577	1.75935	-1.72372
H	-0.07257	-1.64512	3.81151
H	0.40130	-2.73485	2.44835
H	2.20236	-0.71326	-3.26603
H	3.05798	-0.82248	-1.67491
H	-2.51985	-2.17948	-0.94133
H	-3.65809	-4.31146	-1.59915
H	-3.92720	-6.16881	0.07297
H	-3.05489	-5.88212	2.41076
H	-1.93689	-3.76080	3.08086
H	-3.54315	0.49664	0.89267
H	-5.47187	1.47429	2.15834
H	-5.69962	1.06223	4.62588
H	-3.99526	-0.34178	5.82083
H	-2.08725	-1.33045	4.57649
H	-0.62023	0.95141	3.74868
H	-0.37652	2.51268	5.65446
H	1.90489	3.24264	6.42081
H	3.94783	2.37703	5.23911
H	3.72309	0.77534	3.35059
H	2.45872	-2.86270	3.48589
H	4.71833	-3.89591	3.47491
H	6.53969	-2.95142	2.02762
H	6.06917	-0.95614	0.57283
H	3.79906	0.07542	0.55598
H	-0.45252	-0.37665	-3.71054
H	-1.71163	-1.15534	-5.69794
H	-2.15571	-3.60529	-6.04569
H	-1.30255	-5.27304	-4.36872
H	-0.02457	-4.51065	-2.37941
H	0.13422	-3.97751	0.39071
H	1.29046	-6.08462	1.05123
H	3.56040	-6.62720	0.11682
H	4.65492	-5.04104	-1.49339
H	3.50722	-2.94794	-2.17178
H	2.27435	1.21114	-4.42356
H	1.47887	2.65571	-6.28027
H	-0.39968	4.28088	-5.90666
H	-1.49843	4.42386	-3.65196
H	-0.73799	2.93880	-1.78756
H	1.87873	3.24799	0.32317

H	3.84554	4.67645	0.85912
H	6.06319	4.24424	-0.24799
H	6.28064	2.37720	-1.91366
H	4.32027	0.95543	-2.46985
C	-2.66713	0.34560	-1.88849
C	-3.83425	0.46399	-2.71206
C	-1.22460	2.89136	1.04833
H	-2.28013	2.85690	0.69084
C	-0.78787	4.16176	1.64725
C	-6.14966	0.70123	-4.34316
C	-6.19421	-0.05078	-3.15532
C	-5.05412	-0.16957	-2.34820
C	-3.80638	1.21961	-3.91611
C	-4.95099	1.33479	-4.71774
H	-7.04803	0.79442	-4.97511
H	-7.12997	-0.55040	-2.85387
H	-5.09487	-0.75984	-1.41842
H	-2.86965	1.72077	-4.20845
H	-4.90861	1.92788	-5.64660
C	-0.02449	6.67442	2.73343
C	-1.25927	6.53237	2.07673
C	-1.63750	5.29241	1.54216
C	0.44815	4.31534	2.32564
C	0.82265	5.55830	2.85680
H	0.27277	7.64835	3.15491
H	-1.93711	7.39643	1.97989
H	-2.60764	5.19285	1.02678
H	1.10697	3.44386	2.46365
H	1.78509	5.65223	3.38670

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	6.71	0.02265	YES	YES
8	a	12.49	0.11201	YES	YES
9	a	16.26	0.01273	YES	YES
10	a	17.07	0.01255	YES	YES
11	a	21.35	0.01561	YES	YES
12	a	22.09	0.00877	YES	YES
13	a	26.92	0.01662	YES	YES
14	a	27.60	0.00702	YES	YES
15	a	30.58	0.00446	YES	YES
16	a	34.17	0.04273	YES	YES
17	a	34.46	0.00275	YES	YES
18	a	34.79	0.07314	YES	YES
19	a	38.72	0.08688	YES	YES
20	a	40.83	0.08003	YES	YES
21	a	43.24	0.14549	YES	YES

22	a	45.09	0.06783	YES	YES
23	a	45.72	0.05299	YES	YES
24	a	50.40	0.02457	YES	YES
25	a	52.00	0.05474	YES	YES
26	a	53.42	0.02200	YES	YES
27	a	56.16	0.04374	YES	YES
28	a	57.28	0.06024	YES	YES
29	a	59.34	0.07019	YES	YES
30	a	63.26	0.05059	YES	YES
31	a	64.55	0.05306	YES	YES
32	a	69.13	0.28920	YES	YES
33	a	72.05	0.23074	YES	YES
34	a	76.09	0.68233	YES	YES
35	a	81.71	0.71968	YES	YES
36	a	86.40	0.61253	YES	YES
37	a	92.97	0.72567	YES	YES
38	a	97.57	0.88577	YES	YES
39	a	107.17	0.76038	YES	YES
40	a	107.31	0.85439	YES	YES
41	a	112.65	1.24269	YES	YES
42	a	116.42	0.18207	YES	YES
43	a	125.43	2.24694	YES	YES
44	a	142.81	1.26652	YES	YES
45	a	147.61	0.41290	YES	YES
46	a	157.50	0.30338	YES	YES
47	a	161.34	0.43544	YES	YES
48	a	163.99	0.25973	YES	YES
49	a	169.91	0.13754	YES	YES
50	a	171.25	2.25035	YES	YES

S7.17 Complex [4d-*Z*]$^+$

SCF Energy (au) (RI)BP86/SV(P) -4006.3352712970
SCF Energy (au) PBE0/def2-TZVPP -4005.680342212
SCF Energy (au) PBE0/def2-TZVPP -4005.7314016681 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9797648
Chemical potential (kJ mol^{-1}) 2284.25
Dispersion correction (au) PBE0/def2-TZVPP -0.24819490

xyz coordinates

126

C	1.72515	-2.22184	2.32175
C	0.85179	-2.92235	3.18124
H	-0.05395	-2.44220	3.58340
C	1.12719	-4.25476	3.53769
H	0.44649	-4.78304	4.22539
C	2.26403	-4.90497	3.02879
H	2.48101	-5.94723	3.31467
C	3.12762	-4.21757	2.15752
H	4.02242	-4.71965	1.75468
C	2.86336	-2.88478	1.80613
H	3.55762	-2.35277	1.13549
C	3.05874	0.30744	2.23814
C	3.91665	0.77054	1.22102
H	3.61638	0.68760	0.16462
C	5.16377	1.33179	1.55014
H	5.83122	1.67789	0.74428
C	5.55378	1.44362	2.89465
H	6.53023	1.88553	3.15261
C	4.69928	0.98383	3.91472
H	5.00540	1.06332	4.97085
C	3.46001	0.41023	3.59052
H	2.80922	0.03248	4.39723
C	-2.36139	1.62666	2.34993
C	-3.64387	1.70756	1.75779
H	-3.96700	0.94433	1.03072
C	-4.53079	2.73644	2.11197
H	-5.52951	2.77835	1.64690
C	-4.15448	3.69659	3.06805
H	-4.85422	4.49884	3.35401
C	-2.88548	3.62029	3.66392
H	-2.58289	4.36253	4.42043
C	-1.99160	2.59526	3.30568
H	-1.00358	2.56466	3.79015
C	-2.32750	-1.18445	2.54570
C	-2.71591	-2.26796	1.73841
H	-2.38130	-2.30697	0.69092
C	-3.52418	-3.29323	2.26376
H	-3.82521	-4.13416	1.61883
C	-3.93975	-3.24518	3.60356
H	-4.57248	-4.04805	4.01641
C	-3.55216	-2.16502	4.41932

H	-3.88163	-2.11858	5.47039
C	-2.75781	-1.13554	3.89275
H	-2.48638	-0.27991	4.53418
C	0.19321	0.23793	3.01243
H	0.07204	-0.26839	3.99390
H	0.48842	1.29396	3.18680
C	-1.29604	0.27734	-3.61298
C	-0.20197	-0.45765	-4.11526
H	0.51943	-0.91133	-3.41808
C	-0.01850	-0.59164	-5.50363
H	0.83981	-1.16874	-5.88449
C	-0.91898	0.00946	-6.39768
H	-0.77323	-0.09595	-7.48536
C	-2.01173	0.74533	-5.90217
H	-2.72432	1.21633	-6.59913
C	-2.20540	0.87322	-4.51827
H	-3.07953	1.43300	-4.14597
C	-3.35314	0.04284	-1.66414
C	-3.73118	-1.31753	-1.64774
H	-2.95689	-2.10203	-1.66176
C	-5.08700	-1.68105	-1.62747
H	-5.36600	-2.74721	-1.61418
C	-6.08393	-0.68967	-1.62457
H	-7.14848	-0.97471	-1.60936
C	-5.71773	0.66655	-1.64569
H	-6.49400	1.44938	-1.65292
C	-4.36001	1.03325	-1.66535
H	-4.09650	2.10334	-1.68637
C	1.39783	2.99067	-1.81104
C	2.45138	3.83325	-1.38941
H	2.64983	3.98758	-0.31784
C	3.24252	4.51211	-2.33169
H	4.05023	5.17624	-1.98246
C	2.99772	4.35900	-3.70657
H	3.61276	4.90002	-4.44409
C	1.96288	3.51068	-4.13470
H	1.76338	3.37617	-5.21013
C	1.17095	2.82906	-3.19654
H	0.37401	2.16431	-3.56279
C	0.28638	3.46908	0.74844
C	1.25051	3.42918	1.77941
H	1.96454	2.59179	1.83906
C	1.33615	4.47327	2.71769
H	2.10209	4.43188	3.50943
C	0.45775	5.56706	2.63803
H	0.52650	6.38769	3.37082
C	-0.50228	5.61529	1.61243
H	-1.19056	6.47299	1.53814
C	-0.58539	4.57705	0.67026
H	-1.33268	4.64784	-0.13616
C	-1.40493	2.27532	-1.39222
H	-2.14813	2.51694	-0.60079
H	-1.50531	2.99122	-2.23611
C	-0.28808	-3.20366	-0.79639
C	0.49388	-2.24070	-0.96365
C	1.46650	-1.25024	-1.24268

C	2.66339	-1.61690	-1.81440
H	2.77261	-2.70534	-1.99681
C	3.84622	-0.86382	-2.23084
C	5.00993	-1.59825	-2.58976
H	4.98146	-2.70063	-2.54560
C	6.18607	-0.95215	-2.99240
H	7.07395	-1.54786	-3.26157
C	6.23096	0.45208	-3.05813
H	7.15212	0.96449	-3.38094
C	5.08453	1.19599	-2.72210
H	5.10001	2.29588	-2.78839
C	3.90813	0.54915	-2.31551
H	3.01035	1.13865	-2.08390
C	-1.09522	-4.37155	-0.70283
C	-1.92718	-4.75749	-1.79389
H	-1.95711	-4.12543	-2.69562
C	-2.67018	-5.94313	-1.73503
H	-3.29966	-6.23753	-2.59059
C	-2.60432	-6.76281	-0.59226
H	-3.18717	-7.69758	-0.55094
C	-1.78562	-6.39477	0.49212
H	-1.72635	-7.04259	1.38189
C	-1.03465	-5.21361	0.44343
H	-0.38265	-4.92609	1.28269
P	1.43855	-0.46861	1.81097
P	-1.28672	0.19189	1.85556
P	0.27715	2.16141	-0.56766
P	-1.54999	0.44554	-1.78114
Ru	0.09428	-0.13167	-0.13467

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	7.37	0.06809	YES	YES
8	a	15.61	0.01782	YES	YES
9	a	19.76	0.08832	YES	YES
10	a	21.02	0.01751	YES	YES
11	a	22.83	0.01444	YES	YES
12	a	25.01	0.09849	YES	YES
13	a	28.07	0.09778	YES	YES
14	a	28.85	0.07754	YES	YES
15	a	33.34	0.08605	YES	YES
16	a	34.33	0.02106	YES	YES
17	a	36.95	0.08671	YES	YES
18	a	39.02	0.22681	YES	YES
19	a	43.13	0.06376	YES	YES
20	a	45.70	0.06916	YES	YES
21	a	46.80	0.11693	YES	YES

22	a	48.54	0.04603	YES	YES
23	a	49.50	0.01155	YES	YES
24	a	52.26	0.08134	YES	YES
25	a	55.13	0.03485	YES	YES
26	a	55.75	0.05599	YES	YES
27	a	59.14	0.23960	YES	YES
28	a	61.07	0.13591	YES	YES
29	a	65.31	0.04894	YES	YES
30	a	66.26	0.12136	YES	YES
31	a	68.09	0.14353	YES	YES
32	a	72.00	0.03412	YES	YES
33	a	77.71	0.46801	YES	YES
34	a	79.60	0.54428	YES	YES
35	a	81.34	0.13460	YES	YES
36	a	84.45	0.42437	YES	YES
37	a	94.04	1.09115	YES	YES
38	a	100.67	0.19508	YES	YES
39	a	101.97	1.22266	YES	YES
40	a	112.76	1.04695	YES	YES
41	a	118.07	0.38322	YES	YES
42	a	119.45	1.14026	YES	YES
43	a	132.83	2.59192	YES	YES
44	a	151.08	0.08445	YES	YES
45	a	158.22	1.46814	YES	YES
46	a	160.89	0.37913	YES	YES
47	a	165.44	0.09534	YES	YES
48	a	168.65	0.35909	YES	YES
49	a	175.18	2.44640	YES	YES
50	a	182.00	0.72852	YES	YES

S7.18 Complex [4'd-*Z*]$^+$

SCF Energy (au) (RI)BP86/SV(P) -4006.3388213990
SCF Energy (au) PBE0/def2-TZVPP -4005.684556838
SCF Energy (au) PBE0/def2-TZVPP -4005.7350602130 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9801083
Chemical potential (kJ mol^{-1}) 2290.07
Dispersion correction (au) PBE0/def2-TZVPP -0.25261122

xyz coordinates

126

C	-2.16027	1.37719	0.21697
C	-0.96587	2.11602	0.15376
Ru	-0.16936	0.19078	0.05274
P	-0.14929	-0.44144	2.36077
P	1.99590	0.39632	0.86575
P	0.17289	-2.06815	-0.83587
P	0.05927	0.28199	-2.35304
C	1.70670	-0.71536	2.35128
C	0.81312	-1.41635	-2.47522
C	-0.90214	-2.01495	2.98035
C	-2.04942	-2.53805	2.35082
C	-2.64489	-3.71920	2.82886
C	-2.09528	-4.38711	3.93546
C	-0.95088	-3.86837	4.56984
C	-0.35870	-2.68573	4.09918
C	-0.52014	0.70736	3.76637
C	-1.69387	1.49080	3.69759
C	-2.05330	2.32629	4.76878
C	-1.24666	2.39019	5.91749
C	-0.07521	1.61674	5.99058
C	0.28714	0.77950	4.92264
C	2.64417	1.93350	1.69071
C	1.74667	2.80075	2.34872
C	2.22761	3.89582	3.08343
C	3.60730	4.15108	3.15245
C	4.50585	3.30373	2.48306
C	4.03092	2.19672	1.75880
C	3.49776	-0.22873	-0.00645
C	4.37011	-1.17136	0.57876
C	5.54943	-1.55326	-0.08416
C	5.86898	-1.00081	-1.33612
C	5.00450	-0.06103	-1.92591
C	3.82634	0.32447	-1.26486
C	-1.24765	-3.15416	-1.35060
C	-2.56656	-2.66889	-1.26896
C	-3.64699	-3.45980	-1.69711
C	-3.41636	-4.74495	-2.21466
C	-2.10115	-5.23546	-2.30562
C	-1.02129	-4.44797	-1.87473
C	1.39969	-3.35674	-0.30511
C	1.10611	-4.11647	0.85295

C	1.97626	-5.13210	1.28036
C	3.14913	-5.41123	0.55609
C	3.44558	-4.66616	-0.59645
C	2.58036	-3.64233	-1.02281
C	-1.53202	0.25086	-3.30439
C	-1.90151	-0.80641	-4.16218
C	-3.07774	-0.72201	-4.92720
C	-3.89440	0.41826	-4.84842
C	-3.53811	1.47182	-3.98763
C	-2.36922	1.38703	-3.21388
C	1.07113	1.35830	-3.47511
C	0.87898	2.75663	-3.45223
C	1.57254	3.58352	-4.35107
C	2.46391	3.02517	-5.28290
C	2.65711	1.63344	-5.31525
C	1.96375	0.80213	-4.41886
H	2.28516	-0.46089	3.26429
H	1.88342	-1.77729	2.07183
H	0.61015	-2.03727	-3.37387
H	1.90971	-1.26168	-2.37647
H	-2.47435	-2.02672	1.47362
H	-3.54075	-4.11858	2.32670
H	-2.55881	-5.31536	4.30781
H	-0.51819	-4.38684	5.44126
H	0.53211	-2.28754	4.61271
H	-2.32773	1.45351	2.79733
H	-2.96961	2.93527	4.70093
H	-1.52912	3.04598	6.75725
H	0.56586	1.66514	6.88601
H	1.21339	0.18828	5.00426
H	0.66160	2.63533	2.26869
H	1.51284	4.56391	3.58989
H	3.98300	5.01721	3.72155
H	5.58964	3.50232	2.52124
H	4.75266	1.54118	1.24803
H	4.14387	-1.60908	1.56393
H	6.22440	-2.28684	0.38613
H	6.79732	-1.29795	-1.85098
H	5.25035	0.38403	-2.90384
H	3.16609	1.07439	-1.73188
H	-2.74848	-1.65627	-0.87492
H	-4.67248	-3.06390	-1.61996
H	-4.26245	-5.36875	-2.54698
H	-1.91280	-6.24389	-2.70948
H	0.00216	-4.85127	-1.94184
H	0.17782	-3.92969	1.41680
H	1.72760	-5.71691	2.18097
H	3.82727	-6.21494	0.88661
H	4.35734	-4.88194	-1.17702
H	2.83959	-3.07818	-1.93201
H	-1.27828	-1.70959	-4.24877
H	-3.35015	-1.55429	-5.59655
H	-4.80849	0.48777	-5.46067
H	-4.17406	2.36945	-3.91651
H	-2.10550	2.21725	-2.53856
H	0.18597	3.21147	-2.72796

H	1.41453	4.67345	-4.31649
H	3.00628	3.67510	-5.98885
H	3.34651	1.18639	-6.05041
H	2.11789	-0.28743	-4.47514
C	-3.18771	0.66061	0.24908
C	-4.45773	0.01299	0.30688
C	-0.93374	3.48719	0.06909
H	-1.91994	3.98634	0.15756
C	0.16915	4.43265	-0.11432
C	-7.02861	-1.16787	0.43276
C	-6.26032	-1.02695	1.60333
C	-4.98763	-0.44459	1.54662
C	-5.24517	-0.13826	-0.86965
C	-6.51661	-0.72243	-0.80049
H	-8.03240	-1.62057	0.48289
H	-6.66106	-1.36886	2.57149
H	-4.39139	-0.32555	2.46476
H	-4.84329	0.21789	-1.83125
H	-7.11993	-0.82461	-1.71744
C	2.20380	6.38901	-0.48103
C	0.90539	6.78164	-0.10915
C	-0.09665	5.81731	0.06522
C	1.48282	4.06144	-0.49823
C	2.48416	5.02405	-0.67925
H	2.99399	7.14472	-0.62175
H	0.67139	7.84845	0.04157
H	-1.11456	6.13359	0.35124
H	1.70536	2.99821	-0.66673
H	3.49642	4.70752	-0.97961

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	12.17	0.02123	YES	YES
8	a	17.73	0.02985	YES	YES
9	a	22.59	0.02556	YES	YES
10	a	24.07	0.08191	YES	YES
11	a	26.01	0.05363	YES	YES
12	a	28.84	0.12139	YES	YES
13	a	30.13	0.00214	YES	YES
14	a	31.45	0.11839	YES	YES
15	a	34.20	0.04195	YES	YES
16	a	37.62	0.02236	YES	YES
17	a	38.17	0.16063	YES	YES
18	a	39.74	0.01541	YES	YES
19	a	41.71	0.06494	YES	YES
20	a	43.47	0.03257	YES	YES
21	a	46.55	0.05315	YES	YES

22	a	48.12	0.04263	YES	YES
23	a	50.57	0.07805	YES	YES
24	a	51.77	0.09709	YES	YES
25	a	57.23	0.02408	YES	YES
26	a	57.97	0.06608	YES	YES
27	a	60.06	0.02200	YES	YES
28	a	62.41	0.05759	YES	YES
29	a	66.03	0.32809	YES	YES
30	a	68.59	0.04174	YES	YES
31	a	71.94	0.19997	YES	YES
32	a	73.76	0.12544	YES	YES
33	a	77.43	0.00487	YES	YES
34	a	83.63	0.14471	YES	YES
35	a	86.38	0.07212	YES	YES
36	a	91.69	0.92026	YES	YES
37	a	98.78	1.20842	YES	YES
38	a	100.31	0.57792	YES	YES
39	a	102.57	0.48789	YES	YES
40	a	109.15	1.55592	YES	YES
41	a	119.62	0.48851	YES	YES
42	a	128.39	1.59616	YES	YES
43	a	142.91	1.26907	YES	YES
44	a	152.98	0.14951	YES	YES
45	a	156.98	0.75730	YES	YES
46	a	162.51	0.19896	YES	YES
47	a	166.87	0.77034	YES	YES
48	a	174.93	0.31466	YES	YES
49	a	175.47	0.68496	YES	YES
50	a	179.13	0.70898	YES	YES

S7.19 Complex $TS_{[Dd\text{-}Z]+\text{-}[4'd\text{-}Z]}$

SCF Energy (au) (RI)BP86/SV(P) -4006.3087507350
SCF Energy (au) PBE0/def2-TZVPP -4005.652523614
SCF Energy (au) PBE0/def2-TZVPP -4005.7045801208 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.9773334
Chemical potential (kJ mol^{-1}) 2272.31
Dispersion correction (au) PBE0/def2-TZVPP -0.24437589

xyz coordinates

126

C	-1.68366	0.39690	-1.07997
C	-0.83985	1.70227	0.35317
Ru	-0.01303	0.03314	0.03772
P	-1.27328	-1.29510	1.58414
P	1.41543	-0.55821	1.91801
P	0.92502	-1.82864	-1.38351
P	1.52703	0.94933	-1.55200
C	0.22703	-1.87382	2.54802
C	2.27099	-0.69421	-2.04981
C	-2.16183	-2.82073	1.04315
C	-2.62583	-2.93179	-0.28403
C	-3.32108	-4.08523	-0.69031
C	-3.55128	-5.12984	0.22007
C	-3.09212	-5.02062	1.54616
C	-2.40480	-3.86881	1.96019
C	-2.46566	-0.54132	2.77053
C	-3.45951	0.30723	2.23203
C	-4.44242	0.86060	3.06858
C	-4.44135	0.57703	4.44528
C	-3.45286	-0.26317	4.98589
C	-2.46777	-0.82171	4.15404
C	1.56137	0.59599	3.36775
C	0.43521	1.35490	3.75397
C	0.48035	2.15585	4.90732
C	1.65743	2.22992	5.67216
C	2.78925	1.49636	5.27951
C	2.74338	0.67716	4.13797
C	3.08513	-1.34829	1.87489
C	3.36081	-2.55455	2.55382
C	4.66159	-3.08636	2.55674
C	5.70178	-2.41818	1.88886
C	5.43703	-1.21298	1.21546
C	4.13651	-0.68095	1.20599
C	0.07131	-2.46147	-2.90706
C	-0.86872	-1.64254	-3.57137
C	-1.48663	-2.08670	-4.75299
C	-1.17977	-3.35125	-5.28275
C	-0.24724	-4.17171	-4.62551
C	0.37594	-3.73358	-3.44504
C	1.78976	-3.34913	-0.78067
C	1.01766	-4.32501	-0.10705

C	1.60422	-5.52802	0.31924
C	2.96798	-5.77286	0.08036
C	3.74006	-4.81024	-0.59071
C	3.15601	-3.60591	-1.02087
C	0.89257	1.77873	-3.07088
C	0.92998	1.20121	-4.35691
C	0.44449	1.91473	-5.46746
C	-0.08435	3.20537	-5.30355
C	-0.13245	3.78274	-4.02148
C	0.34998	3.07520	-2.90999
C	2.95603	2.03081	-1.10604
C	2.97402	2.71153	0.12733
C	4.05374	3.55018	0.45785
C	5.12440	3.70387	-0.43782
C	5.11244	3.02521	-1.67121
C	4.03037	2.19836	-2.01011
H	0.14335	-1.94785	3.65255
H	0.52595	-2.86137	2.13380
H	2.54406	-0.84254	-3.11577
H	3.18199	-0.81972	-1.42547
H	-2.44660	-2.11070	-0.99689
H	-3.68111	-4.16463	-1.72878
H	-4.09447	-6.03367	-0.10127
H	-3.27699	-5.83549	2.26531
H	-2.06397	-3.78878	3.00642
H	-3.46001	0.53464	1.15349
H	-5.21261	1.52239	2.64022
H	-5.21274	1.01369	5.10048
H	-3.44627	-0.48862	6.06486
H	-1.70290	-1.47677	4.60144
H	-0.48753	1.32807	3.15319
H	-0.41023	2.73510	5.19877
H	1.69404	2.86470	6.57303
H	3.71981	1.55360	5.86869
H	3.63559	0.09790	3.85548
H	2.56547	-3.08826	3.09778
H	4.86265	-4.02816	3.09278
H	6.72252	-2.83423	1.89879
H	6.24889	-0.67618	0.69795
H	3.94778	0.27812	0.69587
H	-1.13372	-0.65829	-3.15685
H	-2.22073	-1.43601	-5.25553
H	-1.66961	-3.69989	-6.20680
H	0.00047	-5.16607	-5.03204
H	1.10206	-4.39325	-2.94612
H	-0.05985	-4.15954	0.06020
H	0.98638	-6.28244	0.83332
H	3.42725	-6.71900	0.41045
H	4.80746	-4.99777	-0.79118
H	3.78108	-2.87641	-1.55927
H	1.33361	0.18910	-4.51334
H	0.48621	1.45505	-6.46832
H	-0.45703	3.76505	-6.17704
H	-0.54447	4.79606	-3.88442
H	0.31056	3.53989	-1.91090
H	2.13517	2.58546	0.82959

H	4.05409	4.08653	1.42044
H	5.97134	4.36025	-0.17899
H	5.94809	3.14987	-2.37933
H	4.01992	1.69148	-2.98990
C	-2.75239	0.65663	-1.66722
C	-3.95365	0.97147	-2.37045
C	-1.46850	2.88754	0.38946
H	-2.35293	2.96392	-0.27034
C	-1.15729	4.11455	1.14485
C	-6.33529	1.60393	-3.77609
C	-6.37918	0.74261	-2.66405
C	-5.20590	0.42755	-1.96678
C	-3.92625	1.84116	-3.49775
C	-5.10571	2.15033	-4.18806
H	-7.26067	1.84914	-4.32244
H	-7.34025	0.31137	-2.33835
H	-5.24062	-0.25074	-1.09907
H	-2.96192	2.26689	-3.81843
H	-5.06739	2.82548	-5.05896
C	-0.65803	6.55990	2.51085
C	-1.77686	6.43394	1.66950
C	-2.02331	5.22877	0.99610
C	-0.03393	4.25941	1.99634
C	0.20998	5.46419	2.66995
H	-0.46281	7.50664	3.04016
H	-2.46656	7.28351	1.53508
H	-2.90441	5.14146	0.33819
H	0.64865	3.40917	2.14388
H	1.08942	5.54822	3.32986

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1	a	-179.32	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	6.22	0.03634	YES	YES
9	a	11.62	0.00122	YES	YES
10	a	15.70	0.01118	YES	YES
11	a	18.06	0.05933	YES	YES
12	a	19.37	0.02535	YES	YES
13	a	21.94	0.16054	YES	YES
14	a	22.75	0.05944	YES	YES
15	a	24.84	0.00480	YES	YES
16	a	28.10	0.01765	YES	YES
17	a	31.33	0.00070	YES	YES
18	a	33.65	0.04247	YES	YES
19	a	36.16	0.04925	YES	YES
20	a	39.56	0.13067	YES	YES
21	a	42.08	0.01663	YES	YES

22	a	43.11	0.08998	YES	YES
23	a	45.10	0.01133	YES	YES
24	a	45.83	0.04709	YES	YES
25	a	46.91	0.03025	YES	YES
26	a	49.50	0.11875	YES	YES
27	a	52.47	0.07499	YES	YES
28	a	57.34	0.26290	YES	YES
29	a	60.32	0.16188	YES	YES
30	a	61.72	0.07834	YES	YES
31	a	63.78	0.09983	YES	YES
32	a	66.38	0.09301	YES	YES
33	a	72.03	0.52860	YES	YES
34	a	77.11	0.01654	YES	YES
35	a	82.22	0.24934	YES	YES
36	a	86.63	0.48491	YES	YES
37	a	88.09	2.92062	YES	YES
38	a	93.51	1.77859	YES	YES
39	a	97.99	0.62334	YES	YES
40	a	107.54	3.43020	YES	YES
41	a	110.32	2.13425	YES	YES
42	a	118.09	0.69327	YES	YES
43	a	127.36	0.92979	YES	YES
44	a	145.62	4.53994	YES	YES
45	a	148.83	1.32699	YES	YES
46	a	155.94	2.38854	YES	YES
47	a	162.97	8.31884	YES	YES
48	a	163.42	1.80885	YES	YES
49	a	173.68	9.49670	YES	YES
50	a	174.71	4.03520	YES	YES

S7.20 Complex [Cf]

SCF Energy (au) (RI)BP86/SV(P) -4234.7732464370
SCF Energy (au) PBE0/def2-TZVPP -4234.120804577
SCF Energy (au) PBE0/def2-TZVPP -4234.1560106665 (CH_2Cl_2 Correction)
Zero Point Energy (au) 1.0279261
Chemical potential (kJ mol^{-1}) 2387.57
Dispersion correction (au) PBE0/def2-TZVPP -0.24829032

xyz coordinates

133

Ru	0.31950	-0.38748	0.12636
C	-1.28342	-0.16760	-1.07424
C	-0.15892	1.41999	0.87660
P	-0.98899	-1.54049	1.71268
P	1.69179	-0.76347	2.10743
P	1.11794	-2.12757	-1.38474
P	1.78664	0.61024	-1.42430
C	0.37280	-1.80790	2.97673
C	2.32237	-0.97220	-2.28017
C	-1.71819	-3.20977	1.37525
C	-2.30262	-3.42691	0.10831
C	-2.91211	-4.65919	-0.18480
C	-2.93426	-5.68572	0.77510
C	-2.34771	-5.47713	2.03597
C	-1.74616	-4.24345	2.33751
C	-2.37617	-0.70713	2.61481
C	-3.12874	0.27363	1.93449
C	-4.22584	0.88162	2.57072
C	-4.57087	0.52756	3.88608
C	-3.81820	-0.44413	4.57014
C	-2.72822	-1.06236	3.93572
C	2.04307	0.57364	3.34973
C	0.96948	1.26321	3.95783
C	1.21767	2.30098	4.87153
C	2.53674	2.67246	5.18242
C	3.60939	1.99978	4.57323
C	3.36563	0.95888	3.66045
C	3.23988	-1.77897	2.25708
C	3.49566	-2.57938	3.39278
C	4.68736	-3.31548	3.49307
C	5.64558	-3.25053	2.46555
C	5.40689	-2.44530	1.33978
C	4.20852	-1.71779	1.23531
C	0.08184	-2.79896	-2.77410
C	-0.46431	-1.91333	-3.73078
C	-1.28022	-2.39998	-4.76560
C	-1.57168	-3.77172	-4.85435
C	-1.04219	-4.65703	-3.90040
C	-0.22298	-4.17481	-2.86483
C	2.14546	-3.62043	-0.97754
C	1.86536	-4.35356	0.19303

C	2.60061	-5.50982	0.50724
C	3.63196	-5.94086	-0.34322
C	3.91692	-5.21906	-1.51625
C	3.17424	-4.07056	-1.83482
C	1.16790	1.73658	-2.75955
C	1.80512	1.82479	-4.01695
C	1.33856	2.72665	-4.98738
C	0.23684	3.55449	-4.70531
C	-0.39820	3.47194	-3.45449
C	0.05798	2.56280	-2.48307
C	3.34232	1.47358	-0.90752
C	3.27711	2.32445	0.21756
C	4.41575	3.03975	0.62703
C	5.62764	2.90516	-0.07226
C	5.69982	2.05405	-1.18926
C	4.56173	1.34430	-1.60860
H	0.14229	-1.48140	4.01307
H	0.69025	-2.87200	2.99582
H	2.22483	-0.98047	-3.38659
H	3.36649	-1.23506	-2.00792
H	-2.27666	-2.62139	-0.64677
H	-3.36614	-4.81592	-1.17687
H	-3.40922	-6.65320	0.54115
H	-2.36203	-6.27874	2.79351
H	-1.30190	-4.09183	3.33606
H	-2.84574	0.55999	0.90820
H	-4.80846	1.64607	2.03099
H	-5.42903	1.01053	4.38291
H	-4.08328	-0.72656	5.60281
H	-2.15656	-1.83251	4.48119
H	-0.07180	1.00270	3.71248
H	0.36810	2.83132	5.33157
H	2.72795	3.48952	5.89794
H	4.64892	2.28136	4.81161
H	4.21793	0.43981	3.19434
H	2.76462	-2.62142	4.21772
H	4.87260	-3.93875	4.38400
H	6.58196	-3.82740	2.54546
H	6.15583	-2.38437	0.53324
H	4.02691	-1.08261	0.35333
H	-0.26692	-0.83198	-3.66732
H	-1.70225	-1.69370	-5.49891
H	-2.21533	-4.15001	-5.66598
H	-1.26271	-5.73607	-3.96140
H	0.18617	-4.88282	-2.12698
H	1.05294	-4.02152	0.85941
H	2.36713	-6.07383	1.42512
H	4.21425	-6.84361	-0.09428
H	4.71935	-5.55743	-2.19311
H	3.39319	-3.52898	-2.77050
H	2.67911	1.19238	-4.24858
H	1.84163	2.78596	-5.96712
H	-0.12706	4.26568	-5.46590
H	-1.26518	4.11431	-3.22872
H	-0.44700	2.48457	-1.50617
H	2.32588	2.42167	0.77027

```
H          4.35196        3.70103        1.50656
H          6.52089        3.46378        0.25394
H          6.64794        1.94408       -1.74209
H          4.63256        0.68982       -2.49413
C         -2.31919       -0.02435       -1.75342
C         -3.50117        0.14053       -2.54094
C         -0.44793        2.56783        1.26846
C         -0.78781        3.87627        1.73416
C         -5.86941        0.46980       -4.11569
C         -5.90644       -0.25445       -2.90238
C         -4.75107       -0.41437       -2.13552
C         -3.48909        0.86502       -3.76220
C         -4.64670        1.03084       -4.54085
O         -7.05496        0.57043       -4.79505
H         -6.86819       -0.68542       -2.58037
H         -4.80005       -0.98003       -1.19111
H         -2.54277        1.31716       -4.10044
H         -4.58091        1.60507       -5.47756
C         -1.46959        6.49476        2.67033
C         -2.07848        5.34875        3.23031
C         -1.74602        4.07212        2.77254
C         -0.19095        5.04258        1.18666
C         -0.52004        6.33061        1.63964
O         -1.86303        7.70119        3.18707
H         -2.82213        5.49132        4.03106
H         -2.23822        3.18966        3.21205
H          0.55168        4.93104        0.38009
H         -0.02700        7.19960        1.17800
C         -1.29186        8.87889        2.65476
C         -7.07481        1.29262       -6.00916
H         -0.18440        8.90891        2.79895
H         -1.74974        9.72437        3.20830
H         -1.51353        8.99581        1.56615
H         -6.78637        2.36208       -5.86422
H         -8.11943        1.24873       -6.38031
H         -6.39881        0.84116       -6.77564

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7        a              11.27         0.00477       YES     YES
     8        a              12.25         0.02528       YES     YES
     9        a              14.35         0.08764       YES     YES
    10        a              15.44         0.12850       YES     YES
    11        a              18.94         0.14673       YES     YES
    12        a              20.87         0.32747       YES     YES
    13        a              22.23         0.02065       YES     YES
    14        a              24.02         0.35150       YES     YES
```

15	a	26.17	0.00238	YES	YES
16	a	28.33	0.29717	YES	YES
17	a	30.35	0.17013	YES	YES
18	a	33.26	0.06997	YES	YES
19	a	37.80	0.04063	YES	YES
20	a	40.06	0.08393	YES	YES
21	a	43.60	0.01152	YES	YES
22	a	46.22	0.08959	YES	YES
23	a	47.35	0.09415	YES	YES
24	a	49.32	0.25332	YES	YES
25	a	50.27	0.07985	YES	YES
26	a	50.57	0.02113	YES	YES
27	a	52.21	0.24900	YES	YES
28	a	52.69	0.00090	YES	YES
29	a	53.27	0.33846	YES	YES
30	a	59.29	0.09685	YES	YES
31	a	60.19	0.34993	YES	YES
32	a	61.66	0.07078	YES	YES
33	a	65.09	0.81945	YES	YES
34	a	70.40	1.56617	YES	YES
35	a	72.99	0.95870	YES	YES
36	a	80.37	0.04517	YES	YES
37	a	81.53	0.76200	YES	YES
38	a	85.53	2.46450	YES	YES
39	a	86.31	0.72670	YES	YES
40	a	95.52	0.42318	YES	YES
41	a	98.70	0.34721	YES	YES
42	a	107.34	0.55830	YES	YES
43	a	113.09	0.40714	YES	YES
44	a	114.94	0.86567	YES	YES
45	a	115.62	3.25247	YES	YES
46	a	140.50	0.10295	YES	YES
47	a	142.09	0.08821	YES	YES
48	a	160.68	0.00296	YES	YES
49	a	161.39	0.45342	YES	YES
50	a	161.69	0.36241	YES	YES

S7.21 Complex $[Df]^+$

SCF Energy (au) (RI)BP86/SV(P) -4235.2041310740
SCF Energy (au) PBE0/def2-TZVPP -4234.549190831
SCF Energy (au) PBE0/def2-TZVPP -4234.6060584902 (CH_2Cl_2 Correction)
Zero Point Energy (au) 1.0403407
Chemical potential (kJ mol^{-1}) 2419.95
Dispersion correction (au) PBE0/def2-TZVPP -0.25127961

xyz coordinates

134

Ru	0.48918	-0.15599	0.36926
C	-1.05863	-0.05878	-0.94088
C	0.04367	1.47999	1.10696
P	-0.80304	-1.44765	1.92289
P	1.91763	-0.73682	2.29061
P	1.36878	-2.02041	-1.18912
P	2.01550	0.78795	-1.22763
C	0.64476	-1.90391	3.03141
C	2.62300	-0.83559	-1.94005
C	-1.58949	-3.05260	1.45904
C	-2.10861	-3.22252	0.15826
C	-2.75497	-4.42326	-0.18656
C	-2.88162	-5.45693	0.75613
C	-2.36258	-5.29138	2.05348
C	-1.72214	-4.09315	2.40729
C	-2.07828	-0.64086	2.98064
C	-2.94193	0.29057	2.36561
C	-3.97948	0.88356	3.10373
C	-4.16027	0.55467	4.45773
C	-3.30297	-0.37333	5.07526
C	-2.26642	-0.97280	4.34090
C	2.18500	0.53791	3.61136
C	1.07868	1.05584	4.32301
C	1.27012	2.01983	5.32724
C	2.56139	2.48949	5.62317
C	3.66279	1.98790	4.90999
C	3.47946	1.01608	3.91105
C	3.52596	-1.64058	2.28972
C	3.78572	-2.68257	3.20654
C	5.04562	-3.30238	3.23507
C	6.06156	-2.88098	2.35966
C	5.81358	-1.83715	1.45275
C	4.55044	-1.22233	1.41321
C	0.40046	-2.61778	-2.64748
C	-0.04278	-1.69626	-3.62300
C	-0.78064	-2.14109	-4.73185
C	-1.09419	-3.50315	-4.87598
C	-0.66301	-4.42240	-3.90541
C	0.07956	-3.98515	-2.79533
C	2.32506	-3.52762	-0.70979
C	1.77084	-4.39879	0.25400

C	2.42326	-5.59753	0.58997
C	3.64066	-5.93349	-0.02524
C	4.19813	-5.07220	-0.98627
C	3.54249	-3.87920	-1.33227
C	1.40168	1.81231	-2.63540
C	1.97707	1.74360	-3.92352
C	1.53631	2.60496	-4.94176
C	0.52697	3.54822	-4.67978
C	-0.04494	3.62366	-3.39831
C	0.38468	2.75635	-2.37999
C	3.54410	1.70438	-0.72940
C	3.48459	2.59251	0.36551
C	4.61502	3.34406	0.73012
C	5.81448	3.21093	0.01066
C	5.88091	2.32757	-1.08169
C	4.75121	1.58067	-1.45436
H	0.49691	-1.79152	4.12607
H	0.94676	-2.95013	2.81305
H	2.68772	-0.89193	-3.04691
H	3.62172	-1.05775	-1.50885
H	-2.00822	-2.41019	-0.58154
H	-3.15906	-4.54700	-1.20424
H	-3.38868	-6.39676	0.48244
H	-2.46303	-6.09822	2.79798
H	-1.33366	-3.97341	3.43292
H	-2.80187	0.54926	1.30344
H	-4.64323	1.61445	2.61472
H	-4.97268	1.02345	5.03684
H	-3.44286	-0.63685	6.13651
H	-1.61143	-1.70459	4.84246
H	0.05372	0.71564	4.10198
H	0.39815	2.40386	5.88145
H	2.70921	3.24364	6.41334
H	4.68042	2.34477	5.13860
H	4.35744	0.62079	3.37697
H	3.01008	-3.01212	3.91702
H	5.23621	-4.11678	3.95298
H	7.05102	-3.36578	2.38837
H	6.60838	-1.49514	0.77000
H	4.37136	-0.39227	0.71000
H	0.17639	-0.62184	-3.52407
H	-1.11981	-1.41070	-5.48374
H	-1.67470	-3.84834	-5.74711
H	-0.89695	-5.49432	-4.01320
H	0.41944	-4.72250	-2.05180
H	0.80442	-4.15479	0.72633
H	1.97374	-6.27341	1.33573
H	4.15448	-6.87202	0.23956
H	5.14803	-5.33513	-1.47996
H	3.98397	-3.23185	-2.10756
H	2.78069	1.02264	-4.14769
H	1.99038	2.54185	-5.94425
H	0.18731	4.22782	-5.47859
H	-0.83753	4.35875	-3.18442
H	-0.07535	2.81569	-1.38183
H	2.54559	2.70088	0.93069

H	4.55557	4.03799	1.58424
H	6.70080	3.79986	0.29810
H	6.81736	2.22435	-1.65419
H	4.81791	0.90529	-2.32389
C	-2.05904	0.05446	-1.67073
C	-3.20535	0.17418	-2.52009
C	-0.23731	2.68500	1.60583
H	0.49535	3.03447	2.36542
C	-1.36033	3.59329	1.31688
C	-5.49447	0.41829	-4.20868
C	-5.55809	-0.33905	-3.01424
C	-4.43990	-0.45626	-2.18966
C	-3.16094	0.93019	-3.71971
C	-4.28184	1.05584	-4.55473
O	-6.63791	0.47165	-4.94265
H	-6.51152	-0.82659	-2.75646
H	-4.50915	-1.04576	-1.26133
H	-2.22253	1.43745	-3.99591
H	-4.20005	1.65605	-5.47305
C	-3.49881	5.40840	0.80500
C	-2.53122	5.70666	1.78913
C	-1.48171	4.80593	2.03261
C	-2.34148	3.30946	0.32666
C	-3.38807	4.19783	0.07735
O	-4.55401	6.20376	0.48434
H	-2.58163	6.63800	2.37212
H	-0.73513	5.05705	2.80504
H	-2.27382	2.37747	-0.26006
H	-4.14598	3.97776	-0.69084
C	-6.64781	1.22191	-6.14673
C	-4.71855	7.43477	1.17131
H	-6.43276	2.30091	-5.96194
H	-7.67037	1.12219	-6.56246
H	-5.91354	0.82423	-6.88677
H	-5.62784	7.90473	0.74629
H	-3.84831	8.11456	1.01280
H	-4.86636	7.27913	2.26613

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	10.67	0.01154	YES	YES
8	a	11.84	0.05060	YES	YES
9	a	13.92	0.00510	YES	YES
10	a	15.21	0.06884	YES	YES
11	a	16.12	0.05369	YES	YES
12	a	19.84	0.04883	YES	YES
13	a	22.73	0.48667	YES	YES

14	a	27.99	0.05247	YES	YES
15	a	30.26	0.01802	YES	YES
16	a	32.34	0.02177	YES	YES
17	a	33.15	0.08910	YES	YES
18	a	36.05	0.27182	YES	YES
19	a	38.58	0.03722	YES	YES
20	a	39.27	0.04760	YES	YES
21	a	42.37	0.03563	YES	YES
22	a	42.59	0.15370	YES	YES
23	a	45.32	0.11170	YES	YES
24	a	46.20	0.11162	YES	YES
25	a	47.10	0.35466	YES	YES
26	a	51.49	0.02818	YES	YES
27	a	53.23	0.06458	YES	YES
28	a	55.27	0.23694	YES	YES
29	a	57.87	0.23265	YES	YES
30	a	59.78	0.43939	YES	YES
31	a	60.97	0.12292	YES	YES
32	a	62.26	0.29840	YES	YES
33	a	65.97	0.60189	YES	YES
34	a	69.31	0.66592	YES	YES
35	a	73.37	1.48325	YES	YES
36	a	73.76	1.20947	YES	YES
37	a	79.90	0.82420	YES	YES
38	a	80.96	0.27115	YES	YES
39	a	84.86	0.83707	YES	YES
40	a	94.63	0.37927	YES	YES
41	a	97.52	0.35276	YES	YES
42	a	106.74	0.73899	YES	YES
43	a	113.72	1.79826	YES	YES
44	a	121.27	2.04094	YES	YES
45	a	126.79	1.29231	YES	YES
46	a	137.97	0.72125	YES	YES
47	a	141.93	0.27027	YES	YES
48	a	155.18	0.08404	YES	YES
49	a	159.33	0.33122	YES	YES
50	a	163.22	0.05578	YES	YES

S7.22 Complex $[Ff]^+$

SCF Energy (au) (RI)BP86/SV(P) -4235.2090162150
SCF Energy (au) PBE0/def2-TZVPP -4234.555965009
SCF Energy (au) PBE0/def2-TZVPP -4234.6094258562 (CH_2Cl_2 Correction)
Zero Point Energy (au) 1.0406652
Chemical potential (kJ mol^{-1}) 2423.64
Dispersion correction (au) PBE0/def2-TZVPP -0.25249907

xyz coordinates

134

C	0.31332	-1.89028	0.28411
C	-1.70397	-0.20023	-2.77470
C	0.99251	0.72117	-3.66035
C	0.57259	-2.07635	-3.09959
C	1.56162	0.21259	2.60446
C	-0.96732	1.72697	3.12060
C	-1.02891	-1.11976	3.32402
C	3.54137	-0.75536	0.60713
P	-2.26284	-0.25582	-0.97899
C	-0.12237	1.94742	-0.63890
P	2.14224	0.42062	0.82363
P	0.13958	-0.39750	-2.47064
P	-0.28596	0.22577	2.29110
Ru	-0.05098	0.11335	-0.11831
C	0.60982	-3.08033	0.50767
C	-3.16195	-1.85334	-0.78697
C	-3.62177	0.98983	-0.80587
C	2.96100	2.07516	0.78541
H	-1.88449	0.81866	-3.17945
H	-2.16401	-0.95027	-3.45246
H	1.92335	1.00020	3.29813
H	1.88690	-0.77777	2.98462
C	-2.23024	-3.16120	4.86971
C	-0.93901	-3.33867	4.34469
C	-0.34212	-2.32908	3.57105
C	-2.32946	-0.94930	3.85323
C	-2.92448	-1.96534	4.61871
H	-2.69457	-3.95424	5.47857
H	-0.38569	-4.27319	4.53108
H	0.65880	-2.50521	3.15046
H	-2.88337	-0.01290	3.68140
H	-3.93603	-1.81371	5.02967
C	-2.22301	3.85942	4.47834
C	-1.07501	3.25567	5.02275
C	-0.45629	2.18653	4.35526
C	-2.11388	2.34244	2.57494
C	-2.74452	3.39800	3.25848
H	-2.71303	4.69122	5.01034
H	-0.66385	3.61177	5.98148
H	0.42047	1.70236	4.81641
H	-2.52072	1.99176	1.61190

H	-3.64466	3.86438	2.82669
C	5.72751	-2.50043	0.25462
C	4.69491	-2.46361	-0.69728
C	3.60093	-1.59852	-0.52036
C	4.58229	-0.79611	1.56347
C	5.66825	-1.66863	1.38804
H	6.58268	-3.18229	0.11619
H	4.72918	-3.12222	-1.57997
H	2.77757	-1.60091	-1.25113
H	4.55545	-0.13636	2.44734
H	6.47563	-1.69456	2.13819
C	4.14044	4.64059	0.65706
C	4.78400	3.53870	0.06992
C	4.19952	2.26150	0.13151
C	2.31213	3.19209	1.35856
C	2.90326	4.46383	1.30088
H	4.60289	5.64017	0.61279
H	5.75679	3.66796	-0.43260
H	4.72420	1.40370	-0.31890
H	1.33307	3.08024	1.85313
H	2.38616	5.32380	1.75604
C	1.23372	-4.65293	-4.04650
C	0.09609	-4.46600	-3.24239
C	-0.23124	-3.18830	-2.76222
C	1.71782	-2.26956	-3.90439
C	2.04457	-3.55366	-4.37328
H	1.48778	-5.65859	-4.41937
H	-0.54147	-5.32464	-2.97760
H	-1.11634	-3.06580	-2.11886
H	2.35463	-1.41518	-4.18311
H	2.93496	-3.68987	-5.00889
C	2.37565	2.35700	-5.49726
C	1.16415	1.74722	-5.87009
C	0.47697	0.92847	-4.95929
C	2.20732	1.33734	-3.29179
C	2.89748	2.14915	-4.20914
H	2.91450	2.99692	-6.21501
H	0.75244	1.90584	-6.88021
H	-0.46277	0.44330	-5.27187
H	2.61255	1.19416	-2.27627
H	3.84449	2.62686	-3.91007
C	-4.64000	-4.22953	-0.43405
C	-3.70691	-3.82927	0.53637
C	-2.96298	-2.64757	0.36115
C	-4.11029	-2.25588	-1.75692
C	-4.83977	-3.44189	-1.58323
H	-5.21799	-5.15816	-0.29613
H	-3.54791	-4.44007	1.43953
H	-2.21521	-2.35172	1.11206
H	-4.29677	-1.63577	-2.65003
H	-5.57451	-3.74888	-2.34547
C	-5.66054	2.91664	-0.44741
C	-4.50305	3.23983	-1.17716
C	-3.48600	2.28699	-1.35123
C	-4.78412	0.67458	-0.06496
C	-5.79509	1.63469	0.11195

```
H         -6.45884        3.66529       -0.31532
H         -4.38306        4.24443       -1.61351
H         -2.57609        2.57206       -1.90260
H         -4.90998       -0.32934        0.37025
H         -6.69926        1.37177        0.68531
C          0.92718       -4.44639        0.78469
C          1.55310       -7.17385        1.35745
C          2.50743       -6.15838        1.59269
C          2.19221       -4.82106        1.30863
C         -0.01878       -5.48818        0.55571
C          0.28520       -6.81984        0.83540
O          1.75135       -8.49718        1.59581
H          3.50235       -6.39921        1.99556
H          2.94848       -4.04037        1.48840
H         -1.01113       -5.22765        0.15442
H         -0.44753       -7.62329        0.65930
C          0.05677        3.13325       -1.23023
C         -0.42636        4.49973       -0.98079
H          0.73713        3.04138       -2.10743
C         -1.31747        7.18384       -0.58520
C         -1.56899        6.18549        0.38744
C         -1.13234        4.87530        0.19195
C         -0.17440        5.51046       -1.93827
C         -0.60991        6.83278       -1.75579
O         -1.78512        8.42850       -0.30000
H         -2.11038        6.47388        1.30233
H         -1.32814        4.12234        0.97014
H          0.37947        5.25656       -2.85800
H         -0.38861        7.58069       -2.53137
C          3.00045       -8.92316        2.11835
C         -1.55662        9.47637       -1.23004
H         -0.46710        9.66051       -1.38318
H         -2.01953       10.38277       -0.79140
H         -2.03378        9.26355       -2.21574
H          3.20500       -8.47048        3.11722
H          3.84091       -8.67895        1.42670
H          2.92834      -10.02371        2.22695

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1                        0.00         0.00000         -       -
     2                        0.00         0.00000         -       -
     3                        0.00         0.00000         -       -
     4                        0.00         0.00000         -       -
     5                        0.00         0.00000         -       -
     6                        0.00         0.00000         -       -
     7        a              10.61         0.00186       YES     YES
     8        a              12.01         0.00228       YES     YES
     9        a              14.50         0.00983       YES     YES
    10        a              17.43         0.05946       YES     YES
    11        a              18.41         0.03717       YES     YES
    12        a              23.23         0.03213       YES     YES
    13        a              25.47         0.17281       YES     YES
```

14	a	27.81	0.12961	YES	YES
15	a	28.50	0.26087	YES	YES
16	a	30.95	0.25715	YES	YES
17	a	32.89	0.27118	YES	YES
18	a	33.25	0.20383	YES	YES
19	a	35.43	0.09355	YES	YES
20	a	39.12	0.06427	YES	YES
21	a	42.38	0.03030	YES	YES
22	a	44.05	0.02402	YES	YES
23	a	46.75	0.13417	YES	YES
24	a	47.78	0.04950	YES	YES
25	a	50.67	0.28057	YES	YES
26	a	52.82	0.31159	YES	YES
27	a	53.98	0.04537	YES	YES
28	a	56.93	0.04475	YES	YES
29	a	58.40	0.39753	YES	YES
30	a	60.16	0.98987	YES	YES
31	a	62.02	0.06798	YES	YES
32	a	65.64	0.05492	YES	YES
33	a	67.36	0.01886	YES	YES
34	a	71.07	0.81656	YES	YES
35	a	74.98	0.23772	YES	YES
36	a	76.63	1.67168	YES	YES
37	a	82.12	0.05735	YES	YES
38	a	85.00	0.30075	YES	YES
39	a	90.07	0.80544	YES	YES
40	a	98.13	1.68848	YES	YES
41	a	100.10	2.75052	YES	YES
42	a	104.54	1.14727	YES	YES
43	a	117.30	0.12917	YES	YES
44	a	123.01	1.19877	YES	YES
45	a	126.84	2.09928	YES	YES
46	a	146.37	1.01387	YES	YES
47	a	148.72	0.39677	YES	YES
48	a	152.20	0.05643	YES	YES
49	a	160.91	0.57861	YES	YES
50	a	166.24	0.44079	YES	YES

S7.23 Complex [3f]

SCF Energy (au) (RI)BP86/SV(P) -4234.7768657230
SCF Energy (au) PBE0/def2-TZVPP -4234.128290494
SCF Energy (au) PBE0/def2-TZVPP -4234.1583984054 (CH_2Cl_2 Correction)
Zero Point Energy (au) 1.0280986
Chemical potential (kJ mol^{-1}) 2381.16
Dispersion correction (au) PBE0/def2-TZVPP -0.24757938

xyz coordinates

133

C	0.17075	-2.01850	0.58963
C	-1.59128	0.17476	-2.73692
C	1.32223	0.75479	-3.36990
C	0.34936	-1.93868	-3.28041
C	1.46358	-0.11454	2.67456
C	-0.69901	1.82617	3.17557
C	-1.35750	-0.93313	3.35660
C	3.54628	-0.76824	0.62548
P	-2.23313	-0.29550	-1.02737
C	-0.19550	1.92164	-0.55685
P	2.05012	0.28377	0.93169
P	0.18976	-0.32081	-2.37807
P	-0.35169	0.21865	2.31428
Ru	-0.07943	-0.06278	-0.03009
C	0.38454	-3.14777	1.08379
C	-3.05810	-1.93296	-1.29020
C	-3.69709	0.79343	-0.66837
C	2.79462	1.97332	0.99573
H	-1.64208	1.28070	-2.81252
H	-2.07079	-0.30089	-3.61888
H	1.93326	0.41009	3.53342
H	1.59562	-1.21256	2.77627
C	-3.03266	-2.59160	4.91564
C	-1.63712	-2.66331	5.05781
C	-0.80224	-1.83942	4.28169
C	-2.76174	-0.86942	3.21460
C	-3.59309	-1.69238	3.99044
H	-3.68547	-3.23904	5.52451
H	-1.18781	-3.37116	5.77378
H	0.28972	-1.91848	4.40193
H	-3.21187	-0.16739	2.49176
H	-4.68750	-1.63050	3.87038
C	-1.26817	4.24966	4.50479
C	-0.71266	3.17011	5.21754
C	-0.43375	1.96327	4.55814
C	-1.25948	2.90776	2.46828
C	-1.54237	4.11487	3.13457
H	-1.48923	5.19752	5.02381
H	-0.50252	3.26677	6.29608
H	-0.02045	1.11567	5.13174
H	-1.44799	2.80758	1.38771

H	-1.97475	4.95676	2.56943
C	5.81112	-2.37820	0.12770
C	4.59738	-2.64608	-0.52808
C	3.46684	-1.84768	-0.27801
C	4.77050	-0.49996	1.27759
C	5.89490	-1.30518	1.03328
H	6.69706	-3.00497	-0.06920
H	4.52532	-3.48409	-1.24128
H	2.50652	-2.06697	-0.77044
H	4.85142	0.35206	1.97316
H	6.84564	-1.08765	1.54823
C	3.99726	4.53189	0.93153
C	3.91429	3.76006	-0.24181
C	3.31198	2.49405	-0.21270
C	2.86272	2.76054	2.16296
C	3.46309	4.03310	2.13006
H	4.46828	5.52865	0.90674
H	4.31076	4.15152	-1.19278
H	3.23835	1.90639	-1.14275
H	2.43981	2.39864	3.11274
H	3.50919	4.63550	3.05255
C	0.48351	-4.40217	-4.65595
C	0.36797	-4.37998	-3.25693
C	0.29938	-3.15448	-2.56844
C	0.46524	-1.96646	-4.69046
C	0.53023	-3.19159	-5.37223
H	0.53766	-5.36389	-5.19349
H	0.32873	-5.32275	-2.68673
H	0.20490	-3.13601	-1.46900
H	0.51106	-1.02420	-5.26165
H	0.62085	-3.20095	-6.47155
C	3.19708	2.35934	-4.75591
C	1.86340	2.77988	-4.62693
C	0.93176	1.98493	-3.93594
C	2.66865	0.34097	-3.49945
C	3.59815	1.13636	-4.18822
H	3.92600	2.98505	-5.29745
H	1.53947	3.74119	-5.05830
H	-0.10382	2.34165	-3.83596
H	2.99704	-0.61577	-3.05994
H	4.64293	0.79614	-4.28180
C	-4.36274	-4.41563	-1.62117
C	-3.53058	-4.19834	-0.51125
C	-2.87855	-2.96266	-0.34390
C	-3.90399	-2.15539	-2.40111
C	-4.54915	-3.39055	-2.56715
H	-4.86759	-5.38728	-1.75389
H	-3.37351	-4.99933	0.22985
H	-2.19881	-2.80195	0.50824
H	-4.07365	-1.35565	-3.14167
H	-5.20288	-3.55384	-3.44030
C	-5.88930	2.46334	-0.01046
C	-4.70740	3.01727	-0.53214
C	-3.61587	2.19295	-0.85160
C	-4.88713	0.24479	-0.13687
C	-5.97266	1.07554	0.19098

```
H         -6.74401        3.11314        0.24142
H         -4.62511        4.10578       -0.68801
H         -2.67998        2.64421       -1.21825
H         -4.97423       -0.84269        0.01546
H         -6.89397        0.62899        0.60129
C          0.59802       -4.45743        1.61923
C          1.01903       -7.08367        2.68302
C          2.05329       -6.42056        1.98871
C          1.83885       -5.13284        1.47088
C         -0.42713       -5.14950        2.33129
C         -0.22357       -6.43035        2.84849
O          1.11910       -8.33670        3.22601
H          3.03532       -6.89599        1.84417
H          2.65743       -4.62567        0.93535
H         -1.39848       -4.65150        2.48006
H         -1.02130       -6.95719        3.39666
C         -0.22219        3.11999       -0.91311
C         -0.26195        4.50921       -1.24513
C         -0.35448        7.30417       -1.87830
C          0.41614        6.83484       -0.78947
C          0.46208        5.47456       -0.48147
C         -1.02853        5.00626       -2.33387
C         -1.08016        6.37447       -2.65185
O         -0.33147        8.65641       -2.09683
H          0.97857        7.57167       -0.19339
H          1.07073        5.12602        0.36730
H         -1.60799        4.29759       -2.94904
H         -1.69255        6.70083       -3.50612
C          2.34201       -9.03293        3.09229
C         -1.09040        9.17730       -3.16886
H         -0.92972       10.27495       -3.15960
H         -2.18152        8.96983       -3.04831
H         -0.75625        8.77055       -4.15430
H          3.18725       -8.49019        3.58088
H          2.60447       -9.21431        2.02181
H          2.20049      -10.00969        3.59881

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7        a               7.14         0.13112      YES     YES
     8        a               9.55         0.02099      YES     YES
     9        a              12.71         0.08841      YES     YES
    10        a              14.26         0.02676      YES     YES
    11        a              15.54         0.03227      YES     YES
    12        a              16.71         0.05607      YES     YES
    13        a              20.55         0.03506      YES     YES
    14        a              23.10         0.14980      YES     YES
```

15	a	24.08	0.23393	YES	YES
16	a	24.86	0.06926	YES	YES
17	a	27.68	0.00474	YES	YES
18	a	30.38	0.22034	YES	YES
19	a	32.63	0.10142	YES	YES
20	a	35.09	0.01829	YES	YES
21	a	35.58	0.10487	YES	YES
22	a	36.98	0.07653	YES	YES
23	a	38.77	0.60359	YES	YES
24	a	43.04	0.07066	YES	YES
25	a	44.42	0.19543	YES	YES
26	a	47.03	0.15224	YES	YES
27	a	49.09	0.05154	YES	YES
28	a	51.56	0.02322	YES	YES
29	a	54.57	0.04472	YES	YES
30	a	56.93	0.51134	YES	YES
31	a	58.27	0.81711	YES	YES
32	a	59.39	0.08545	YES	YES
33	a	63.47	0.01792	YES	YES
34	a	67.69	1.61515	YES	YES
35	a	73.83	1.28762	YES	YES
36	a	74.13	0.33801	YES	YES
37	a	80.27	0.48452	YES	YES
38	a	90.07	1.18673	YES	YES
39	a	92.35	2.26898	YES	YES
40	a	97.97	0.55984	YES	YES
41	a	101.69	3.29076	YES	YES
42	a	105.91	0.20325	YES	YES
43	a	117.05	0.04937	YES	YES
44	a	118.31	0.47925	YES	YES
45	a	124.43	1.74093	YES	YES
46	a	134.21	0.07905	YES	YES
47	a	146.18	0.13495	YES	YES
48	a	150.16	0.03579	YES	YES
49	a	159.56	0.55590	YES	YES
50	a	163.45	0.22989	YES	YES

S7.24 Complex $[4f]^+$

SCF Energy (au) (RI)BP86/SV(P) -4235.2433512890
SCF Energy (au) PBE0/def2-TZVPP -4234.590645656
SCF Energy (au) PBE0/def2-TZVPP -4234.6453806515 (CH_2Cl_2 Correction)
Zero Point Energy (au) 1.0430186
Chemical potential (kJ mol^{-1}) 2438.19
Dispersion correction (au) PBE0/def2-TZVPP -0.25601834

xyz coordinates

134

C	1.71582	-1.86429	2.74507
C	2.17876	-2.00844	4.07443
H	2.34876	-1.12042	4.70676
C	2.44294	-3.28214	4.60009
H	2.80118	-3.38186	5.63797
C	2.26291	-4.42648	3.80033
H	2.47639	-5.42637	4.21259
C	1.81815	-4.28898	2.47623
H	1.67860	-5.18014	1.84296
C	1.54305	-3.01408	1.94797
H	1.18847	-2.91439	0.91184
C	3.07794	0.56448	2.33513
C	4.10092	0.19552	1.43056
H	3.86827	-0.45623	0.57157
C	5.41485	0.65283	1.62111
H	6.20443	0.35093	0.91349
C	5.72338	1.48658	2.71139
H	6.75552	1.84302	2.86153
C	4.71269	1.85653	3.61417
H	4.95005	2.50148	4.47624
C	3.39600	1.39577	3.43089
H	2.62233	1.68226	4.16226
C	-2.34871	1.98502	2.72938
C	-3.37404	2.43528	1.86971
H	-3.51714	1.96217	0.88465
C	-4.23905	3.46902	2.26992
H	-5.04326	3.79976	1.59225
C	-4.08105	4.07281	3.52823
H	-4.75878	4.88295	3.84369
C	-3.05835	3.63422	4.38733
H	-2.93034	4.10016	5.37808
C	-2.20215	2.59231	3.99528
H	-1.42281	2.24917	4.69473
C	-2.31248	-0.82516	3.04818
C	-1.69663	-1.86580	3.77831
H	-0.60191	-1.91503	3.87936
C	-2.47189	-2.87374	4.37715
H	-1.97097	-3.67333	4.94672
C	-3.87079	-2.86279	4.25233
H	-4.47728	-3.65067	4.72816
C	-4.49163	-1.83518	3.52134

H	-5.58935	-1.81107	3.42207
C	-3.72087	-0.82364	2.92515
H	-4.23178	-0.01813	2.37463
C	0.23698	0.63582	3.29443
H	0.18999	0.19986	4.31541
H	0.49206	1.71591	3.36525
C	-1.17322	0.74789	-3.25494
C	-0.11197	1.42126	-3.89937
H	0.48668	2.17403	-3.36143
C	0.20065	1.13284	-5.23761
H	1.02688	1.67016	-5.73065
C	-0.52964	0.16023	-5.94157
H	-0.28140	-0.06424	-6.99180
C	-1.57514	-0.52580	-5.30106
H	-2.15306	-1.28990	-5.84642
C	-1.89682	-0.23654	-3.96458
H	-2.72605	-0.77508	-3.47839
C	-3.40045	0.87027	-1.44650
C	-3.97831	-0.25205	-0.81828
H	-3.33417	-0.99664	-0.32381
C	-5.37413	-0.42690	-0.82885
H	-5.81489	-1.31367	-0.34507
C	-6.19967	0.52255	-1.45354
H	-7.29369	0.38704	-1.45755
C	-5.62832	1.64538	-2.08118
H	-6.27252	2.38850	-2.57932
C	-4.23484	1.81595	-2.08634
H	-3.79739	2.68755	-2.60218
C	1.69362	3.39966	-0.96389
C	3.00100	3.03743	-0.57441
H	3.15359	2.24836	0.17906
C	4.11819	3.67381	-1.14210
H	5.13088	3.38163	-0.81957
C	3.94503	4.67078	-2.11653
H	4.82074	5.16734	-2.56536
C	2.64698	5.03687	-2.51163
H	2.49949	5.82385	-3.26934
C	1.52828	4.41329	-1.93342
H	0.52359	4.74755	-2.23829
C	0.11186	3.96068	1.26591
C	1.14893	4.03903	2.22386
H	1.99067	3.32734	2.19096
C	1.14651	5.04519	3.20306
H	1.96999	5.09592	3.93440
C	0.10913	5.99291	3.23925
H	0.10921	6.78764	4.00296
C	-0.92073	5.92730	2.28747
H	-1.73429	6.67069	2.29930
C	-0.92077	4.91958	1.30701
H	-1.73851	4.90432	0.57052
C	-1.23668	2.88711	-1.17847
H	-2.08623	3.29323	-0.59112
H	-1.09850	3.51510	-2.08308
C	-0.47266	-1.88467	-0.56032
C	0.56528	-1.36339	-1.13243
C	1.41468	-0.31574	-1.31842

C	2.51170	0.02956	-2.04576
H	2.90314	1.05345	-1.92833
C	3.25212	-0.80557	-2.99297
C	2.94554	-2.16218	-3.26042
H	2.10060	-2.63947	-2.73696
C	3.69133	-2.92246	-4.16996
H	3.41665	-3.97354	-4.34244
C	4.78476	-2.33698	-4.85256
O	5.57180	-2.98144	-5.75170
C	5.10783	-0.98228	-4.59993
H	5.96089	-0.53934	-5.13741
C	4.35675	-0.23994	-3.68999
H	4.62255	0.81491	-3.50524
C	-1.32461	-3.04535	-0.57340
C	-1.23623	-3.96150	-1.65963
H	-0.52644	-3.75315	-2.47652
C	-2.03370	-5.10953	-1.72265
H	-1.92997	-5.78519	-2.58447
C	-2.96057	-5.38298	-0.68786
O	-3.78236	-6.46148	-0.64952
C	-3.06062	-4.48257	0.39930
H	-3.77917	-4.70992	1.20170
C	-2.26173	-3.34037	0.45381
H	-2.34461	-2.66335	1.31511
P	1.39802	-0.16399	2.06075
P	-1.31245	0.52518	2.23929
P	0.25161	2.65259	-0.05655
P	-1.56515	1.06882	-1.48005
Ru	-0.05890	0.30396	0.18517
C	5.30762	-4.34404	-6.05117
C	-3.72822	-7.41174	-1.70497
H	-2.72005	-7.88184	-1.78238
H	-3.99684	-6.95239	-2.68499
H	-4.47408	-8.19142	-1.45287
H	4.29156	-4.47882	-6.49117
H	5.40526	-4.99006	-5.14721
H	6.06906	-4.64674	-6.79726

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	12.39	0.02972	YES	YES
8	a	15.41	0.26108	YES	YES
9	a	18.11	0.15999	YES	YES
10	a	20.65	0.00820	YES	YES
11	a	22.45	0.28164	YES	YES
12	a	25.96	0.09356	YES	YES
13	a	28.29	0.42804	YES	YES

14	a	32.33	0.14491	YES	YES
15	a	33.08	0.09505	YES	YES
16	a	36.58	0.01665	YES	YES
17	a	39.33	0.01124	YES	YES
18	a	40.95	0.09479	YES	YES
19	a	42.28	0.02055	YES	YES
20	a	44.61	0.10182	YES	YES
21	a	45.40	0.09462	YES	YES
22	a	45.71	0.06936	YES	YES
23	a	48.29	0.07996	YES	YES
24	a	50.10	0.19858	YES	YES
25	a	51.04	0.12871	YES	YES
26	a	52.49	0.28212	YES	YES
27	a	53.63	0.05196	YES	YES
28	a	57.79	0.17713	YES	YES
29	a	60.71	0.30883	YES	YES
30	a	64.69	0.11630	YES	YES
31	a	65.54	0.22203	YES	YES
32	a	69.62	0.63080	YES	YES
33	a	74.84	0.19869	YES	YES
34	a	75.57	0.08984	YES	YES
35	a	78.10	1.91525	YES	YES
36	a	79.77	0.29737	YES	YES
37	a	81.70	0.22718	YES	YES
38	a	90.41	0.08660	YES	YES
39	a	94.72	0.15416	YES	YES
40	a	100.58	0.16670	YES	YES
41	a	105.90	0.58539	YES	YES
42	a	110.59	0.31242	YES	YES
43	a	116.69	1.18750	YES	YES
44	a	132.42	1.22854	YES	YES
45	a	134.25	0.89028	YES	YES
46	a	142.25	0.60537	YES	YES
47	a	151.58	0.39777	YES	YES
48	a	163.34	0.11450	YES	YES
49	a	166.90	0.38039	YES	YES
50	a	170.71	1.09595	YES	YES

S7.25Complex $[4'f]^+$

SCF Energy (au) (RI)BP86/SV(P) -4235.2450738280
SCF Energy (au) PBE0/def2-TZVPP -4234.592607205
SCF Energy (au) PBE0/def2-TZVPP -4234.6463803025 (CH_2Cl_2 Correction)
Zero Point Energy (au) 1.0426673
Chemical potential (kJ mol^{-1}) 2431.54
Dispersion correction (au) PBE0/def2-TZVPP -0.25518875

xyz coordinates

134

C	-1.83907	0.35840	0.06354
C	-1.02292	1.48394	0.12816
Ru	0.45139	0.00637	0.06331
P	0.66209	-0.34559	2.41914
P	2.28421	1.22658	0.79181
P	1.74296	-1.89761	-0.75443
P	0.62334	0.15808	-2.30456
C	2.38778	0.39480	2.47269
C	1.94147	-1.15486	-2.47818
C	0.79444	-2.02866	3.17910
C	0.01289	-3.07534	2.64697
C	0.05879	-4.35834	3.22000
C	0.89083	-4.60741	4.32414
C	1.67659	-3.56917	4.85748
C	1.62725	-2.28482	4.29138
C	-0.31838	0.55727	3.71149
C	-1.69264	0.79465	3.49182
C	-2.47201	1.42199	4.47961
C	-1.88974	1.81903	5.69419
C	-0.52139	1.58638	5.92123
C	0.25976	0.95872	4.93777
C	2.14121	3.03859	1.19281
C	1.27400	3.45734	2.22757
C	1.16634	4.81683	2.56289
C	1.90555	5.78180	1.85716
C	2.75539	5.37676	0.81458
C	2.87730	4.01531	0.48556
C	4.00105	1.15365	0.09395
C	5.11736	0.92793	0.92887
C	6.41874	0.94811	0.40018
C	6.62554	1.20451	-0.96585
C	5.52216	1.44115	-1.80287
C	4.21846	1.41281	-1.27777
C	1.00206	-3.56825	-1.10509
C	-0.39505	-3.72537	-1.02549
C	-0.99443	-4.95936	-1.33285
C	-0.19817	-6.05056	-1.71858
C	1.19837	-5.90214	-1.79947
C	1.79860	-4.66966	-1.49366
C	3.45121	-2.38624	-0.21846
C	3.59529	-2.95999	1.06672

C	4.85318	-3.38746	1.52178
C	5.98672	-3.24977	0.70147
C	5.85231	-2.68550	-0.57736
C	4.59381	-2.25683	-1.03579
C	-0.83367	-0.38223	-3.30770
C	-0.94337	-1.65554	-3.90500
C	-2.07365	-1.98128	-4.67668
C	-3.10700	-1.04570	-4.85042
C	-3.01319	0.21849	-4.23953
C	-1.88630	0.54910	-3.47158
C	1.20130	1.61251	-3.29031
C	1.09513	2.91392	-2.75819
C	1.50606	4.02329	-3.51921
C	2.03329	3.83851	-4.80790
C	2.14301	2.54113	-5.34278
C	1.72217	1.43215	-4.59221
H	2.64815	1.05380	3.32837
H	3.11842	-0.44081	2.40761
H	1.87004	-1.86512	-3.32913
H	2.91384	-0.62158	-2.53823
H	-0.62582	-2.88922	1.76873
H	-0.55481	-5.16797	2.79294
H	0.93026	-5.61411	4.77145
H	2.33148	-3.75997	5.72363
H	2.24846	-1.48280	4.72358
H	-2.15727	0.49353	2.54060
H	-3.54201	1.60665	4.29088
H	-2.50142	2.31279	6.46698
H	-0.05704	1.89382	6.87267
H	1.32962	0.78617	5.14065
H	0.66602	2.72490	2.78135
H	0.49315	5.12016	3.38111
H	1.82168	6.84857	2.12205
H	3.34455	6.12379	0.25755
H	3.57003	3.71995	-0.31730
H	4.98528	0.74464	2.00688
H	7.27838	0.76841	1.06627
H	7.64832	1.22716	-1.37638
H	5.67292	1.65643	-2.87349
H	3.36624	1.62422	-1.94328
H	-1.01927	-2.86958	-0.72231
H	-2.08958	-5.06189	-1.26310
H	-0.66408	-7.02194	-1.95299
H	1.82911	-6.75566	-2.09832
H	2.89472	-4.57176	-1.55212
H	2.71306	-3.09558	1.71338
H	4.94409	-3.83948	2.52311
H	6.97354	-3.58902	1.05676
H	6.73261	-2.58095	-1.23235
H	4.51933	-1.82781	-2.04703
H	-0.15212	-2.41055	-3.77896
H	-2.13900	-2.97526	-5.14892
H	-3.98661	-1.29946	-5.46464
H	-3.82109	0.95760	-4.36600
H	-1.82209	1.54638	-3.00552
H	0.68575	3.05648	-1.74600

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H          1.41252        5.03789       -3.09896
H          2.35714        4.70830       -5.40275
H          2.55077        2.39318       -6.35632
H          1.79280        0.42177       -5.02966
C         -2.39402       -0.77026        0.04919
C         -3.26974       -1.89275        0.05026
C         -1.27602        2.82549        0.14494
H         -0.40307        3.49711        0.22445
C         -2.56433        3.52254        0.09436
C         -5.12476       -4.05368        0.06976
C         -4.51571       -3.61796        1.27442
C         -3.60946       -2.56168        1.26517
C         -3.88019       -2.34711       -1.15028
C         -4.79476       -3.40772       -1.14608
O         -5.99855       -5.07951        0.18678
H         -4.78909       -4.12794        2.21122
H         -3.15816       -2.22344        2.21110
H         -3.63399       -1.84635       -2.09961
H         -5.25478       -3.71914       -2.09527
C         -5.00422        5.00875        0.00568
C         -3.76688        5.67998        0.12174
C         -2.57724        4.93826        0.16378
C         -3.82414        2.87047       -0.02352
C         -5.01452        3.59304       -0.06664
O         -6.21790        5.61655       -0.04541
H         -3.71923        6.77735        0.17994
H         -1.61846        5.47660        0.25682
H         -3.86610        1.77167       -0.08626
H         -5.98763        3.08519       -0.15870
C         -6.28086        7.03349        0.02002
C         -6.67683       -5.55518       -0.97036
H         -7.35592        7.29594       -0.03928
H         -5.74107        7.50871       -0.83258
H         -5.86287        7.41963        0.97936
H         -7.29780       -4.75550       -1.43614
H         -7.33720       -6.37308       -0.62106
H         -5.96298       -5.95798       -1.72603

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1                        0.00         0.00000         -       -
     2                        0.00         0.00000         -       -
     3                        0.00         0.00000         -       -
     4                        0.00         0.00000         -       -
     5                        0.00         0.00000         -       -
     6                        0.00         0.00000         -       -
     7        a              11.99         0.02671       YES     YES
     8        a              13.30         0.01887       YES     YES
     9        a              17.56         0.13565       YES     YES
    10        a              18.81         0.31015       YES     YES
    11        a              20.99         0.24407       YES     YES
    12        a              23.61         0.00781       YES     YES
    13        a              26.76         0.18448       YES     YES
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14	a	28.39	0.02314	YES	YES
15	a	31.02	0.17419	YES	YES
16	a	31.74	0.16701	YES	YES
17	a	34.91	0.17160	YES	YES
18	a	35.84	0.38417	YES	YES
19	a	38.39	0.07563	YES	YES
20	a	39.92	0.01966	YES	YES
21	a	41.70	0.06019	YES	YES
22	a	42.12	0.23058	YES	YES
23	a	44.39	0.19210	YES	YES
24	a	47.83	0.10677	YES	YES
25	a	48.18	0.12651	YES	YES
26	a	50.80	0.20900	YES	YES
27	a	52.52	0.24425	YES	YES
28	a	55.92	0.19507	YES	YES
29	a	58.74	0.01295	YES	YES
30	a	59.15	0.24746	YES	YES
31	a	64.26	0.26516	YES	YES
32	a	65.17	0.17178	YES	YES
33	a	68.53	0.19449	YES	YES
34	a	71.28	0.49184	YES	YES
35	a	75.28	0.22538	YES	YES
36	a	78.67	1.71051	YES	YES
37	a	82.74	0.37507	YES	YES
38	a	85.85	0.45923	YES	YES
39	a	94.85	0.62484	YES	YES
40	a	95.08	2.25595	YES	YES
41	a	100.39	0.07449	YES	YES
42	a	107.55	0.01191	YES	YES
43	a	120.85	1.77909	YES	YES
44	a	123.03	2.04306	YES	YES
45	a	129.45	2.74713	YES	YES
46	a	137.78	0.93783	YES	YES
47	a	152.37	0.20478	YES	YES
48	a	160.80	0.06300	YES	YES
49	a	164.91	0.44711	YES	YES
50	a	166.43	0.15861	YES	YES

S7.26 Complex $TS_{[Df]+-[4'f]}$

SCF Energy (au) (RI)BP86/SV(P) -4235.1980395000
SCF Energy (au) PBE0/def2-TZVPP -4234.544643834
SCF Energy (au) PBE0/def2-TZVPP -4234.5992187806 (CH_2Cl_2 Correction)
Zero Point Energy (au) 1.0397846
Chemical potential (kJ mol^{-1}) 2417.55
Dispersion correction (au) PBE0/def2-TZVPP -0.25264172

xyz coordinates

134

C	-1.14013	0.09847	-0.77042
C	-0.21008	1.36577	0.78944
Ru	0.54120	-0.30249	0.33002
P	-0.71063	-1.61607	1.88953
P	1.97676	-0.85131	2.20664
P	1.50763	-2.12075	-1.10996
P	2.08307	0.65311	-1.21971
C	0.78667	-2.13567	2.89738
C	2.86158	-0.96829	-1.73628
C	-1.57311	-3.16683	1.38190
C	-2.05261	-3.28878	0.06069
C	-2.73937	-4.45191	-0.33162
C	-2.94464	-5.49558	0.58613
C	-2.46834	-5.37618	1.90518
C	-1.78952	-4.21438	2.30562
C	-1.92367	-0.84253	3.04495
C	-2.87072	0.04938	2.49309
C	-3.86057	0.62049	3.31018
C	-3.91211	0.31181	4.68028
C	-2.97036	-0.57253	5.23485
C	-1.97992	-1.14930	4.42241
C	2.14585	0.39777	3.57494
C	0.99360	1.08516	4.02004
C	1.07932	2.01472	5.06951
C	2.31846	2.28727	5.67545
C	3.46876	1.61529	5.23213
C	3.38582	0.67172	4.19251
C	3.64689	-1.64352	2.19154
C	3.92384	-2.82871	2.90567
C	5.22273	-3.36527	2.91570
C	6.26099	-2.72162	2.22158
C	5.99615	-1.53594	1.51456
C	4.69701	-1.00092	1.49594
C	0.68550	-2.73032	-2.65811
C	-0.23258	-1.89050	-3.32745
C	-0.83264	-2.31177	-4.52638
C	-0.53151	-3.57363	-5.06615
C	0.37640	-4.41561	-4.40158
C	0.98299	-4.00007	-3.20436
C	2.37282	-3.64121	-0.50824
C	1.60610	-4.60906	0.18204

C	2.19465	-5.80925	0.61383
C	3.55601	-6.05791	0.36602
C	4.32361	-5.10254	-0.32056
C	3.73672	-3.90230	-0.75812
C	1.46713	1.50201	-2.73730
C	1.68423	1.03016	-4.04835
C	1.21410	1.76463	-5.15192
C	0.52379	2.97188	-4.95620
C	0.29528	3.44211	-3.64999
C	0.75945	2.71108	-2.54596
C	3.46749	1.76142	-0.70208
C	3.38384	2.46391	0.51788
C	4.42181	3.32961	0.90699
C	5.55022	3.49022	0.08612
C	5.63883	2.79083	-1.13221
C	4.59933	1.93599	-1.53088
H	0.69235	-2.15303	4.00368
H	1.09867	-3.14076	2.53844
H	3.14942	-1.09752	-2.80068
H	3.76371	-1.10124	-1.10120
H	-1.89012	-2.46841	-0.65781
H	-3.11259	-4.54024	-1.36471
H	-3.48134	-6.40711	0.27575
H	-2.63301	-6.19085	2.62950
H	-1.43421	-4.12691	3.34639
H	-2.82931	0.29915	1.42023
H	-4.59188	1.31732	2.86978
H	-4.68815	0.76279	5.32029
H	-3.00555	-0.81833	6.30889
H	-1.25299	-1.84040	4.87957
H	0.01417	0.89276	3.55373
H	0.16730	2.52946	5.41357
H	2.38582	3.02133	6.49497
H	4.44495	1.81749	5.70277
H	4.29770	0.14601	3.87135
H	3.13090	-3.34256	3.47181
H	5.42384	-4.29139	3.47841
H	7.28017	-3.14127	2.23722
H	6.80663	-1.01742	0.97655
H	4.50832	-0.05640	0.95890
H	-0.49611	-0.91001	-2.90175
H	-1.55000	-1.64646	-5.03383
H	-1.00808	-3.90427	-6.00373
H	0.61734	-5.40859	-4.81563
H	1.69042	-4.67470	-2.69808
H	0.53164	-4.43764	0.36156
H	1.58055	-6.55764	1.14110
H	4.01733	-7.00102	0.70199
H	5.38936	-5.29304	-0.52723
H	4.35704	-3.17834	-1.30962
H	2.21829	0.08474	-4.23073
H	1.39453	1.38730	-6.17183
H	0.16350	3.54920	-5.82351
H	-0.24942	4.38603	-3.48546
H	0.57118	3.08827	-1.52712
H	2.50104	2.33165	1.16348

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H          4.34585        3.87925        1.85917
H          6.36451        4.16716        0.39255
H          6.52048        2.91997       -1.78133
H          4.66890        1.41070       -2.49856
C         -2.20354        0.31441       -1.38766
C         -3.39462        0.54178       -2.14025
C         -0.61296        2.57569        1.18039
H          0.01457        2.84641        2.06363
C         -1.60517        3.59611        0.81557
C         -5.77653        1.05333       -3.62322
C         -5.82094        0.29076       -2.42977
C         -4.65758        0.04212       -1.70526
C         -3.36650        1.29214       -3.34633
C         -4.53321        1.54856       -4.08009
O         -6.96566        1.25278       -4.24601
H         -6.79736       -0.09013       -2.09156
H         -4.70976       -0.54761       -0.77619
H         -2.40289        1.68693       -3.70712
H         -4.46443        2.13807       -5.00621
C         -3.51072        5.63582        0.22646
C         -2.73405        5.70650        1.40418
C         -1.79835        4.69845        1.68225
C         -2.38529        3.55018       -0.36895
C         -3.31877        4.54582       -0.65643
O         -4.44802        6.54820       -0.14386
H         -2.84889        6.54041        2.11215
H         -1.20299        4.76992        2.60848
H         -2.25312        2.71400       -1.06945
H         -3.92686        4.50141       -1.57340
C         -4.69612        7.66012        0.70263
C         -7.00361        2.04100       -5.42721
H         -5.49255        8.25094        0.20784
H         -3.78876        8.29844        0.82159
H         -5.05226        7.33903        1.70976
H         -6.63868        3.07830       -5.23932
H         -8.06784        2.08031       -5.73457
H         -6.40381        1.58268       -6.24779

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1        a            -149.87         0.00000       YES     YES
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7                        0.00         0.00000        -       -
     8        a               3.63         0.17476       YES     YES
     9        a               8.74         0.00806       YES     YES
    10        a              12.06         0.18188       YES     YES
    11        a              14.24         0.21666       YES     YES
    12        a              15.09         0.08326       YES     YES
    13        a              20.87         0.16124       YES     YES
```

14	a	23.84	0.04666	YES	YES
15	a	26.48	0.29430	YES	YES
16	a	30.29	0.12252	YES	YES
17	a	33.74	0.15307	YES	YES
18	a	34.95	0.08609	YES	YES
19	a	35.16	0.15717	YES	YES
20	a	37.44	0.20585	YES	YES
21	a	39.25	0.09763	YES	YES
22	a	40.85	0.13073	YES	YES
23	a	42.68	0.10680	YES	YES
24	a	44.28	0.28358	YES	YES
25	a	46.09	0.13618	YES	YES
26	a	47.06	0.09210	YES	YES
27	a	50.68	0.04583	YES	YES
28	a	52.50	0.04115	YES	YES
29	a	55.97	0.63864	YES	YES
30	a	57.29	1.19004	YES	YES
31	a	59.78	0.05053	YES	YES
32	a	61.85	0.01575	YES	YES
33	a	65.92	0.45100	YES	YES
34	a	70.06	0.26188	YES	YES
35	a	73.40	0.69525	YES	YES
36	a	78.00	2.00640	YES	YES
37	a	80.07	0.53546	YES	YES
38	a	83.11	0.45152	YES	YES
39	a	88.44	3.67964	YES	YES
40	a	96.57	1.06642	YES	YES
41	a	98.28	1.64111	YES	YES
42	a	104.15	4.20516	YES	YES
43	a	111.05	0.68385	YES	YES
44	a	116.25	2.29829	YES	YES
45	a	123.20	5.01345	YES	YES
46	a	137.33	5.49657	YES	YES
47	a	143.25	0.09247	YES	YES
48	a	152.94	0.60566	YES	YES
49	a	154.90	24.59411	YES	YES
50	a	162.44	0.03988	YES	YES

S7.27 Proton sponge

SCF Energy (au) (RI)BP86/SV(P) -653.3309117434
SCF Energy (au) PBE0/def2-TZVPP -653.2525919652
SCF Energy (au) PBE0/def2-TZVPP -653.2597464086 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.2845876
Chemical potential (kJ mol^{-1}) 639.28
Dispersion correction (au) PBE0/def2-TZVPP -0.03935925

xyz coordinates

34

C	-1.19098	0.53183	-0.18474
C	-2.43133	0.68416	-0.82711
C	-0.43033	-0.69353	-0.40094
C	0.96434	-0.89962	-0.02803
C	1.48791	-2.20346	-0.05031
C	0.73824	-3.30123	-0.53515
C	-0.52065	-3.09628	-1.07394
C	-1.11878	-1.80004	-1.04044
C	-2.39914	-1.60018	-1.63992
H	-1.08323	-3.92639	-1.53231
H	1.19436	-4.30560	-0.54247
H	2.53396	-2.37333	0.24371
C	-3.01540	-0.36165	-1.58046
H	-2.88092	-2.44939	-2.15198
H	-3.99589	-0.20023	-2.05935
H	-3.00640	1.61042	-0.68395
N	-0.70963	1.54633	0.67079
N	1.79035	0.18672	0.33088
C	-0.40969	1.18631	2.05222
C	-1.25866	2.88184	0.54868
C	1.93567	1.27974	-0.62414
C	3.00938	-0.07548	1.06934
H	-1.30290	3.18716	-0.51832
H	-0.59228	3.59474	1.08441
H	-2.28641	2.99460	0.99005
H	2.09475	2.24661	-0.09446
H	1.02948	1.37327	-1.25050
H	2.81121	1.10643	-1.30481
H	3.38168	0.88116	1.50039
H	3.84000	-0.50106	0.44254
H	2.81189	-0.77698	1.90738
H	-1.30969	1.32017	2.70983
H	0.41077	1.82327	2.45415
H	-0.09167	0.12965	2.11893

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -

2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	56.65	0.75068	YES	YES
8	a	95.96	1.88692	YES	YES
9	a	106.49	3.46773	YES	YES
10	a	116.44	0.37149	YES	YES
11	a	122.24	1.01804	YES	YES
12	a	142.95	0.35398	YES	YES
13	a	171.79	0.79922	YES	YES
14	a	208.02	0.07219	YES	YES
15	a	233.79	0.40761	YES	YES
16	a	258.99	4.16322	YES	YES
17	a	287.71	1.27664	YES	YES
18	a	300.14	1.52157	YES	YES
19	a	303.53	7.51256	YES	YES
20	a	326.67	0.22660	YES	YES
21	a	344.70	1.30912	YES	YES
22	a	354.84	2.60517	YES	YES
23	a	375.38	1.69839	YES	YES
24	a	434.14	1.27962	YES	YES
25	a	464.48	5.09684	YES	YES
26	a	476.91	2.65129	YES	YES
27	a	520.66	4.59137	YES	YES
28	a	521.81	2.55716	YES	YES
29	a	527.79	0.09692	YES	YES
30	a	534.06	1.63894	YES	YES
31	a	619.37	1.34967	YES	YES
32	a	641.61	8.37534	YES	YES
33	a	663.05	7.50533	YES	YES
34	a	747.34	0.46734	YES	YES
35	a	754.41	8.70185	YES	YES
36	a	757.41	56.90380	YES	YES
37	a	769.82	2.52115	YES	YES
38	a	835.61	12.51615	YES	YES
39	a	845.80	0.45021	YES	YES
40	a	866.55	4.22332	YES	YES
41	a	894.69	3.68403	YES	YES
42	a	940.69	30.24377	YES	YES
43	a	944.00	0.81855	YES	YES
44	a	952.02	0.88688	YES	YES
45	a	1029.30	96.79414	YES	YES
46	a	1036.39	30.68533	YES	YES
47	a	1051.75	5.60632	YES	YES
48	a	1057.74	7.86744	YES	YES
49	a	1080.56	12.56245	YES	YES
50	a	1083.60	3.51040	YES	YES

S7.28 [HProton sponge]$^+$

SCF Energy (au) (RI)BP86/SV(P) -653.7298291209
SCF Energy (au) PBE0/def2-TZVPP -653.6546459553
SCF Energy (au) PBE0/def2-TZVPP -653.7122924463 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.2956309
Chemical potential (kJ mol^{-1}) 668.18
Dispersion correction (au) PBE0/def2-TZVPP -0.04071040

xyz coordinates

35

C	-1.27799	0.31178	0.06919
C	-2.66241	0.28108	-0.04830
C	-0.46650	-0.76409	-0.43187
C	0.96715	-0.82075	-0.35632
C	1.68159	-1.89765	-0.86427
C	1.00586	-2.98296	-1.47904
C	-0.37738	-2.97021	-1.57446
C	-1.14315	-1.88003	-1.06306
C	-2.56647	-1.87336	-1.16424
H	-0.90884	-3.80981	-2.05093
H	1.58709	-3.82943	-1.87686
H	2.78107	-1.91899	-0.79481
C	-3.31385	-0.81623	-0.66821
H	-3.06477	-2.72943	-1.64706
H	-4.41192	-0.81996	-0.75101
H	-3.26843	1.11470	0.34147
N	-0.59950	1.45146	0.71265
N	1.66982	0.31336	0.28383
C	-0.93897	1.59105	2.15386
C	-0.78473	2.72921	-0.02508
C	2.54960	1.06195	-0.65959
C	2.38978	-0.07397	1.53071
H	-0.50600	2.58647	-1.08868
H	-0.13430	3.50777	0.42670
H	-1.84076	3.07733	0.02221
H	2.92705	1.97548	-0.15466
H	1.96499	1.34639	-1.55718
H	3.41431	0.43932	-0.97459
H	2.76780	0.84269	2.02966
H	3.24780	-0.74163	1.30251
H	1.69061	-0.60577	2.20662
H	-2.00128	1.89082	2.29427
H	-0.28795	2.36812	2.60726
H	-0.77311	0.62333	2.66890
H	0.68380	1.02196	0.58040

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN

1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	34.37	0.01558	YES	YES
8	a	103.23	0.58780	YES	YES
9	a	128.83	0.47567	YES	YES
10	a	155.64	178.20337	YES	YES
11	a	160.54	150.56855	YES	YES
12	a	176.14	3.66330	YES	YES
13	a	192.97	0.21471	YES	YES
14	a	218.46	0.40887	YES	YES
15	a	223.22	0.10700	YES	YES
16	a	235.70	0.17979	YES	YES
17	a	247.24	126.64666	YES	YES
18	a	262.93	9.98622	YES	YES
19	a	274.09	0.18349	YES	YES
20	a	306.35	298.06269	YES	YES
21	a	314.75	0.08619	YES	YES
22	a	335.71	808.52357	YES	YES
23	a	370.53	11.54635	YES	YES
24	a	439.80	9.31732	YES	YES
25	a	450.13	105.78460	YES	YES
26	a	469.98	0.79636	YES	YES
27	a	502.20	15.79133	YES	YES
28	a	523.59	7.68487	YES	YES
29	a	526.37	0.02396	YES	YES
30	a	549.63	11.91848	YES	YES
31	a	580.31	280.29650	YES	YES
32	a	633.72	0.23689	YES	YES
33	a	657.21	0.01022	YES	YES
34	a	717.68	71.64922	YES	YES
35	a	768.69	138.47574	YES	YES
36	a	769.89	0.43902	YES	YES
37	a	772.75	6.22060	YES	YES
38	a	776.94	66.60926	YES	YES
39	a	855.52	4.20483	YES	YES
40	a	885.08	17.73469	YES	YES
41	a	905.04	0.04216	YES	YES
42	a	913.49	17.17444	YES	YES
43	a	923.75	2.41372	YES	YES
44	a	978.22	0.00630	YES	YES
45	a	989.70	0.00229	YES	YES
46	a	999.59	31.21941	YES	YES
47	a	1001.32	16.37569	YES	YES
48	a	1007.64	15.29921	YES	YES
49	a	1025.75	103.65308	YES	YES
50	a	1056.64	0.52381	YES	YES

S7.29 Pyridine

SCF Energy (au) (RI)BP86/SV(P) -248.1066297523
SCF Energy (au) PBE0/def2-TZVPP -248.0746694250
SCF Energy (au) PBE0/def2-TZVPP -248.0817570498 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.0862104
Chemical potential (kJ mol^{-1}) 154.10
Dispersion correction (au) PBE0/def2-TZVPP -0.00841146

xyz coordinates

11

N	1.07664	0.21029	-1.19060
C	0.58344	1.25382	-0.50176
C	-0.35332	1.12930	0.54051
C	-0.80080	-0.15631	0.88513
C	-0.29292	-1.25536	0.17378
C	0.64024	-1.01484	-0.85125
H	0.95671	2.25306	-0.79746
H	-0.72214	2.02371	1.06935
H	-1.53445	-0.29978	1.69631
H	-0.61253	-2.28441	0.40709
H	1.05914	-1.85947	-1.43112

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	361.91	0.00003	YES	YES
8	a	407.02	2.95124	YES	YES
9	a	590.49	4.11585	YES	YES
10	a	649.86	0.36676	YES	YES
11	a	695.42	50.99604	YES	YES
12	a	743.57	4.37772	YES	YES
13	a	870.11	0.00009	YES	YES
14	a	923.22	0.01539	YES	YES
15	a	964.42	0.00030	YES	YES
16	a	981.28	9.00977	YES	YES
17	a	984.79	0.00594	YES	YES
18	a	1021.65	3.04290	YES	YES
19	a	1049.67	0.00031	YES	YES
20	a	1062.35	4.80612	YES	YES
21	a	1129.82	1.34523	YES	YES
22	a	1206.31	3.23261	YES	YES
23	a	1325.59	0.84605	YES	YES
24	a	1338.35	0.10751	YES	YES

25	a	1436.78	23.84228	YES	YES
26	a	1471.44	2.86106	YES	YES
27	a	1592.98	20.10630	YES	YES
28	a	1594.27	10.53416	YES	YES
29	a	3059.94	36.96739	YES	YES
30	a	3063.27	9.71276	YES	YES
31	a	3093.85	3.78534	YES	YES
32	a	3107.88	25.02201	YES	YES
33	a	3115.74	7.59709	YES	YES

S7.30 [Hpyridine]$^+$

SCF Energy (au) (RI)BP86/SV(P) -248.4713768608
SCF Energy (au) PBE0/def2-TZVPP -248.4444248666
SCF Energy (au) PBE0/def2-TZVPP -248.5220537530 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.0999681
Chemical potential (kJ mol^{-1}) 189.99
Dispersion correction (au) PBE0/def2-TZVPP -0.00900921

xyz coordinates

12

N	0.89280	0.17525	-0.98532
C	0.43271	1.27304	-0.32821
C	-0.49625	1.11288	0.69939
C	-0.93444	-0.18336	1.03082
C	-0.43424	-1.29539	0.32704
C	0.49358	-1.09127	-0.69380
H	0.82847	2.24755	-0.65221
H	-0.87026	2.00014	1.23280
H	-1.66840	-0.32759	1.84041
H	-0.75885	-2.31988	0.56503
H	0.93544	-1.90163	-1.29328
H	1.57943	0.31026	-1.74268

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	379.71	0.97251	YES	YES
8	a	392.46	0.00006	YES	YES
9	a	601.74	0.01395	YES	YES
10	a	625.26	0.13623	YES	YES
11	a	661.56	96.95914	YES	YES
12	a	725.49	62.95160	YES	YES
13	a	834.39	10.81840	YES	YES
14	a	846.20	0.00002	YES	YES
15	a	954.98	2.59017	YES	YES
16	a	970.82	0.00016	YES	YES
17	a	999.53	3.13975	YES	YES
18	a	1016.83	0.45173	YES	YES
19	a	1017.04	0.06264	YES	YES
20	a	1049.39	4.44995	YES	YES
21	a	1056.00	5.27538	YES	YES
22	a	1152.92	1.12395	YES	YES
23	a	1183.07	1.04674	YES	YES

24	a	1269.02	0.08873	YES	YES
25	a	1349.76	1.24634	YES	YES
26	a	1391.24	9.58071	YES	YES
27	a	1473.55	19.91942	YES	YES
28	a	1534.35	45.90459	YES	YES
29	a	1612.92	23.14023	YES	YES
30	a	1636.56	27.31715	YES	YES
31	a	3131.83	0.56118	YES	YES
32	a	3146.52	2.76912	YES	YES
33	a	3148.08	13.64381	YES	YES
34	a	3159.25	25.24800	YES	YES
35	a	3160.51	0.95182	YES	YES
36	a	3399.94	152.11996	YES	YES

S7.31(MeOH)$_4$

SCF Energy (au) (RI)BP86/SV(P) -462.5583485669
SCF Energy (au) PBE0/def2-TZVPP -462.6005360868
SCF Energy (au) PBE0/def2-TZVPP -462.6081871275 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.2058545
Chemical potential (kJ mol^{-1}) 423.66
Dispersion correction (au) PBE0/def2-TZVPP -0.01271465

xyz coordinates

24

H	0.69462	1.93326	2.13806
C	0.68224	2.55564	1.20913
H	1.67882	3.04992	1.11066
H	-0.08283	3.35212	1.33554
O	0.35883	1.80851	0.04747
H	1.02320	1.02930	-0.04311
O	-0.36090	-1.80726	0.04671
H	0.08259	-3.35352	1.33097
C	-0.68156	-2.55555	1.20840
H	-0.68965	-1.93457	2.13832
H	-1.67931	-3.04799	1.11266
O	1.80681	-0.35907	-0.04825
C	2.55587	-0.68230	-1.20871
H	3.04987	-1.67896	-1.10961
H	1.93507	-0.69436	-2.13870
H	3.35267	0.08270	-1.33355
H	1.02745	-1.02352	0.04122
O	-1.80906	0.36055	-0.04602
C	-2.55552	0.68153	-1.20886
H	-1.93299	0.68977	-2.13772
H	-3.35333	-0.08255	-1.33280
H	-3.04801	1.67930	-1.11362
H	-1.02535	-1.02780	-0.04151
H	-1.02952	1.02483	0.04330

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	29.35	0.00002	YES	YES
8	a	48.73	0.51164	YES	YES
9	a	74.42	5.90094	YES	YES
10	a	74.48	5.90298	YES	YES
11	a	82.12	0.00240	YES	YES

12	a	91.69	0.00652	YES	YES
13	a	105.85	1.61481	YES	YES
14	a	105.96	1.60694	YES	YES
15	a	110.61	2.96789	YES	YES
16	a	117.55	0.23557	YES	YES
17	a	135.89	0.14289	YES	YES
18	a	136.39	8.46882	YES	YES
19	a	136.39	8.32329	YES	YES
20	a	165.70	0.00010	YES	YES
21	a	257.17	0.00010	YES	YES
22	a	338.43	58.23423	YES	YES
23	a	338.47	58.20314	YES	YES
24	a	347.43	6.52222	YES	YES
25	a	915.92	6.77407	YES	YES
26	a	1038.49	178.64670	YES	YES
27	a	1038.61	178.34815	YES	YES
28	a	1058.28	0.01169	YES	YES
29	a	1064.47	259.68936	YES	YES
30	a	1082.28	81.45276	YES	YES
31	a	1082.37	81.23976	YES	YES
32	a	1096.06	0.00184	YES	YES
33	a	1129.03	39.26083	YES	YES
34	a	1136.17	40.88916	YES	YES
35	a	1136.19	40.88476	YES	YES
36	a	1148.35	0.00005	YES	YES
37	a	1156.86	33.07660	YES	YES
38	a	1156.89	33.17810	YES	YES
39	a	1157.23	6.90137	YES	YES
40	a	1256.55	0.00261	YES	YES
41	a	1425.88	21.91580	YES	YES
42	a	1428.36	15.24609	YES	YES
43	a	1428.39	15.11610	YES	YES
44	a	1432.29	0.00002	YES	YES
45	a	1434.71	28.01388	YES	YES
46	a	1434.74	28.11472	YES	YES
47	a	1435.26	0.58493	YES	YES
48	a	1437.83	0.00198	YES	YES
49	a	1442.39	42.46358	YES	YES
50	a	1442.39	42.62973	YES	YES

S7.32 $[H(MeOH)_4]^+$

SCF Energy (au) (RI)BP86/SV(P) -462.9201903133
SCF Energy (au) PBE0/def2-TZVPP -462.9701893694
SCF Energy (au) PBE0/def2-TZVPP -463.0317625936 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.2149554
Chemical potential (kJ mol^{-1}) 437.97
Dispersion correction (au) PBE0/def2-TZVPP -0.01193877

xyz coordinates

25

H	5.27259	0.08659	0.62411
C	4.31660	-0.45897	0.46977
H	4.33383	-1.42164	1.02744
H	4.19105	-0.66531	-0.61138
O	3.19810	0.36129	0.86217
H	3.24764	0.58397	1.81655
H	0.08433	-0.22476	-0.12646
O	-0.88548	-0.88268	0.23131
H	-1.67569	-1.71648	-1.55303
C	-1.20321	-2.02133	-0.59288
H	-0.25796	-2.55997	-0.80249
H	-1.88461	-2.69587	-0.03416
O	1.07095	0.34318	-0.51197
C	0.87800	1.64925	-1.09065
H	0.56008	2.39337	-0.32687
H	1.82784	1.97707	-1.55921
H	0.10119	1.56138	-1.87648
H	1.90619	0.31693	0.11812
O	-2.94091	0.38683	1.06521
C	-4.08283	0.72171	0.25298
H	-3.69446	0.97780	-0.75260
H	-4.79375	-0.13047	0.16581
H	-4.60791	1.60895	0.66806
H	-1.73427	-0.37284	0.55459
H	-3.22730	0.18197	1.98205

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	17.61	0.27981	YES	YES
8	a	29.76	0.19242	YES	YES
9	a	41.03	0.38854	YES	YES
10	a	47.60	1.76431	YES	YES

11	a	55.79	2.27203	YES	YES
12	a	70.30	8.76178	YES	YES
13	a	80.78	1.95901	YES	YES
14	a	89.66	1.47813	YES	YES
15	a	97.91	2.31500	YES	YES
16	a	108.10	0.46828	YES	YES
17	a	113.13	6.22458	YES	YES
18	a	123.17	1.51265	YES	YES
19	a	150.84	4.10865	YES	YES
20	a	154.17	1.43986	YES	YES
21	a	182.97	2.47060	YES	YES
22	a	287.62	49.92567	YES	YES
23	a	323.30	234.91437	YES	YES
24	a	372.20	111.89787	YES	YES
25	a	421.13	129.40268	YES	YES
26	a	571.02	27.95533	YES	YES
27	a	949.32	406.89352	YES	YES
28	a	973.91	325.32751	YES	YES
29	a	992.53	643.14029	YES	YES
30	a	1021.50	179.87823	YES	YES
31	a	1027.17	16.94326	YES	YES
32	a	1046.50	25.73077	YES	YES
33	a	1083.71	35.07033	YES	YES
34	a	1092.37	35.29998	YES	YES
35	a	1122.49	327.92452	YES	YES
36	a	1133.05	16.81579	YES	YES
37	a	1135.77	48.29859	YES	YES
38	a	1138.96	5.87035	YES	YES
39	a	1140.35	40.24077	YES	YES
40	a	1157.58	43.24470	YES	YES
41	a	1216.28	1423.65572	YES	YES
42	a	1320.95	146.08575	YES	YES
43	a	1348.45	47.24867	YES	YES
44	a	1350.54	34.41105	YES	YES
45	a	1403.39	31.64265	YES	YES
46	a	1419.93	1.61287	YES	YES
47	a	1428.09	16.68445	YES	YES
48	a	1429.22	4.11042	YES	YES
49	a	1434.63	65.72452	YES	YES
50	a	1435.49	17.57504	YES	YES

S8. References

1. B. Chaudret, G. Commenges and R. Poilblanc, *J. Chem. Soc., Dalton Trans.*, **1984**, 1635.
2. S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis-Stuttgart*, **1980**, 627.
3. S. Marqués-González, M. Parthey, D. S. Yufit, J. A. K. Howard, M. Kaupp and P. J. Low, *Organomet.*, **2014**, *33*, 4947.
4. F. J. Arnaiz, *J. Chem. Educ.*, **1997**, *74*, 1332.
5. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, **1997**, *62*, 7512.
6. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, **1996**, *96*, 877.
7. G. M. Sheldrick, *Acta Crystallogr., Sect.A*, **2008**, *64*, 112.
8. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl. Cryst.*, **2009**, *42*, 339.
9. A. Klamt and G. Schuurmann, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 799.
10. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, **2010**, *132*, 154104.
11. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, **2011**, *32*, 1456.
12. P. Csaszar and P. Pulay, *J. Mol. Struct.*, **1984**, *114*, 31.
13. R. Ahlrichs, M. Bar, M. Haser, H. Horn and C. Kolmel, *Chem. Phys. Lett.*, **1989**, *162*, 165.
14. K. Eichkorn, O. Treutler, H. Ohm, M. Haser and R. Ahlrichs, *Chem. Phys. Lett.*, **1995**, *240*, 283.
15. O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, **1995**, *102*, 346.
16. K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, **1997**, *97*, 119.
17. M. von Arnim and R. Ahlrichs, *J. Chem. Phys.*, **1999**, *111*, 9183.
18. P. Deglmann and F. Furche, *J. Chem. Phys.*, **2002**, *117*, 9535.
19. P. Deglmann, F. Furche and R. Ahlrichs, *Chem. Phys. Lett.*, **2002**, *362*, 511.
20. P. Deglmann, K. May, F. Furche and R. Ahlrichs, *Chem. Phys. Lett.*, **2004**, *384*, 103.