Supporting Information

Metal-Metal Communication Between 1,1'-Bis(diphenylphosphino)cobaltocenium and an Organonickel Moiety

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Contents

List of Figures

List of Tables

1 Experimental

^{1}H NMR, $\{^{1}H\}^{11}B$ NMR, $\{^{1}H\}^{13}C$ NMR and ^{31}P NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1299986 MHz, 26.866 MHz, 62.8954017 MHz, 101.2544800 MHz respectively. ^{1}H NMR and $\{^{1}H\}^{13}C$ NMR spectra were referenced against remanent solvent peak. ^{31}P NMR spectra were referenced against H_3PO_4 as external standard. IR spectra were recorded on a Nicolet 6700 FT-IR. UV-vis-NIR absorption spectra were obtained on J&M TIDAS spectrophotometer. Cyclic voltammetry was carried out in a 0.1 M $^{n}Bu_4NPF_6$ solution in acetonitrile using a three-electrode configuration (glassy carbon working, Pt wire counter, and Ag reference electrode) on a Metrohm Autolab potentiostat. The couple $[Fe(C_5H_5)_2]/[Fe(C_5H_5)_2]^+$ ($FeCp_2/FeCp_2^+$) served as internal reference in all experiments. All solvents were degassed by passing through argon prior to use. Spectroelectrochemistry was performed at -30 °C using an optically transparent thin-layered electrode (OTTLE) [1] and a liquid nitrogen cryostat previously described. [2] A suitable crystals of **[1]**$_2(Fe_2OCl_6)$ [ac465a], **[1]**PF_6 [ac539 sqd], **[2]**$(BF_4)_n(PF_6)_m$ [ac500/] and **[2]**$(BF_4)_2$ [ac535] were selected and measured on an Apex II, Brucker diffractometer. Using Olex2 [3] the structures were solved with the ShelXS structure solution program using Direct Methods and refined with the least squared refinement. [4]

Density functional theory (DFT) calculations were performed using the molecular structure of $\mathbf{[1]}^+$. A computational analysis was performed by means of restricted Kohn-Sham density functional theory (DFT) using TPSS [5] functional in combination with the D3 dispersion correction [6]with the def2-TZVP and Weigend J auxiliary basis set. [7,8] Geometry optimizations were realized with the ORCA program package with TightSCF convergence (1.0e-7 a.u.). [9] Solvation in CH_2Cl_2 was modeled using the CPCM solvation model. [10] Open-shell calculations on the structure $\mathbf{[1]}^0$, $\mathbf{[1]}^{-1}$ (S =3) and compared to restricted KS for and $\mathbf{[1]}^{-1}$ were determined by adding the requisite number of electrons, and calculations were performed by means of (un)restricted Kohn–Sham DFT using the same basis set, functionals, and solvent models as $\mathbf{[1]}^+$.

Density functional theory (DFT) calculations were performed using the molecular structure of $[\mathbf{2}]^{2+}$. A computational analysis was performed by means of restricted Kohn-Sham density functional theory (DFT) using TPSS [5] functional in combination with the D3 dispersion correction [6] with the def2-TZVP and Weigend J auxiliary basis set. [7,8] Geometry optimizations were realized with the ORCA program package with TightSCF convergence (10^{-7} a.u.). [9] Solvation in $CH_2Cl_2$was modeled using the CPCM solvation model. [10] Open-shell calculations on the structure $[\mathbf{1}]^0$, $[\mathbf{1}]^{-1}$ (S =3) and compared to restricted KS for and $[\mathbf{1}]^{-1}$ were determined by adding the requisite number of electrons, and calculations were performed by means of (un)restricted Kohn–Sham DFT using the same basis set, functionals, and solvent models as $[\mathbf{1}]^+$.

1,1'-bis(diphenylphosphino)cobaltocenium $(dppc)^+$: A solution of chlorodiphenylphosphine (10 mL, 12 g, 54 mmol, 1.1 equiv.) in THF (100 mL) was cooled to -78 C and a solution of sodium cyclopentadienide (4.35 g, 49.4 mmol, 1 equiv.) in THF (40 mL) was added slowly. After the addition the dry-ice/acetone bath was removed, and the solution was allowed react for 30 min at room temperature. The color turned bright yellow. The reaction solution was again cooled to -78 C and ^{n}BuLi was added (2.5 M in hexanes, 22 mL, 55 mmol, 1.1 equiv.). The reaction mixture was stirred for 15 min and anhydrous $CoCl_2$ (3.56 g, 27.4 mmol, 0.55 equive) was added as a solid against a counterflow of argon. The reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched with acetic acid (1.6 mL) in water (4 mL) and air was purged through the solution for 3 h to oxidize the product. The resulting suspension was filtered through celite and a solution of NH4PF6 (5.2 g) in water (5 mL) was added. The mixture was diluted with ethanol (80 mL) and the solvent volume was reduced to 50 mL under reduced pressure. Filtration gave a brown solid which was recrystal-lized from DCM/Et2O to give an orange crystalline solid (2.450 g, 3.282 mmol, 13%). ^{1}H NMR (CD3CN): $\delta =$ 7.48-7.28 (m, 20H), 5.77 (t, J = 2.0 Hz, 4H), 5.34 ppm (t, J = 2.0 Hz, 4H). ^{31}P NMR (CD3CN): $\delta =$ -22.9 ppm (s), -144.4 ppm (sep).

$[Ni(dppc)Cl_2]Cl\bullet CH_3CN$: $[Et_4N]_2[NiCl_4]$ (100 mg, 0.217 mmol, 1 equiv.) and (dppc)PF6 (175 mg, 0.234 mmol, 1.1 equiv.) were each dissolved in Acetonitrile (35 mL in total), combined and heated to reflux for 5 min. After cooling to 20 C the formed brown precipitate was filtered off and recrystallized from Acetonitrile giving a brown crystalline solid (149 mg, 0.185 mmol, 85%). Elemental analysis calcd. (%) for $C_{36}H_{31}NCl_6CoFeNiO_2P_2$: C 56.63, H 4.092, N 1.83; found C 65.56, H 4.040, N 1.76.

References

[1] M. Krejcik, M. Danek, and F. Hartl, "Simple construction of an infrared optically transparent thin-layer electrochemical cell: Applications to the redox reactions of ferrocene, $Mn_2(CO)_{10}$ and $Mn(CO)_3(3,5-di-t-butyl-catecholate)^-$," *J. Electroanal. Chem. Interfacial Electrochem.*, vol. 317, no. 1–2, pp. 179–187, 1991.

[2] T. Mahabiersing, H. Luyten, R. C. Nieuwendam, and F. Hartl, "Synthesis, spectroscopy and spectroelectrochemistry of chlorocarbonyl 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene-κ^2-N,N'rhodium(i)," *Collect. Czech. Chem. Commun.*, vol. 68, no. 9, pp. 1687–1709, 2003.

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[9] F. Neese, "The orca program system," *WIREs Comput Mol Sci*, vol. 2, no. 1, pp. 73–78, 2012.

[10] Y. Takano and K. N. Houk, "Benchmarking the conductor-like polarizable continuum model (cpcm) for aqueous solvation free energies of neutral and ionic organic molecules," *J. Chem. Theory Comput.*, vol. 1, no. 1, pp. 70–77, 2005.

2 Crystallography

Table S1: Selected Bond Lengths $[\mathbf{2}]^{2+}$

Bond / Å	$[\mathbf{2}](PF_6)_n(BF_4)_m$	$[\mathbf{2}](BF_4)_2$
Ni1-Co1	4.165(2)	4.106(3)
Ni1-P1	2.174(3)	2.1681(4)
Ni1-P2	2.156(3)	2.1744(4)
Ni1-Cp(centroid)	1.729	1.727

Table S2: Crystallographic Information for $[\mathbf{1}]_2(Fe_2OCl_6)$

Identification code	ac465a
Empirical formula	$C_{36}H_{28}Cl_3CoFeNiO_{2.5}P_2$
Formula weight	842.40
Temperature/K	135.0
Crystal system	triclinic
Space group	P-1
a/Å	10.1357(5)
b/Å	17.5973(8)
c/Å	21.6427(11)
α/°	68.911(3)
β/°	80.097(4)
γ/°	74.415(3)
Volume/Å^3	3457.0(3)
Z	4
ϱ_{calc}g/cm^3	1.6184
μ/mm^{-1}	10.952
F(000)	1688.3
Crystal size/mm^3	0.09 × 0.047 × 0.038
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	4.4 to 133.3
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 20, -25 ≤ l ≤ 24
Reflections collected	46677
Independent reflections	11746 [R_{int} = 0.1107, R_{sigma} = 0.0978]
Data/restraints/parameters	11746/0/838
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0509, wR_2 = 0.0978
Final R indexes [all data]	R_1 = 0.1008, wR_2 = 0.1164
Largest diff. peak/hole / e Å^{-3}	0.85/-0.94

Table S3: Crystallographic Information for $[\mathbf{2}](PF_6)_{1.58}(BF_4)_{0.42}$

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No syntax errors found.                          CIF dictionary
Please wait while processing ....                Interpreting this report
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Datablock: ac500

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Bond precision:      C-C = 0.0168 A              Wavelength=0.71073
Cell:          a=19.107(2)     b=10.7707(12)   c=18.508(2)
               alpha=90        beta=96.858(5)  gamma=90
Temperature:140 K
                    Calculated                      Reported
Volume              3781.6(7)                       3781.6(7)
Space group         P 21/c                          P 1 21/c 1
Hall group          -P 2ybc                         -P 2ybc
Moiety formula      C39 H33 Co Ni P2, 1.582(F6 P),  C39 H33 Co Ni P2, 1.58(F6 P),
                    0.418(B F4) [+ solvent]         0.42(B F4)
Sum formula         C39 H33 B0.42 Co F11.16 Ni      C39 H33 B0.42 Co F11.16 Ni
                    P3.58 [+ solvent]               P3.58
Mr                  946.84                          946.84
Dx,g cm-3           1.663                           1.706
Z                   4                               4
Mu (mm-1)           1.174                           1.196
F000                1913.2                          1965.8
F000'               1918.44
h,k,lmax            23,13,23                        23,13,23
Nref                7787                            7711
Tmin,Tmax           0.871,0.912                     0.653,0.888
Tmin'               0.595
Correction method= # Reported T Limits: Tmin=0.653
Tmax=0.888 AbsCorr = NUMERICAL
Data completeness= 0.990        Theta(max)= 26.430
R(reflections)= 0.1324( 5089)                   wR2(reflections)=
                                                0.3628( 7711)
S = 1.047             Npar= 410
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

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PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) ...................       0.36 Report
PLAT097_ALERT_2_B Large Reported Max.  (Positive) Residual Density       3.09 eA-3
PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X)  Ni1       --P4      .      16.3 s.u.
PLAT341_ALERT_3_B Low Bond Precision on  C-C Bonds ...............    0.01678 Ang.
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Alert level C

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ABSMU01_ALERT_1_C  The ratio of given/expected absorption coefficient lies
            outside the range 0.99 <> 1.01
           Calculated value of mu =     1.174
           Value of mu given      =     1.196
DENSD01_ALERT_1_C  The ratio of the submitted crystal density and that
           calculated from the formula is outside the range 0.99 <> 1.01
           Crystal density given    =     1.706
           Calculated crystal density =     1.663
DIFMN02_ALERT_2_C  The minimum difference density is < -0.1*ZMAX*0.75
           _refine_diff_density_min given =     -2.580
           Test value =     -2.100
DIFMN03_ALERT_1_C  The minimum difference density is < -0.1*ZMAX*0.75
           The relevant atom site should be identified.
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
           The relevant atom site should be identified.
PLAT046_ALERT_1_C Reported Z, MW and D(calc) are Inconsistent ....      1.663 Check
PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms ..     Please Check
PLAT082_ALERT_2_C High R1 Value ..................................       0.13 Report
PLAT098_ALERT_2_C Large Reported Min.  (Negative) Residual Density      -2.58 eA-3
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.6 Note
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        3.0 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       P1A      0.121 Check
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
            C39 H33 Co Ni P2
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Alert level G

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PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         51 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          3 Report
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT014_ALERT_1_G No       _shelx_fab_checksum Found in CIF ......     Please Check
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.17 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      84.37 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records        12 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records        13 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records        61 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records         3 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )       28% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )      100% Note
And 3 other PLAT302 Alerts
More ...
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And 3 other PLAT304 Alerts
More ...
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                                          1-x,1/2+y,1/2-z  =     2_655 Check
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                                            x,1+y,z  =     1_565 Check
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                                            x,-1/2-y,1/2+z  =     4_556 Check
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PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
            F6 P
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          4 Note
            F6 P
PLAT794_ALERT_5_G Tentative Bond Valency for Co1       (III)     .       3.48 Info
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PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....         ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       93 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File        12 Note
PLAT982_ALERT_1_G The Co-f'=    0.3565 Deviates from  IT-value =       0.3494 Check
And 2 other PLAT982 Alerts
More ...
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And 2 other PLAT983 Alerts
More ...
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   0 ALERT level A = Most likely a serious problem - resolve or explain
   4 ALERT level B = A potentially serious problem, consider carefully
  13 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  37 ALERT level G = General information/check it is not something unexpected

  14 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  16 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
  18 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert

Table S4: Crystallographic Information for [**1**]PF_6

ac539_sqd

Table 1 Crystal data and structure refinement for ac539_sqd.

Identification code	ac539_sqd
Empirical formula	$C_{37}H_{30}Cl_2CoF_6NiO_2P_3$
Formula weight	902.06
Temperature/K	140.01
Crystal system	monoclinic
Space group	C2/c
a/Å	15.8614(11)
b/Å	12.6538(9)
c/Å	40.759(3)
α/°	90
β/°	93.232(4)
γ/°	90
Volume/Å^3	8167.6(10)
Z	8
ϱ_{calc}g/cm^3	1.467
μ/mm^{-1}	1.174
F(000)	3648.0
Crystal size/mm^3	0.512 × 0.353 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.004 to 56.746
Index ranges	-21 ≤ h ≤ 21, -16 ≤ k ≤ 16, -54 ≤ l ≤ 54
Reflections collected	71525
Independent reflections	10165 [R_{int} = 0.0477, R_{sigma} = 0.0322]
Data/restraints/parameters	10165/0/469
Goodness-of-fit on F^2	1.122
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1055
Final R indexes [all data]	R_1 = 0.0622, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.52/-0.42

Table S5: Crystallographic Information for $[\mathbf{2}](BF_4)_2$

ac535

Table 1 Crystal data and structure refinement for ac535.

Identification code	ac535
Empirical formula	$C_{39}H_{33}B_2CoF_8NiP_2$
Formula weight	854.85
Temperature/K	139.99
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.0540(14)
b/Å	10.2096(8)
c/Å	20.0648(16)
α/°	90
β/°	92.827(4)
γ/°	90
Volume/Å^3	3489.3(5)
Z	4
ϱ_{calc}g/cm^3	1.627
μ/mm^{-1}	1.180
F(000)	1736.0
Crystal size/mm^3	0.536 × 0.514 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.064 to 61.036
Index ranges	-24 ≤ h ≤ 24, -8 ≤ k ≤ 14, -28 ≤ l ≤ 28
Reflections collected	56875
Independent reflections	10610 [R_{int} = 0.0264, R_{sigma} = 0.0249]
Data/restraints/parameters	10610/86/540
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0652
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.0724
Largest diff. peak/hole / e Å^{-3}	0.78/-0.41

3 Cyclic Voltammetry

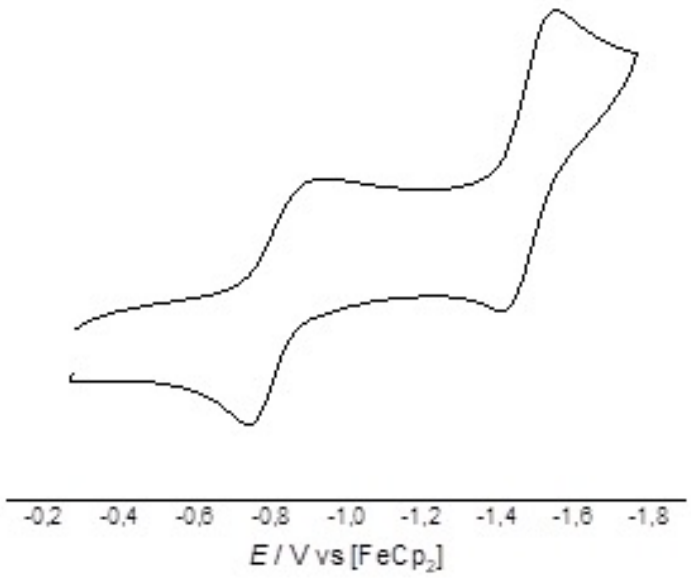


Figure S1: Cyclicvoltammogram of $[\mathbf{2}]^{2+}$ in 0.1 M $^{n}Bu_4NPF_6$ in MeCN

4 NMR Spectroscopy

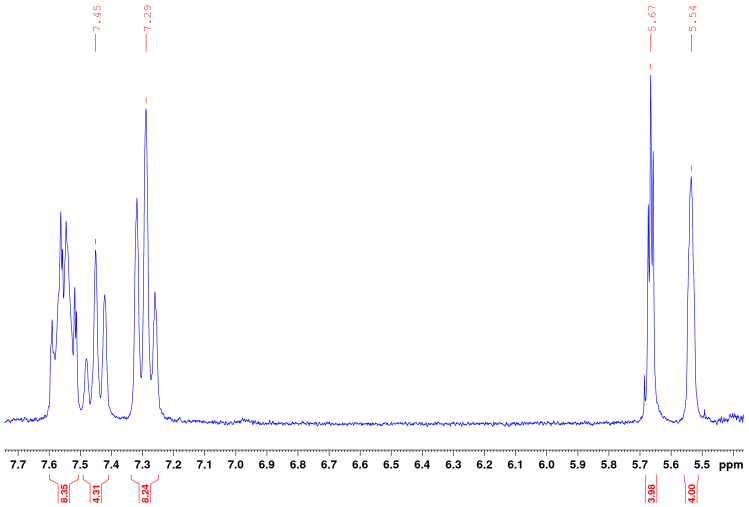


Figure S2: ^{1}H NMR of $(dppc)^{+}$ in CD_3CN.

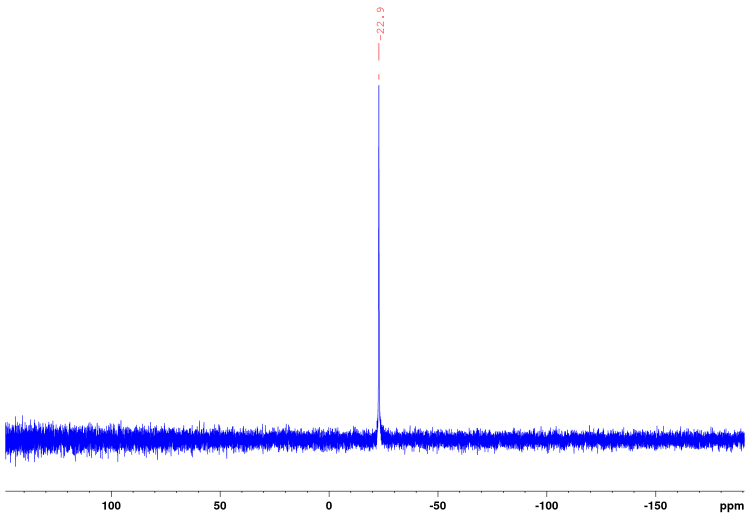


Figure S3: ^{31}P NMR of (dppc)BF_4 in CD_3CN.

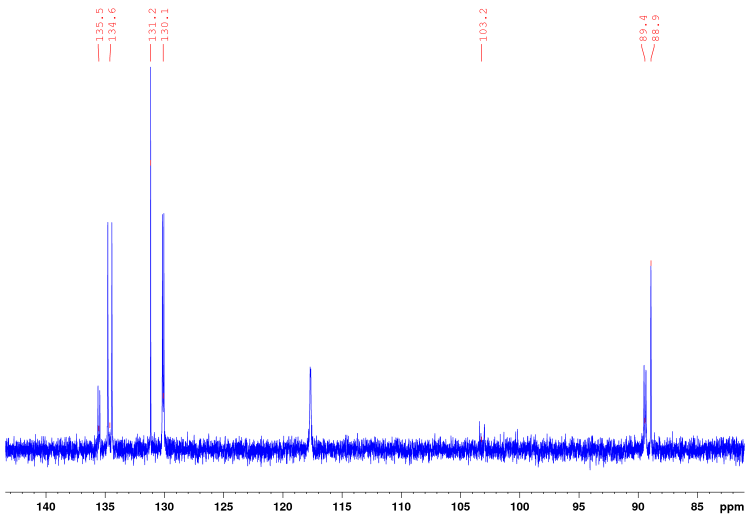


Figure S4: ^{13}C NMR of (dppc)BF_4 in CD_3CN.

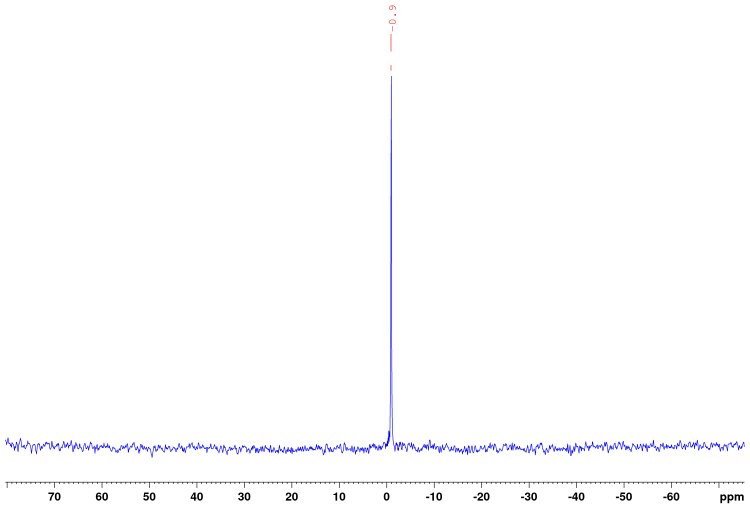


Figure S5: ^{11}B NMR of (dppc)BF_4 in CD_3CN.

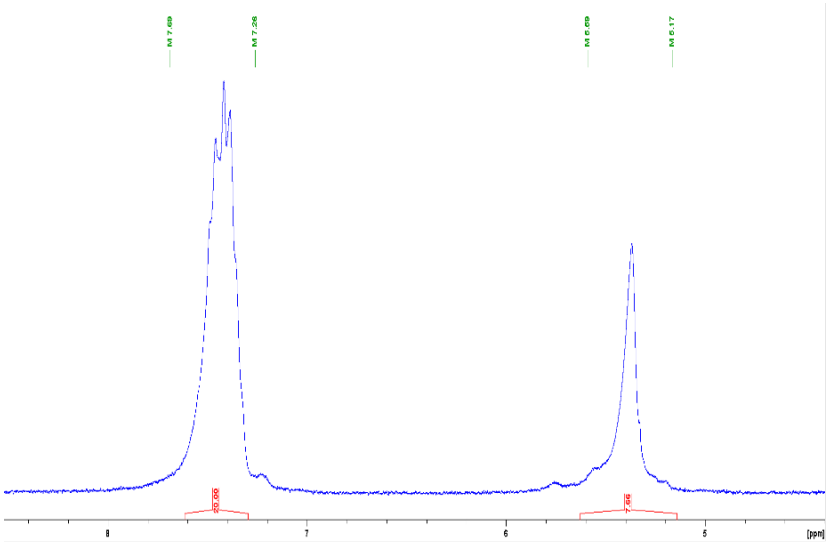


Figure S6: ^{1}H NMR of $[\mathbf{1}]_2(Fe_2OCl_6)$ in CD_3CN.

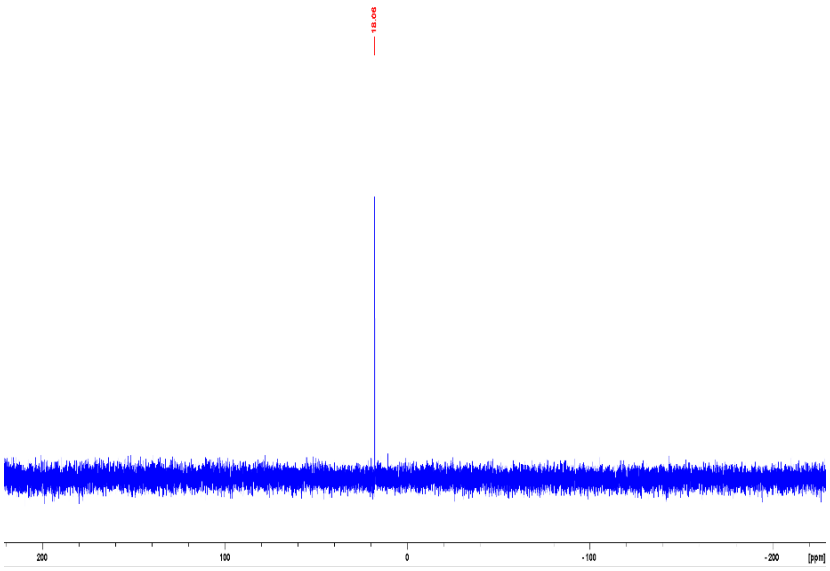


Figure S7: ^{31}P NMR of $[\mathbf{1}]_2(Fe_2OCl_6)$ in CD_3CN.

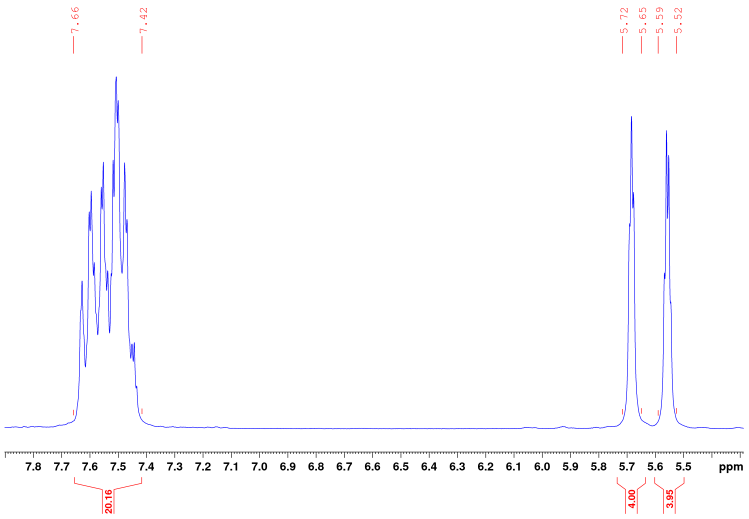


Figure S8: ^{1}H NMR of $[\mathbf{1}]PF_6$ in CD_3CN.

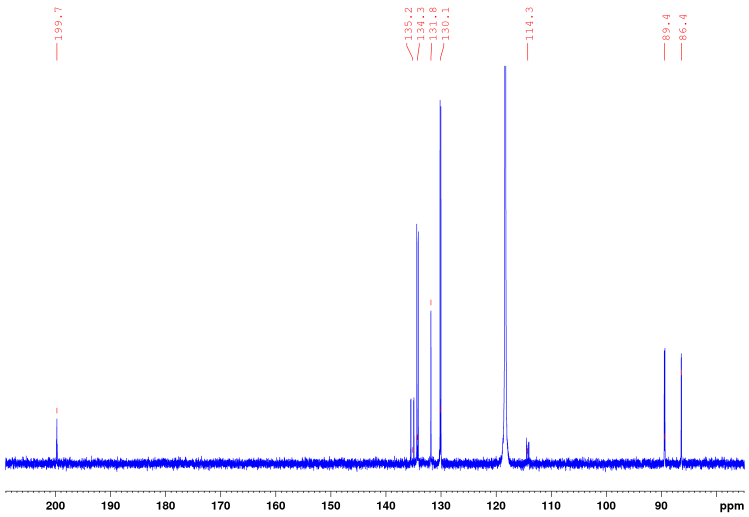


Figure S9: ^{13}C NMR of [**1**]PF_6 in CD_3CN.

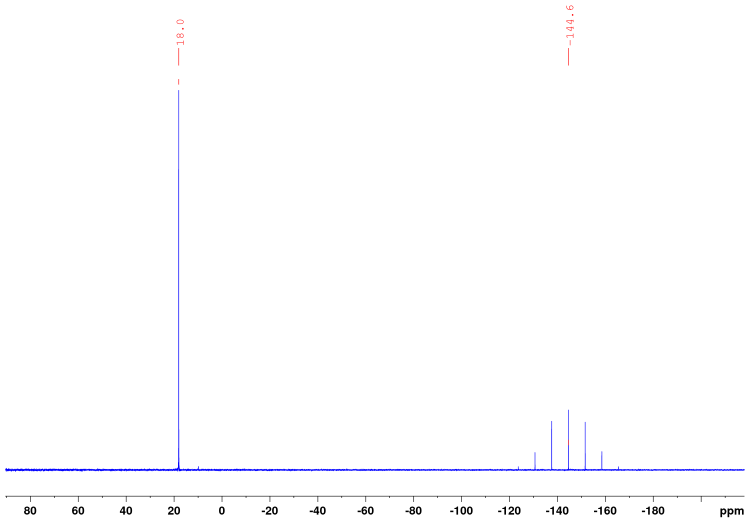


Figure S10: ^{31}P NMR of [**1**]PF_6 in CD_3CN.

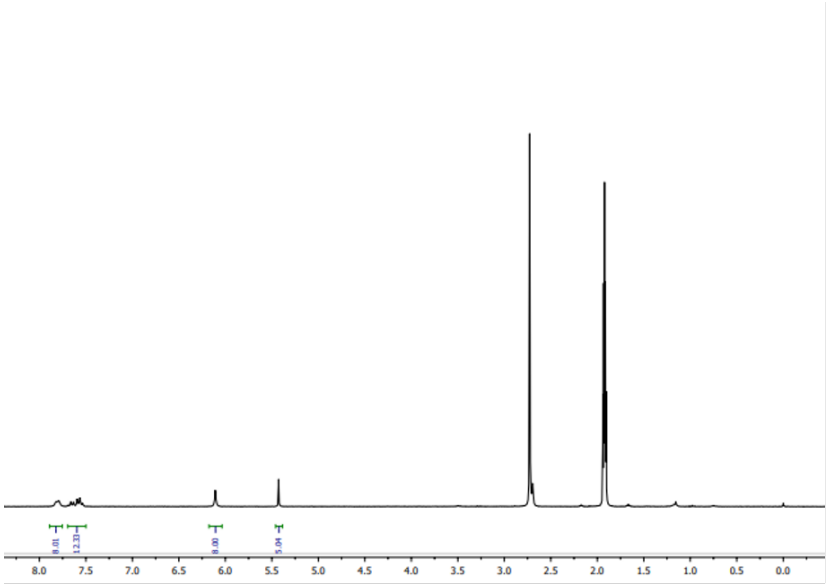


Figure S11: ^{1}H NMR of **[2]**$(PF_6)_n(BF_4)_m$ in $CDCl_3$.

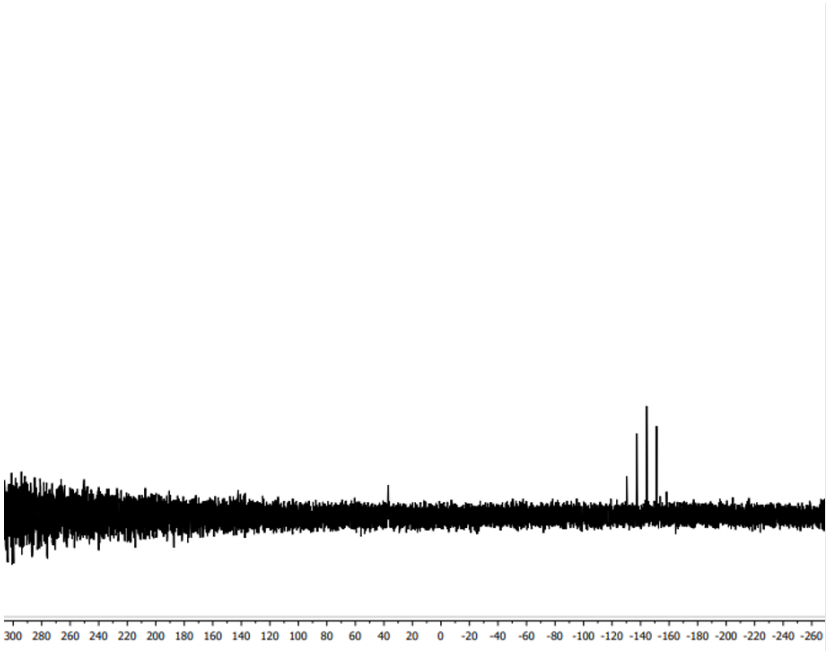


Figure S12: ^{31}P NMR of **[2]**$(PF_6)_n(BF_4)_m$ in $CDCl_3$.

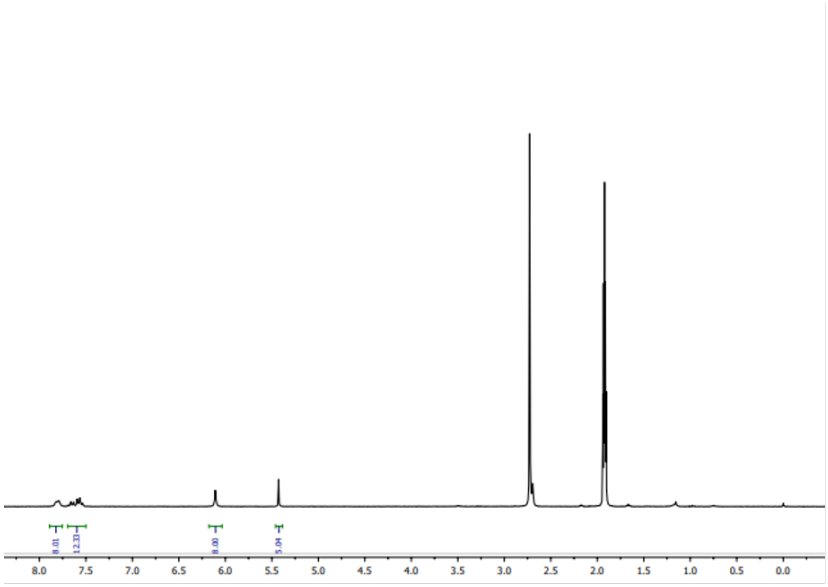


Figure S13: ^{1}H NMR of [**2**]$(PF_6)_n(BF_4)_m$ in $CDCl_3$.

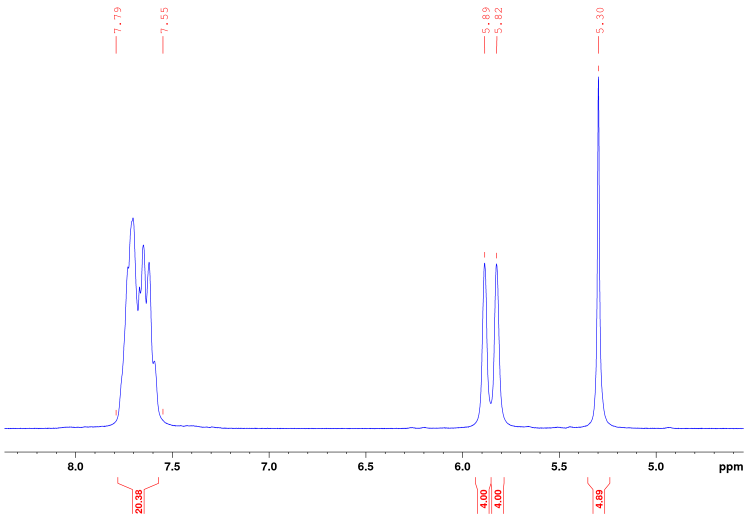


Figure S14: ^{1}H NMR of [**2**]$(BF_4)_2$ in $CDCl_3$.

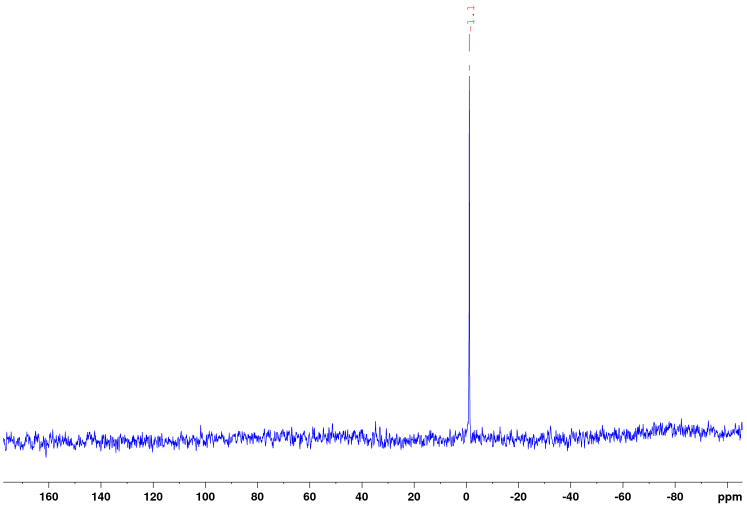


Figure S15: ^{11}B NMR of **[2]**$(BF_4)_2$ in $CDCl_3$.

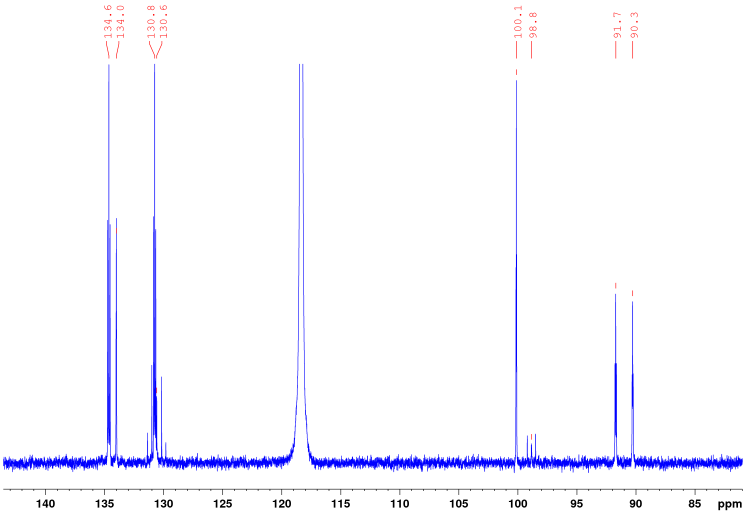


Figure S16: ^{13}C NMR of **[2]**$(BF_4)_2$ in $CDCl_3$.

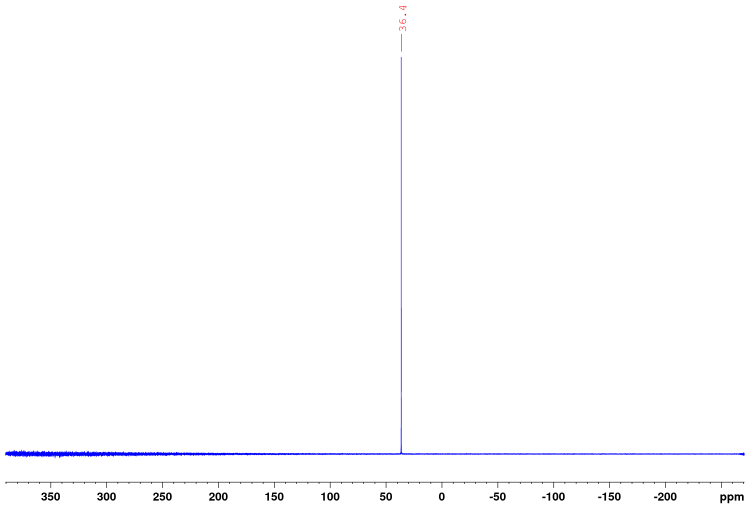


Figure S17: ^{31}P sNMR of $[\mathbf{2}](BF_4)_2$ in $CDCl_3$.

5 Absorption Spectroscopy

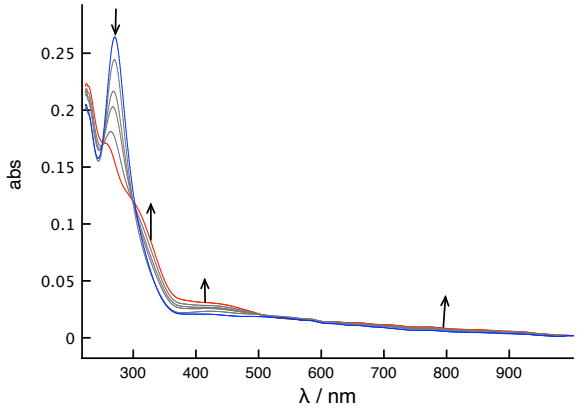


Figure S18: UV-Vis-NIR SEC of cathodic process $[\mathbf{1}]^{+/0}$ in 0.1 M $^{n}Bu_4NPF_6$ in MeCN.

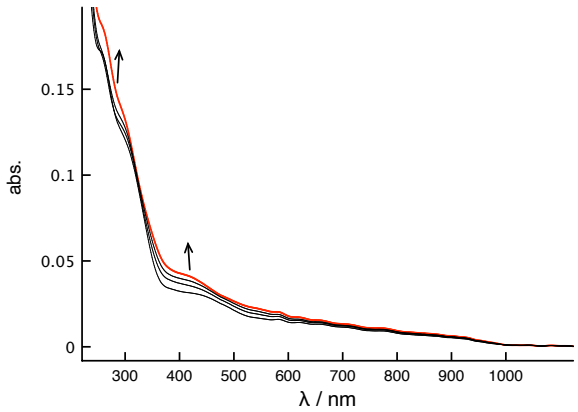


Figure S19: UV-Vis-NIR SEC of cathodic process $[\mathbf{1}]^{0/-1}$ in 0.1 M $^{n}Bu_4NPF_6$ in MeCN.

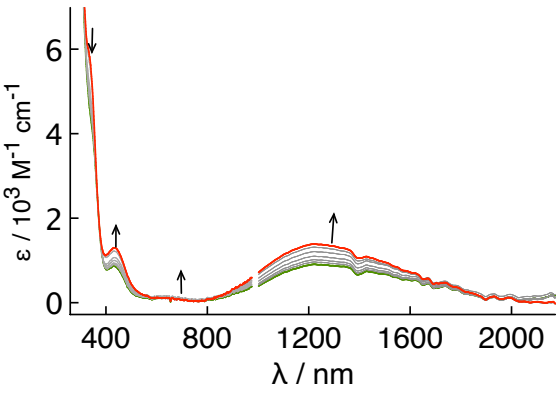


Figure S20: UV-Vis-NIR SEC of cathodic process $[\mathbf{2}]^{+/0}$ in 0.1 M $^{n}Bu_4NPF_6$ in MeCN.

6 Electron Paramagnetic Resonance

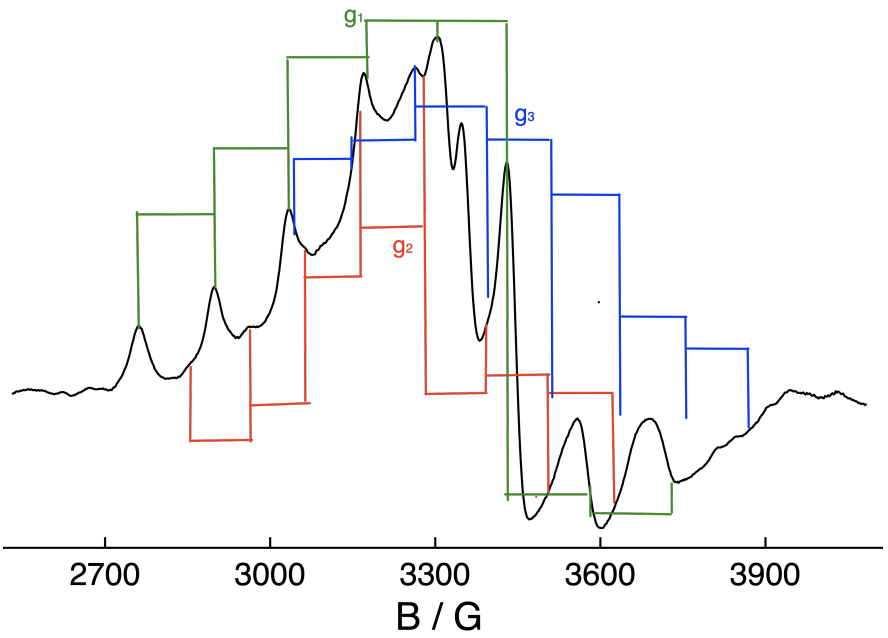


Figure S21: EPR spectrum of $[\mathbf{2}]^{+}$ in 0.1 M $^{n}Bu_4NPF_6$ in CH_2Cl_2 at 100K

6.1 TD-DFT

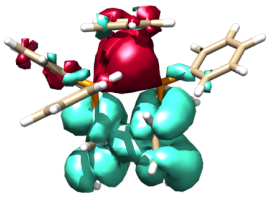
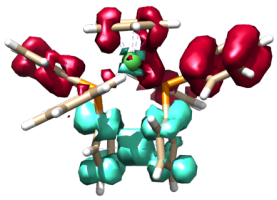
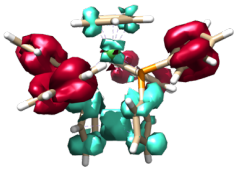
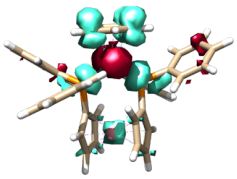
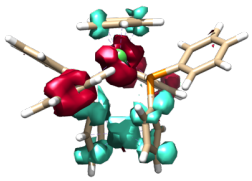
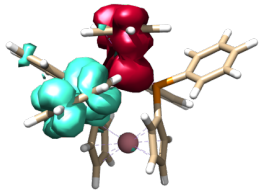
CpNidppc2+ RKS PBE0 RIJCOSX def2-TZVP def2/J D3BJ NormalPrint Grid5 CPCM(acetonitrile) Isosurface = 0.002, green denotes gain of electron density Tranistions below 5% were omitted	
	STATE 4: E= 0.056117 au 1.527 eV 12316.3 cm**-1 173a -> 175a : 0.927641 (c= 0.96314113) 173a -> 177a : 0.071125 (c= -0.26669304)
	STATE 7: E= 0.077377 au 2.106 eV 16982.3 cm**-1 171a -> 175a : 0.941013 (c= -0.97005810)
	STATE 10: E= 0.088209 au 2.400 eV 19359.7 cm**-1 170a -> 175a : 0.943741 (c= 0.97146332)
	STATE 12: E= 0.097158 au 2.644 eV 21323.6 cm**-1 173a -> 175a : 0.061441 (c= -0.24787196) 173a -> 177a : 0.822517 (c= -0.90692719)
	STATE 18: E= 0.098942 au 2.692 eV 21715.3 cm**-1 163a -> 175a : 0.073032 (c= -0.27024348) 165a -> 175a : 0.753275 (c= -0.86791407) 166a -> 175a : 0.064593 (c= 0.25415155)
	STATE 26: E= 0.097610 au 2.656 eV 21422.9 cm**-1 172a -> 177a : 0.120752 (c= 0.34749334) 174a -> 179a : 0.858999 (c= 0.92682191)

Figure S22: TDDFT transitions for $[\mathbf{2}]^{2+}$ green denotes gain, red denotes loss.

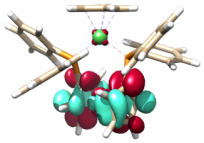
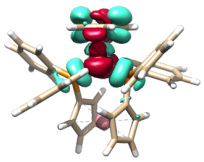
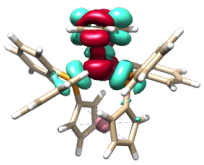
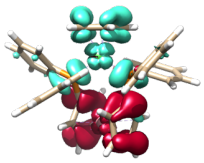
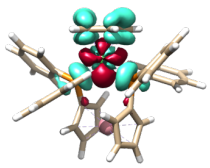
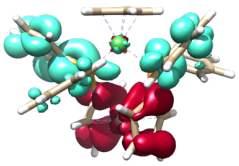
CpNidppc_+ UKS PBE0 RIJCOSX def2-TZVP def2/J D3BJ NormalPrint Grid5 CPCM(acetonitrile) Isosurface = 0.002, green denotes gain of electron density Tranistions below 5% were omitted	
	STATE 1: E= 0.022236 au 0.605 eV 4880.3 cm**-1 175a -> 177a : 0.909918 (c= -0.95389643)
	STATE 2: E= 0.030207 au 0.822 eV 6629.7 cm**-1 155a -> 176a : 0.054197 (c= -0.23280260) 174a -> 176a : 0.374785 (c= 0.61219656) 154b -> 175b : 0.069590 (c= 0.26379846) 174b -> 175b : 0.409706 (c= 0.64008254)
	STATE 6: E= 0.059170 au 1.610 eV 12986.2 cm**-1 174a -> 176a : 0.458178 (c= 0.67688813) 174b -> 175b : 0.406821 (c= -0.63782530)
	STATE 9: E= 0.056001 au 1.524 eV 12290.8 cm**-1 175a -> 176a : 0.952844 (c= 0.97613734)
	STATE 17: E= 0.104472 au 2.843 eV 22928.8 cm**-1 155a -> 176a : 0.065952 (c= -0.25681153) 156a -> 176a : 0.163132 (c= -0.40389593) 157a -> 176a : 0.170243 (c= -0.41260538) 155b -> 175b : 0.274344 (c= -0.52377853)
	STATE 23: E= 0.114282 au 3.110 eV 25082.0 cm**-1 175a -> 180a : 0.876538 (c= 0.93623601)

Figure S23: TDDFT transitions for $[\mathbf{2}]^+$ green denotes gain, red denotes loss.

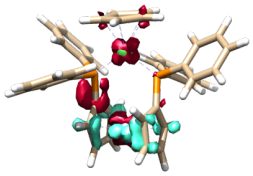
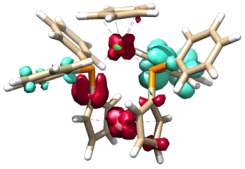
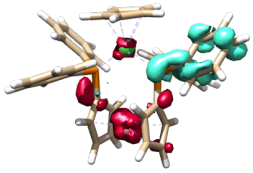
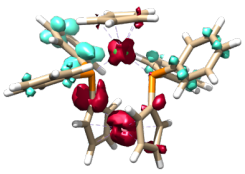
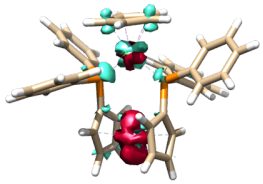
CpNidppc0 RKS PBE0 RIJCOSX def2-TZVP def2/J D3BJ NormalPrint Grid5 CPCM(acetonitrile) Isosurface = 0.002, green denotes gain of electron density Tranistions below 5% were omitted	
	STATE 1: E= 0.021020 au 0.572 eV 4613.4 cm**-1 175a -> 177a : 0.180424 (c= -0.42476399) 175a -> 179a : 0.079465 (c= -0.28189508) 175a -> 180a : 0.336490 (c= 0.58007765) 175a -> 181a : 0.213628 (c= 0.46219948)
	STATE 3: E= 0.054193 au 1.475 eV 11893.9 cm**-1 175a -> 176a : 0.106578 (c= 0.32646358) 175a -> 177a : 0.342006 (c= 0.58481287) 175a -> 178a : 0.443173 (c= 0.66571243)
	STATE 5: E= 0.064692 au 1.760 eV 14198.3 cm**-1 173a -> 176a : 0.024194 (c= 0.15554497) 175a -> 176a : 0.444551 (c= -0.66674646) 175a -> 177a : 0.039200 (c= 0.19798895) 175a -> 178a : 0.143990 (c= 0.37945958) 175a -> 179a : 0.147491 (c= 0.38404604) 175a -> 180a : 0.010835 (c= 0.10409110) 175a -> 182a : 0.038183 (c= 0.19540484) 175a -> 183a : 0.021561 (c= -0.14683722)
	STATE 7: E= 0.070649 au 1.922 eV 15505.7 cm**-1 175a -> 176a : 0.090239 (c= -0.30039728) 175a -> 179a : 0.417752 (c= -0.64633713) 175a -> 180a : 0.256787 (c= -0.50674175)
	STATE 15: E= 0.087834 au 2.390 eV 19277.4 cm**-1 170a -> 176a : 0.065388 (c= -0.25571142) 173a -> 176a : 0.572129 (c= 0.75639224) 175a -> 185a : 0.058675 (c= -0.24222834)

Figure S24: TDDFT transitions for $[\mathbf{2}]^0$ green denotes gain, red denotes loss.