Supporting Information

CO_2 Cleavage by Tantalum/M (M = Iridium, Osmium) Heterobimetallic Complexes

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Authors Contributions

A. Lachguar and C. Z. Ye conducted the synthetic experimental work, with C. Z. Ye focusing on the synthesis of the starting materials [Cp*ReH_6] and [Cp*OsH_5], and A. Lachguar handling the remaining aspects. S. N. Kelly and E. Jeanneau recorded and interpreted the XRD data. A. Lachguar drafted the original version of the manuscript. I. Del Rosal and L. Maron carried out the computational work. J. Arnold, C. Camp conceptualized the research by securing funding and administered the project. J. Arnold, C. Camp, L. Veyre and C. Thieuleux supervised the work, interpreted the data, revised and edited subsequently the manuscript. All authors have read and agreed to the published version of the manuscript.

Content

A. Experimental section

General Considerations. Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an MBRAUN glovebox under an atmosphere of purified argon or nitrogen (<1 ppm of O_2/H_2O). Glassware and cannulas were stored in an oven at ~100 °C for at least 16 h prior to use. THF and *n*-pentane were purified by passage through a column of activated alumina, dried over Na/benzophenone, vacuum-transferred to a storage flask, and freeze−pump−thaw degassed prior to use. Deuterated solvents (toluene-d_8, THF-d_8 and C_6D_6) were dried over Na/benzophenone, vacuum-transferred to a storage flask, and freeze-pump-thaw degassed prior to use. Compounds [Cp*OsH_5],[1] [Ta(CH*t*Bu)(CH_2*t*Bu)$_3$][2] and [Ta(CH_2*t*Bu)$_3$(H)$_2$IrCp*][3] were prepared according to the literature procedures. All other reagents were acquired from commercial sources and used as received.

IR Spectroscopy. The samples were prepared in a glovebox (diluted in dry KBr), sealed under argon in a DRIFT cell fitted with KBr windows, then analyzed using a Nicolet 670 FT-IR spectrometer.

Elemental Analyses. Elemental analyses were performed under an inert atmosphere at either Mikroanalytisches Labor Pascher (Germany) or the Microanalytical Facility at the College of Chemistry, University of California, Berkeley (USA).

Mass Spectroscopy. High-resolution mass spectrometry (HRMS) was performed at the Centre Commun de Spectrométrie de Masse (CCSM) in Villeurbanne (France), using the Bruker QTOF Impact II spectrometer, with the APCI source and direct introduction *via* Solid Probe.

NMR Spectroscopy. Solution NMR spectra were recorded on Bruker AV-300, AV-500 and AV-600 spectrometers. ^{1}H and ^{13}C chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. ^{1}H and ^{13}C NMR assignments were confirmed by ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and HMBC experiments. NMR data recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) J (Hz), relative integral].

Synthesis of [Ta(CH_2*t*Bu)$_3$(μ-H)$_3$Os(Cp*)] (2). A colourless pentane solution (5 mL) of Cp*OsH_5 (143 mg, 0.431 mmol, 1 equiv.) was added dropwise to a dark-brown pentane solution (5 mL) of Ta(CH*t*Bu)(CH_2*t*Bu)$_3$ (200 mg, 0.431 mmol, 1 equiv.). The reaction mixture turned red and was stirred at room temperature for 2 h. Volatiles were removed under vacuum affording pure **2** as a red powder (305 mg, 0.422 mmol, 98%). Single crystals of **2** suitable for X-ray diffraction were obtained through recrystallization in a minimal amount of pentane at -35 °C. ^{1}H-NMR (600 MHz, toluene-d_8, 302 K) δ ppm 2.20 (s, 15 H, 5 C$\underline{H_3}^{Cp^*}$), 1.29 (s, 27 H, 3 C(C$\underline{H_3}$)$_3$), 0.32 (s, 6 H, 3 C$\underline{H_2}$C(CH_3)$_3$), -6.90 (s, 3 H, Os$\underline{H_3}$). ^{1}H-NMR (300 MHz, C_6D_6, 298 K) δ ppm 2.21 (s, 15 H, 5 C$\underline{H_3}^{Cp^*}$), 1.32 (s, 27 H, 3 C(C$\underline{H_3}$)$_3$),

0.34 (s, 6 H, 3 C$\underline{H_2}$C(CH_3)$_3$), -6.80 (s, 3 H, Os$\underline{H_3}$). ^{13}C{^{1}H}-NMR (151 MHz, toluene-d_8, 302 K) δ ppm 120.12 (s, 3 C, 3 Ta$\underline{C}$H$_2$C(CH_3)$_3$), 86.76 (s, 5 C, $\underline{C_5}$(CH_3)$_5$), 35.21 (s, 3 C, 3 TaCH$\underline{C}$(CH_3)$_3$), 34.86 (s, 9 C, 3 TaCHC($\underline{C}$H$_3$)$_3$), 11.71 (s, 5 C, C_5($\underline{C}$H$_3$)$_5$). FTIR (293 K, cm^{-1}) ν = 2924 (br s, ν_{C-H}), 2856 (s, ν_{C-H}), 2735 (s, ν_{C-H}), 2670 (s, ν_{C-H}), 1957 (s, ν_{Os-H}), 1339 (s), 1230 (s), 1071 (s), 1033 (s), 933(s), 913 (s), 754 (s), 547 (s), 488 (s). Anal. Calcd for $C_{25}H_{51}OsTa$: C, 41.54; H, 7.11 Found: C, 42.34; H, 7.05.

Reactivity of compound 1 (or 2) with CO_2.

In a J-Young NMR tube, a solution of complex **1** (or **2**) (10 mg, 0.014 mmol) in THF-d_8 (1 mL) was freeze-pumped and subsequently exposed to a CO_2 atmosphere (1 atm, ca. 2 mL headspace, ca. 0.08 mmol). The solution turned colourless within a few minutes (ca. 10 min), indicating the complete consumption of complex **1** (or **2**). Note that diffusion of CO_2 gas in the solution is more limiting (slower) than the chemical kinetics with both complexes, preventing the accurate measurement of kinetics. The quantitative and clean formation of compounds **3** (or **4**) and **5** was determined by ^{1}H NMR analysis of the crude reaction (refer to Figures 7 and 8). The volatiles were evaporated under vacuum. The resulting crude product was then washed with pentane (3x1 mL) and dried under vacuum to yield [Ta(O)(CH_2tBu)$_3$]$_x$ **5** as a white powder with a yield of 94% (5.3 mg) and 95% (5.4 mg) respectively from compound **1** and **2**. The solutions resulting from the pentane washings of the residue were combined, and the pentane was evaporated to yield: complex **3** as a light yellow solid with a yield of 96% (4.7 mg), and complex **4** as a white solid with a yield of 45% (2.2 mg). A similar yield was also obtained from similar procedure starting with 100 mg (0.14 mmol) of compound **1** (or **2**) dissolved in 5 mL of THF and exposed to CO_2 (1 atm, 70.5 mL headspace, 2.84 mmol).

Characterization of compound 3: ^{1}H-NMR (500 MHz, C_6D_6, 298 K) δ ppm 1.88 (s, 15 H, 5 C$\underline{H_3}^{Cp^*}$), -15.75 (s, 2 H, Ir$\underline{H_2}$). ^{13}C{^{1}H}-NMR (126 MHz, C_6D_6, 298 K) δ ppm 97.16 (s, 5 C, $\underline{C_5}$(CH_3)$_5$), 10.69 (s, 5 C, C_5($\underline{C}$H$_3$)$_5$). These data agree with the previously published ones.[4,5]

Characterization of compound 4: ^{1}H-NMR (500 MHz, THF-d_8, 298 K) δ ppm 2.26 (s, 15 H, 5 C$\underline{H_3}^{Cp^*}$), -10.47 (s*, 1 H, trans Os$\underline{H}$), -12.50 (s*, 2 H, cis Os$\underline{H}$). ^{13}C{^{1}H}-NMR (126 MHz, THF-d8, 298 K) δ ppm 184.63 (s, 1 C, $\underline{C}$O), 98.46 (s, 5 C, $\underline{C_5}$(CH_3)$_5$), 11.64 (s, 5 C, C_5($\underline{C}$H$_3$)$_5$). These data agree with the previously published ones.[6] *Note that in the original publication the NMR data was recorded at -50°C in CD_2Cl_2 and the hydride signals appeared as a doublet and a triplet due to mutual coupling. However, under our experimental conditions (500 MHz, THF-d_8, 298 K) the fine structure is not visible and thus these ^{1}H hydride signals appear as pseudo-singlets. (see Figure S13).

Characterization of compound 5: ^{1}H-NMR (500 MHz, THF-d_8, 298 K) δ ppm 1.12 (s, 27 H, 3 C(C$\underline{H_3}$)$_3$), 0.55 (s, 6 H, 3 C$\underline{H_2}$C(CH_3)$_3$). ^{13}C{^{1}H}-NMR (126 MHz, THF-d_8, 298 K) δ ppm 104.44 (s, 3 C, 3 Ta(O)$\underline{C}$H$_2$C(CH_3)$_3$), 35.13 (s, 3 C, 3 Ta(O)CH$_2\underline{C}$(CH_3)$_3$), 34.40 (s, 9 C, 3 Ta(O)CH$_2$C($\underline{C}$H$_3$)$_3$). HRMS (APCI-SP$^+$)) Calcd for $C_{15}H_{34}OTa$ [M+H]$^+$: 411.2084 Found: 411.2086. Anal. Calcd for $C_{15}H_{33}OTa$: C, 43.90; H, 8.11; Found: C, 43.45; H, 7.95.

B. NMR, DRIFT and HRMS spectra

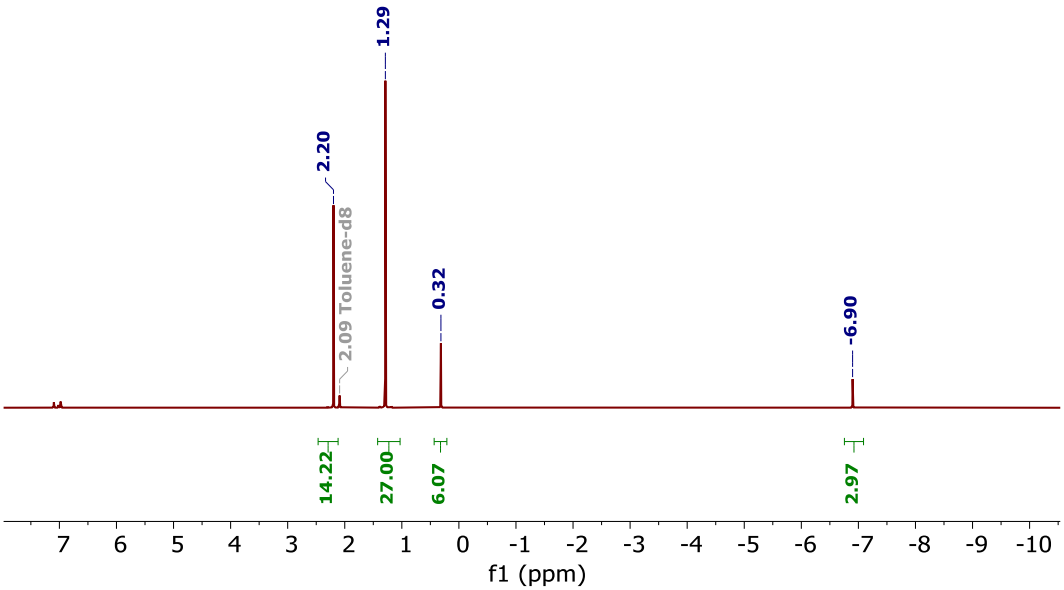

Figure S1. ^{1}H-NMR spectrum (600 MHz, toluene-d_8, 302 K) of compound **2**.

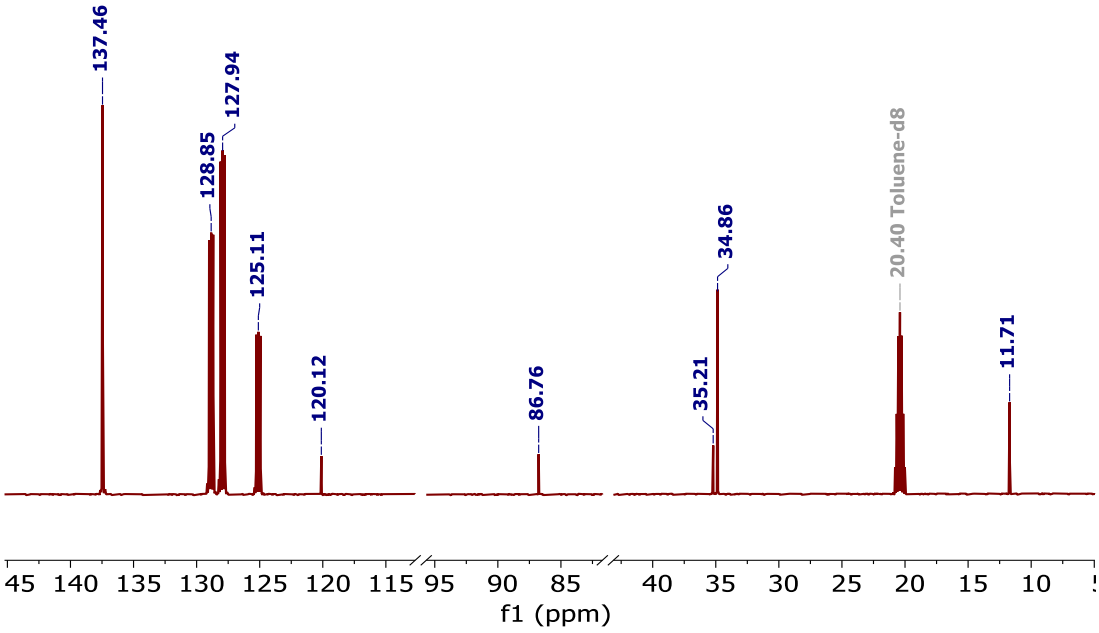

Figure S2. ^{13}C{^{1}H}-NMR spectrum (151 MHz, toluene-d_8, 302 K) of compound **2**.

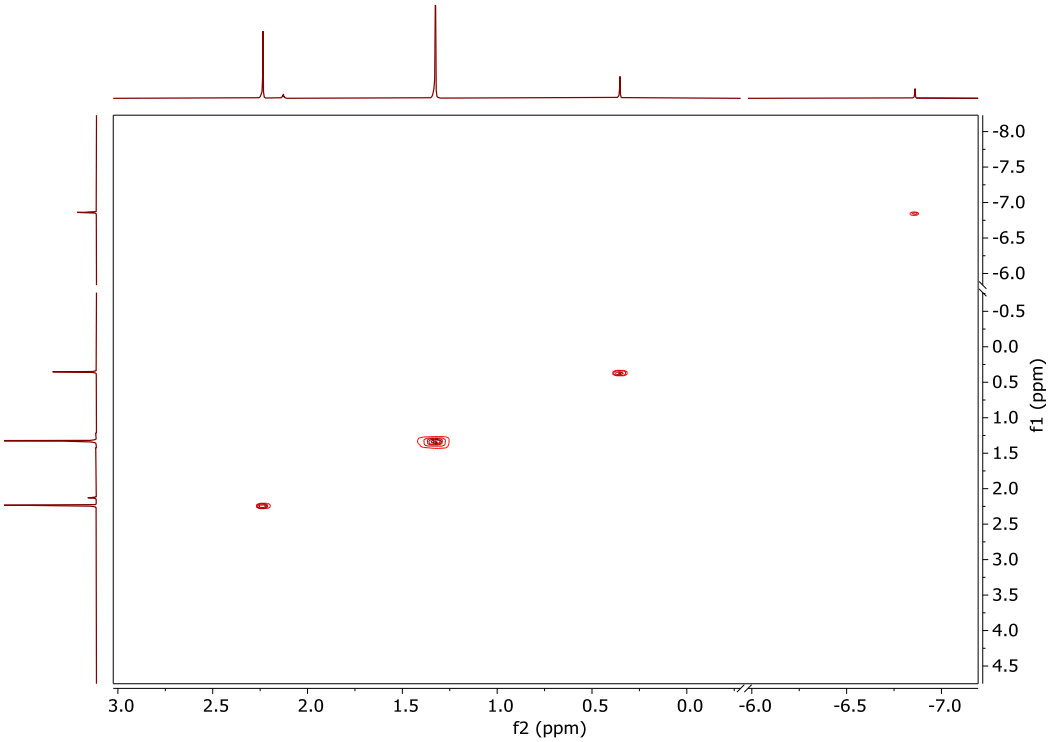

Figure S3. ^{1}H-^{1}H COSY NMR spectrum **(**600 MHz, toluene-d_8, 302 K) of compound **2**.

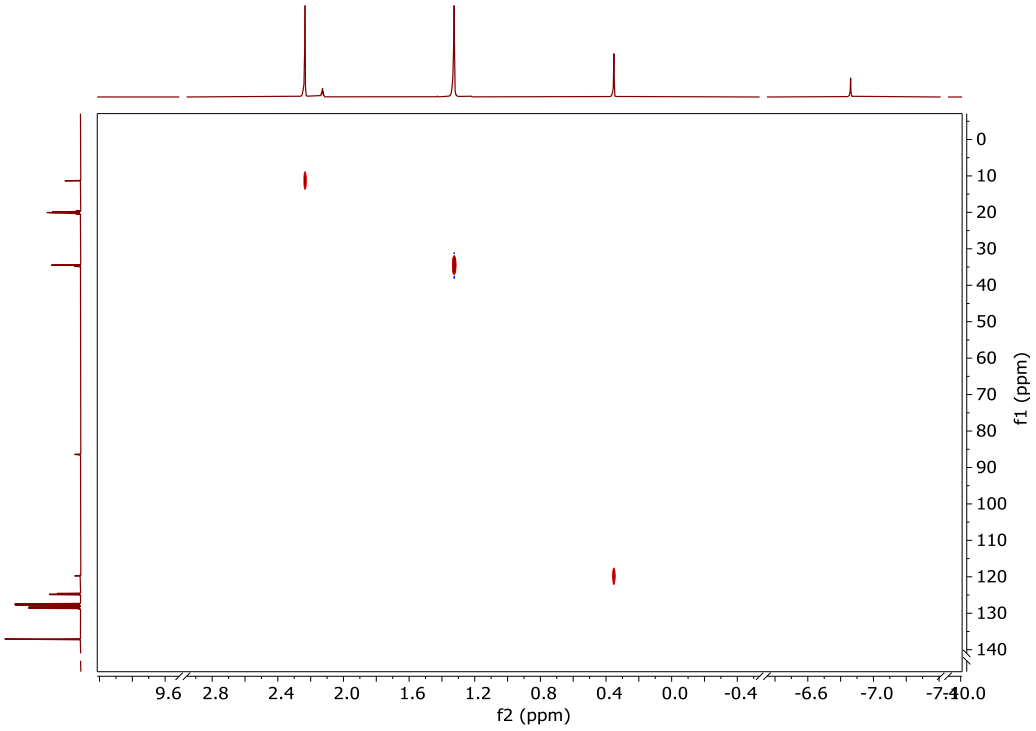

Figure S4. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz, toluene-d_8, 302 K) of compound **2**.

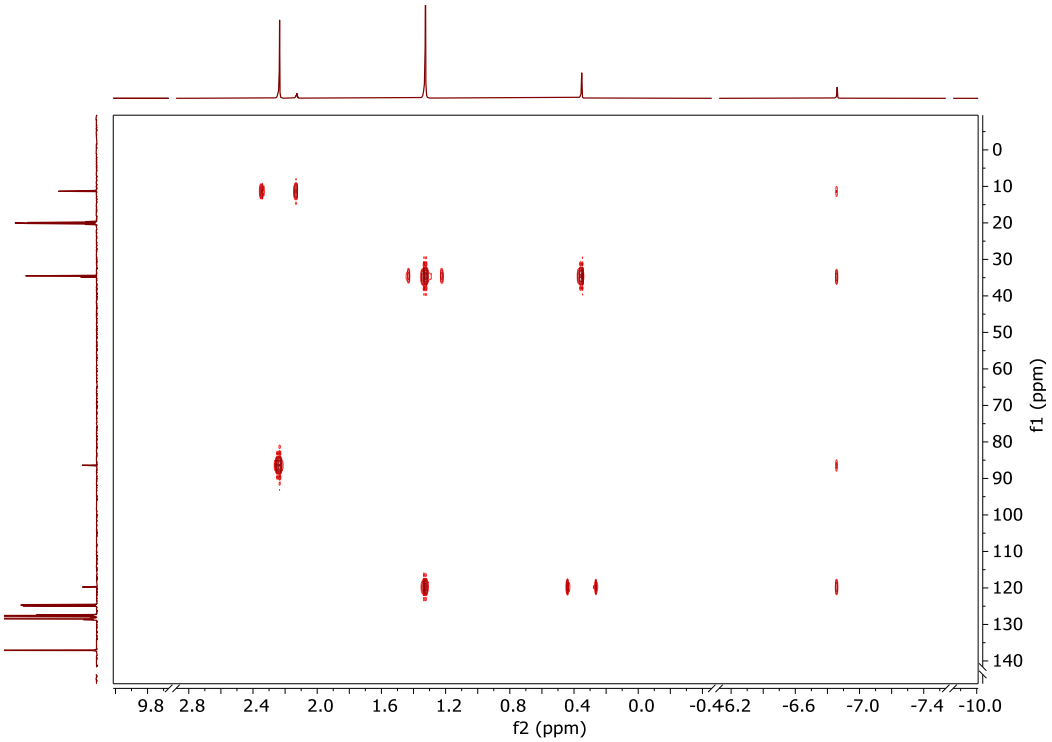

Figure S5. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz, toluene-d_8, 302 K) of compound **2**.

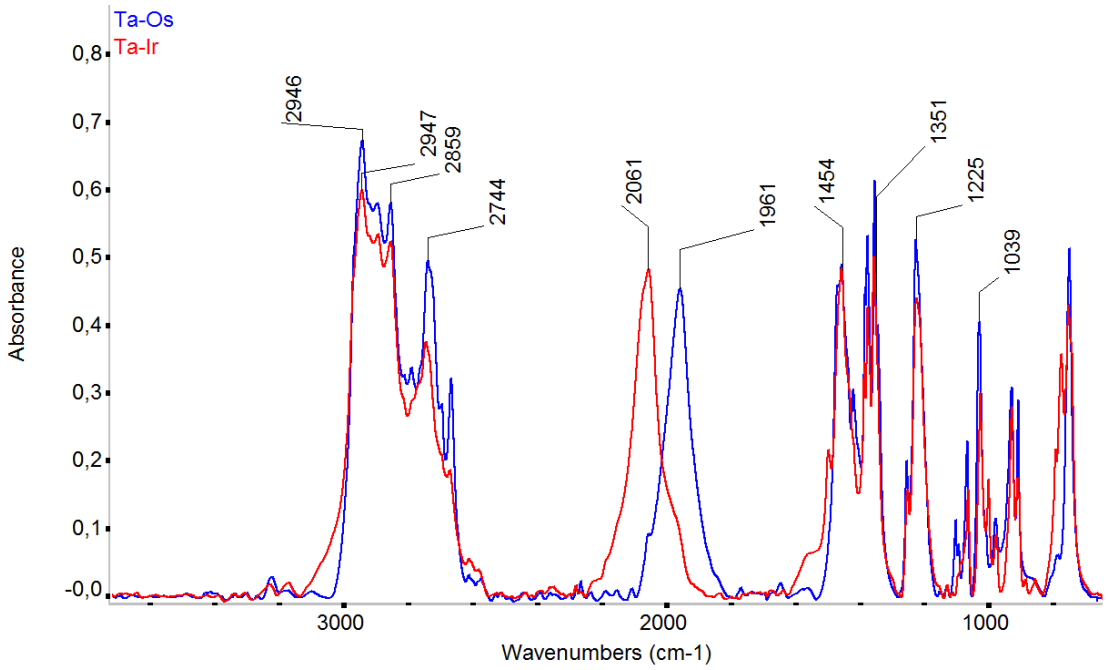

Figure S6. DRIFT (293 K, cm^{-1}) spectra of compounds **1** (in red) and **2** (in blue).

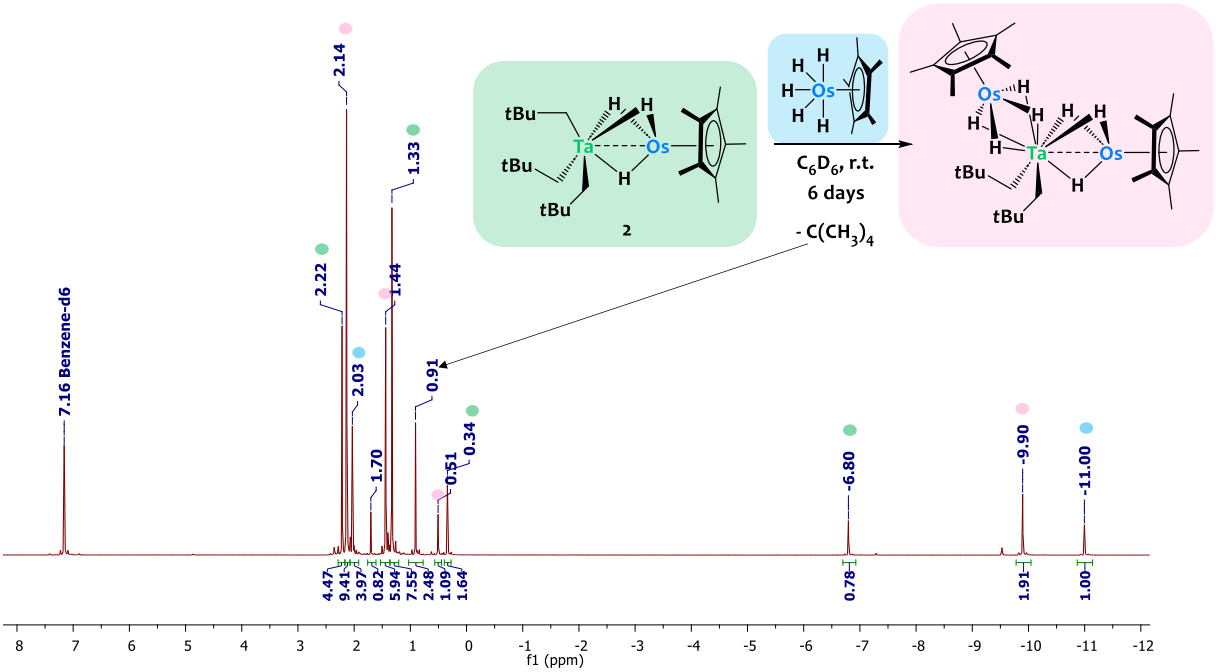

Figure S7. ^{1}H-NMR spectrum (300 MHz, C_6D_6, 298 K) of the crude reaction mixture of **2** with Cp^*OsH_5 after 6 days in C_6D_6. We observe the slow formation of a new trinuclear species by protonolysis and formation of neopentane (δ ^{1}H = 0.91 ppm). A similar iridium analogue was isolated previously in our group (S. Lassalle et al., *J. Catal.*, 2020, **392**, 287–301). Attempts to heat the reaction mixture to speed up the process lead instead to the decomposition of the starting materials.

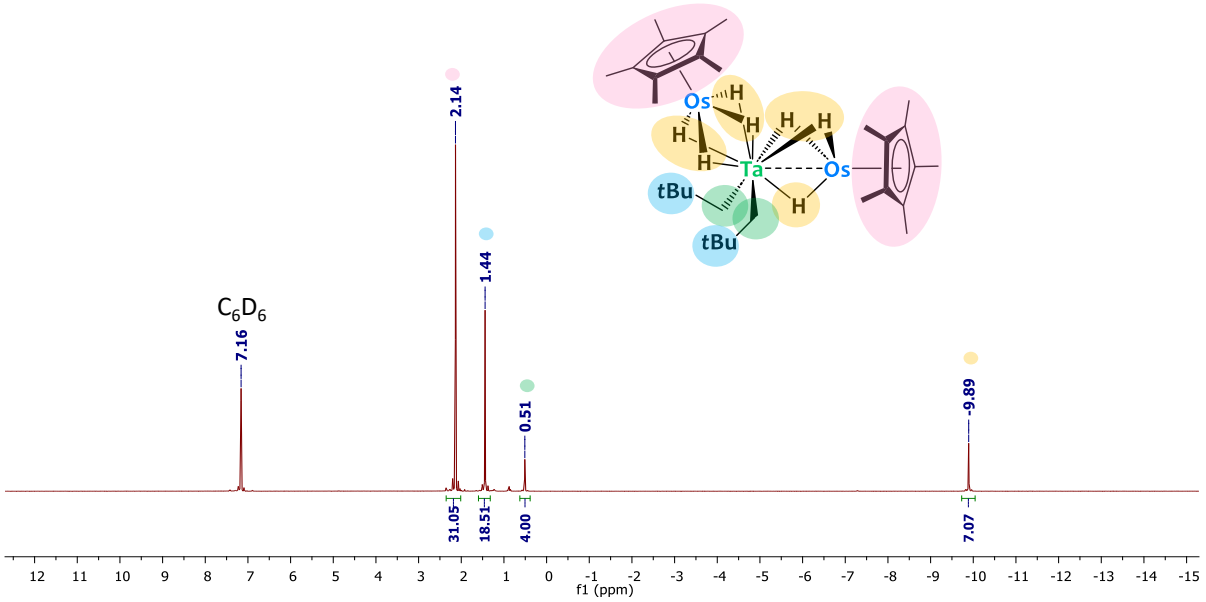

Figure S8. ^{1}H-NMR spectrum (300 MHz, C_6D_6, 298 K) of the trinuclear $TaOs_2$ complex isolated in 10% yield as a black precipitate upon taking the reaction mixture from Figure S7 to dryness, extraction in pentane and cooling to -40°C for 1 night.

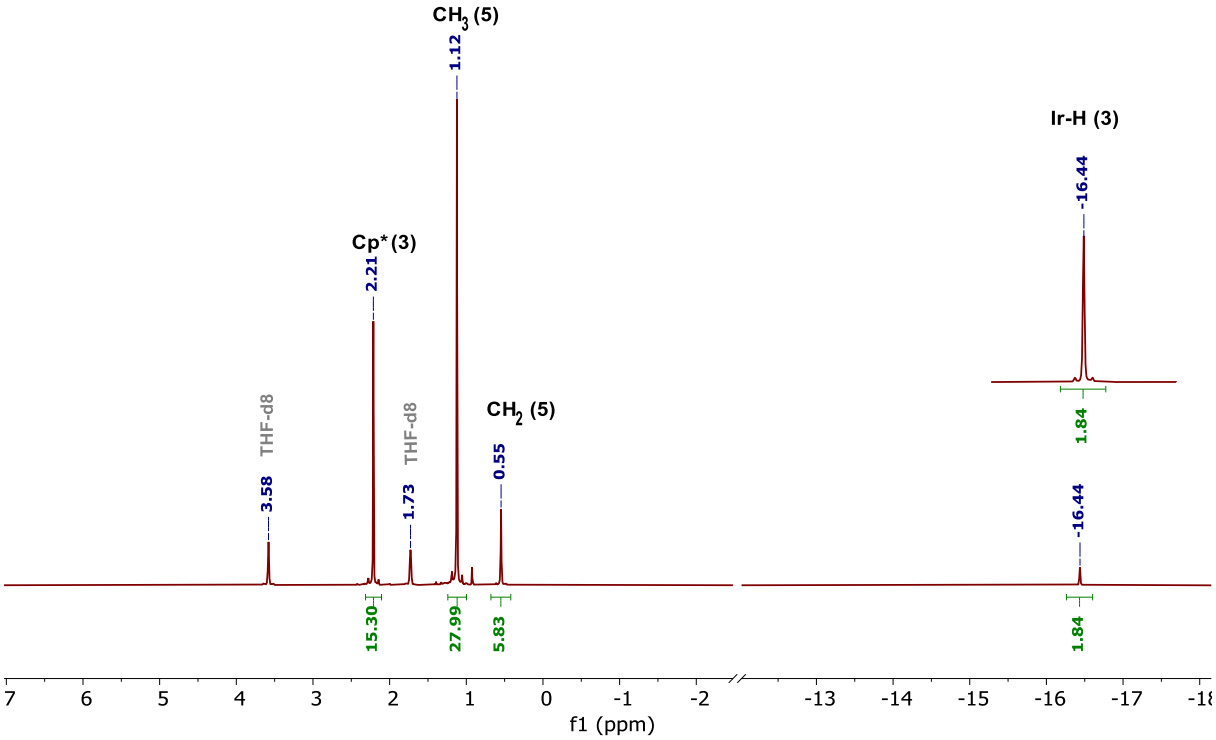

Figure S9. ^{1}H-NMR spectrum (300 MHz, THF-d_8, 298 K) of the crude reaction mixture of **1** with 1 atm of CO_2 after 60 min in THF-d_8. We observe the complete consumption of complex **1** and the quantitative formation of Cp*Ir(CO)H_2 **3** and $[Ta(O)(CH_2tBu)_3]_x$ **5**.

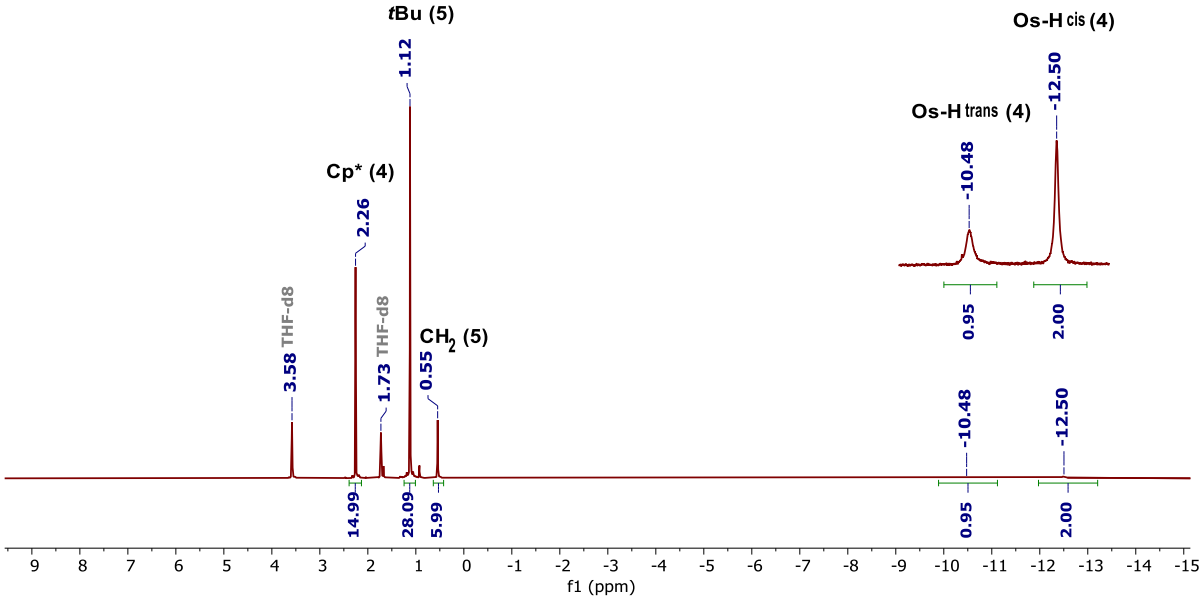

Figure S10. ^{1}H-NMR spectrum (300 MHz, THF-d_8, 298 K) of the crude reaction mixture of **2** with 1 atm of CO_2 after 90 min in THF-d_8. We observe the complete consumption of complex **2** and the quantitative formation of Cp*Os(CO)H_3 **4** and $[Ta(O)(CH_2tBu)_3]_x$ **5.**

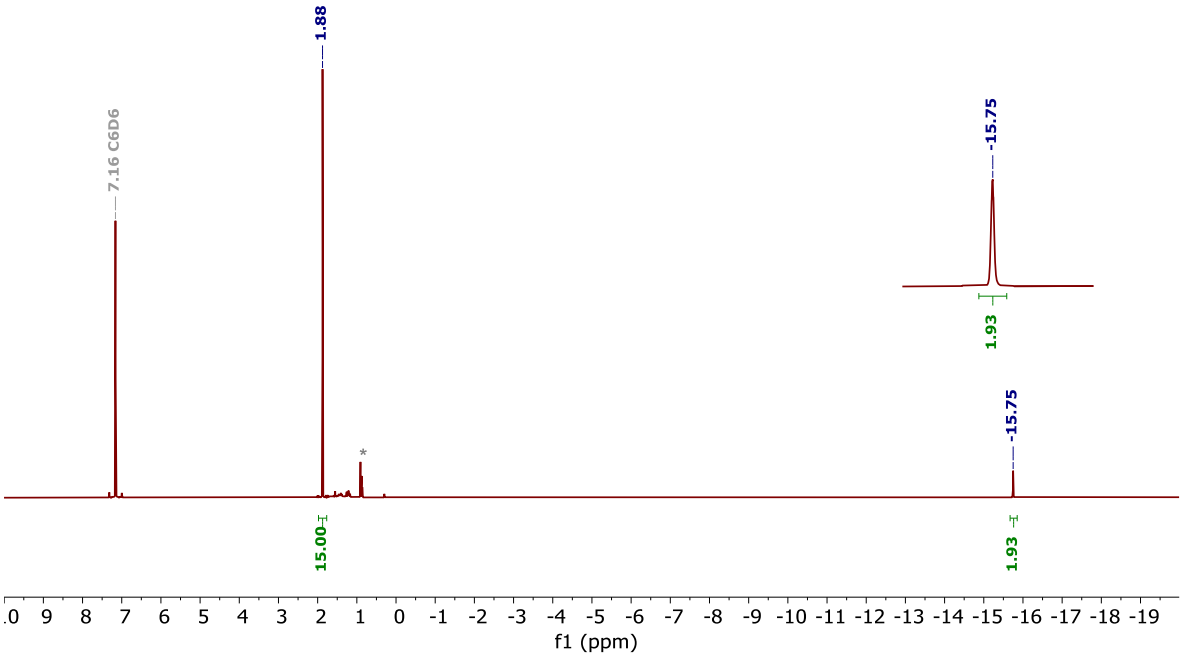

Figure S11. ^{1}H-NMR spectrum (500 MHz, C_6D_6, 298 K) of compound **3**.
(* = trace amounts of pentane)

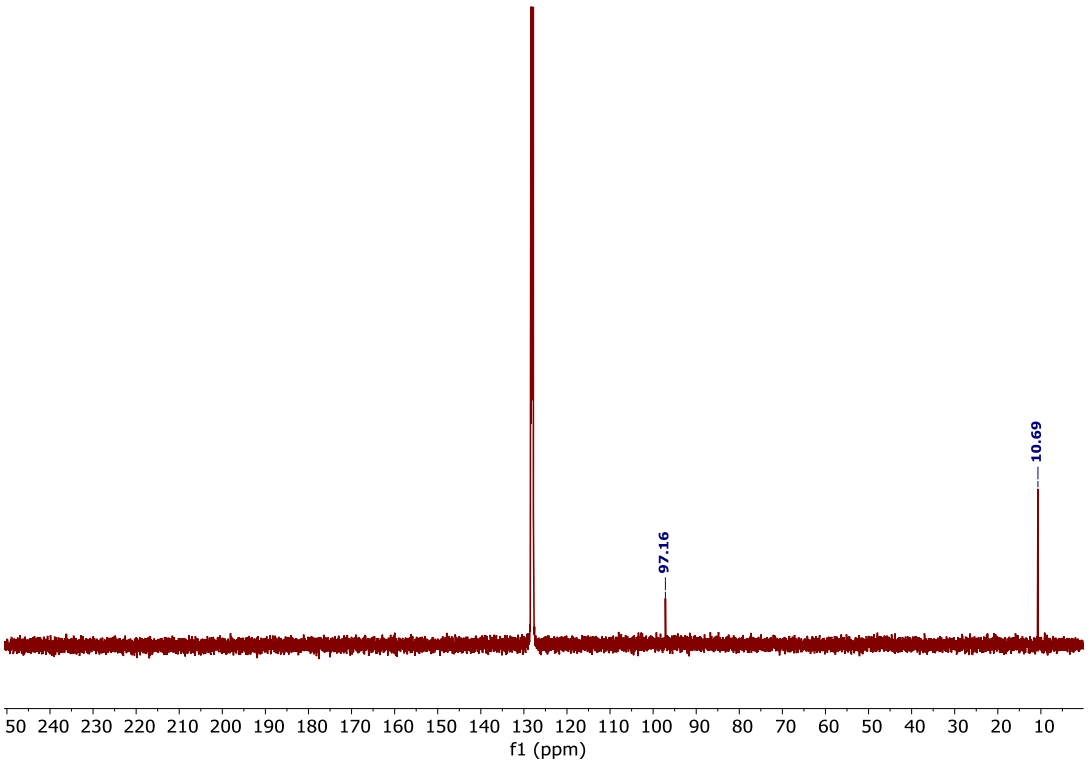

Figure S12. ^{13}C{^{1}H}-NMR spectrum (126 MHz, C_6D_6, 298 K) of [Cp*Ir(CO)H_2], **3**.

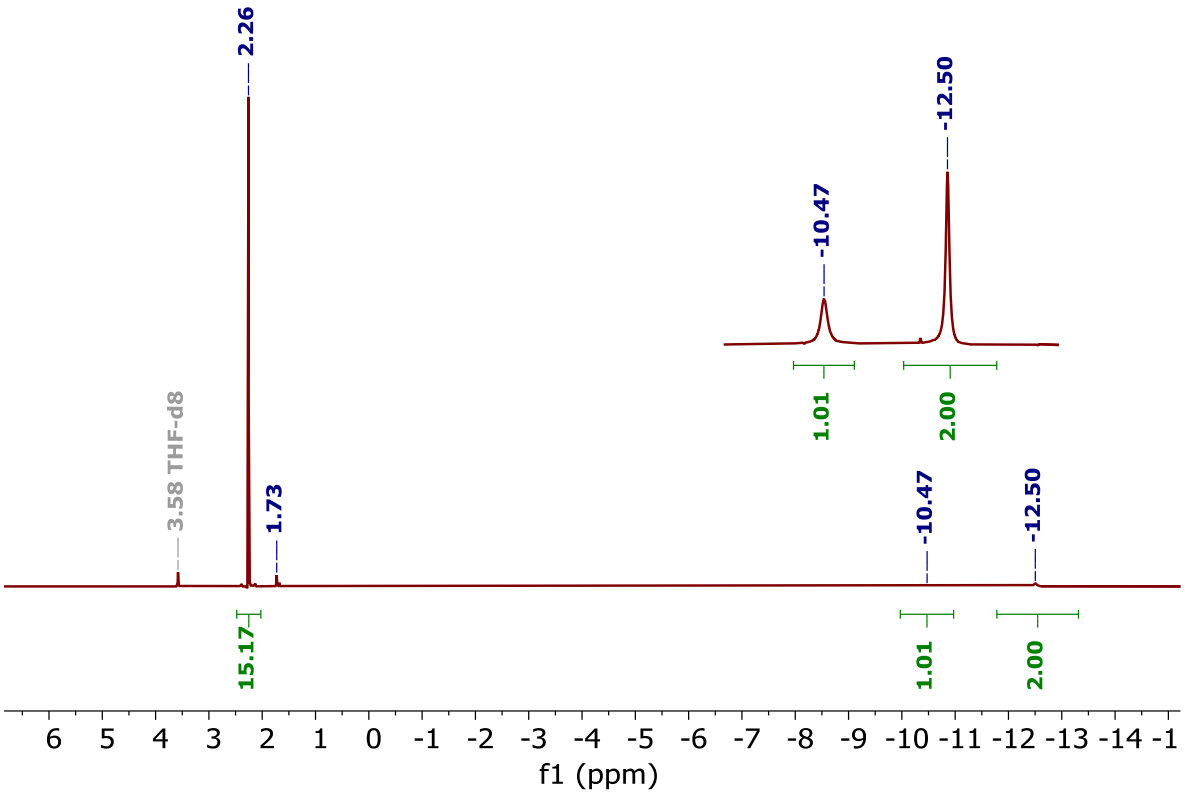

Figure S13. ^{1}H-NMR spectrum (500 MHz, THF-d_8, 298 K) of compound **4**.

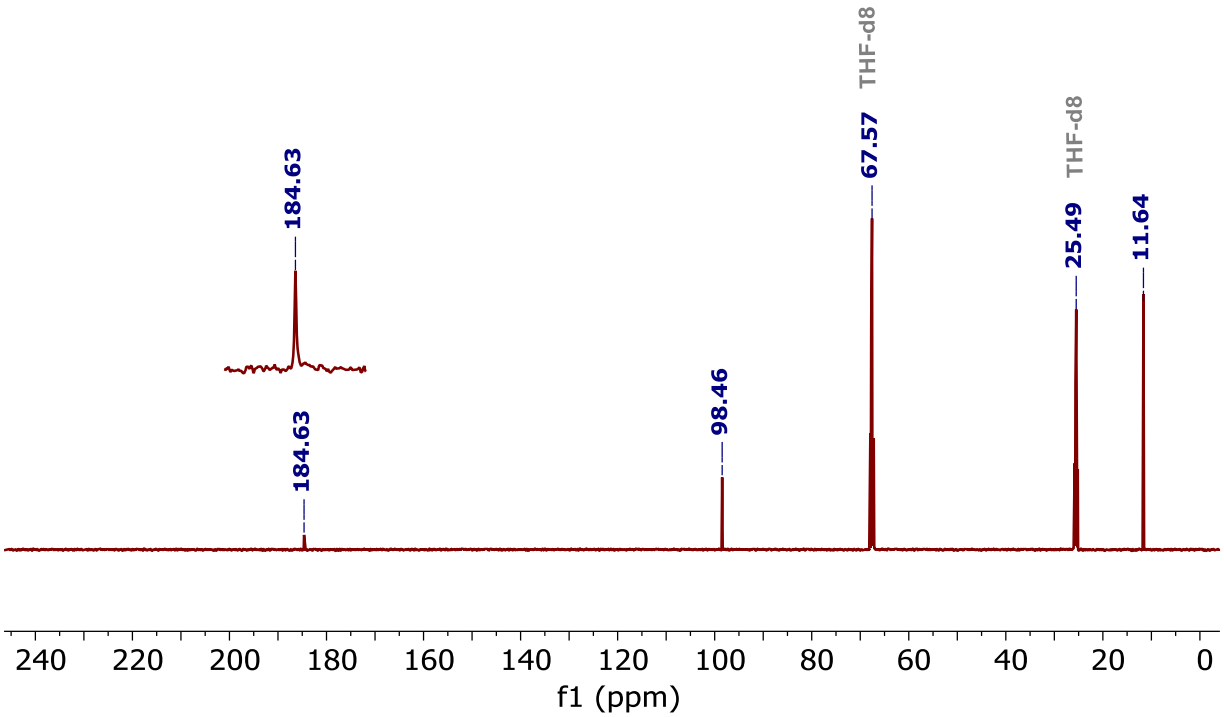

Figure S14. ^{13}C{^{1}H}-NMR spectrum (126 MHz, THF-d_8, 298 K) of compound **4**.

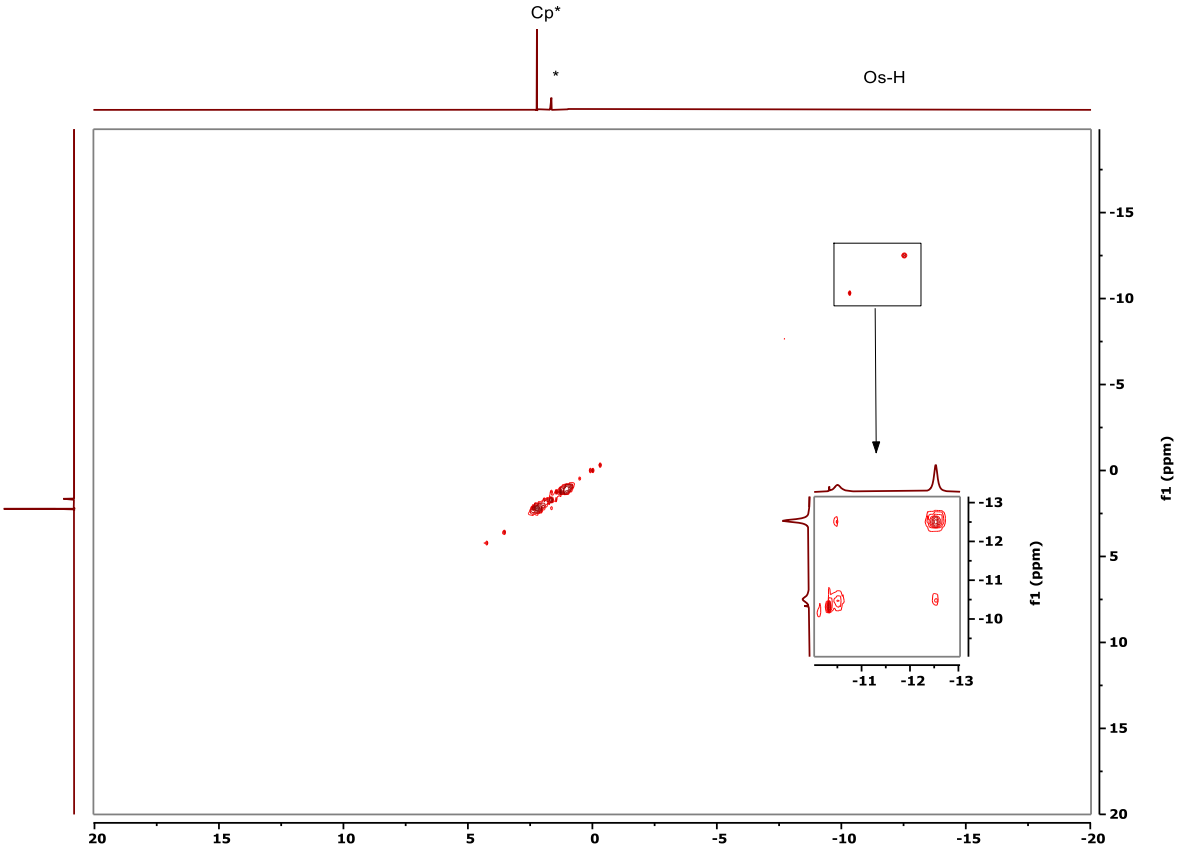

Figure S15. ^{1}H-^{1}H COSY NMR spectrum **(**400 MHz, THF-d_8, 302 K) of compound **4**, showing clear coupling of the two hydride signals. *(⁎ = Impurity resulting from the decomposition of **4** in the timeframe of the experiment)*

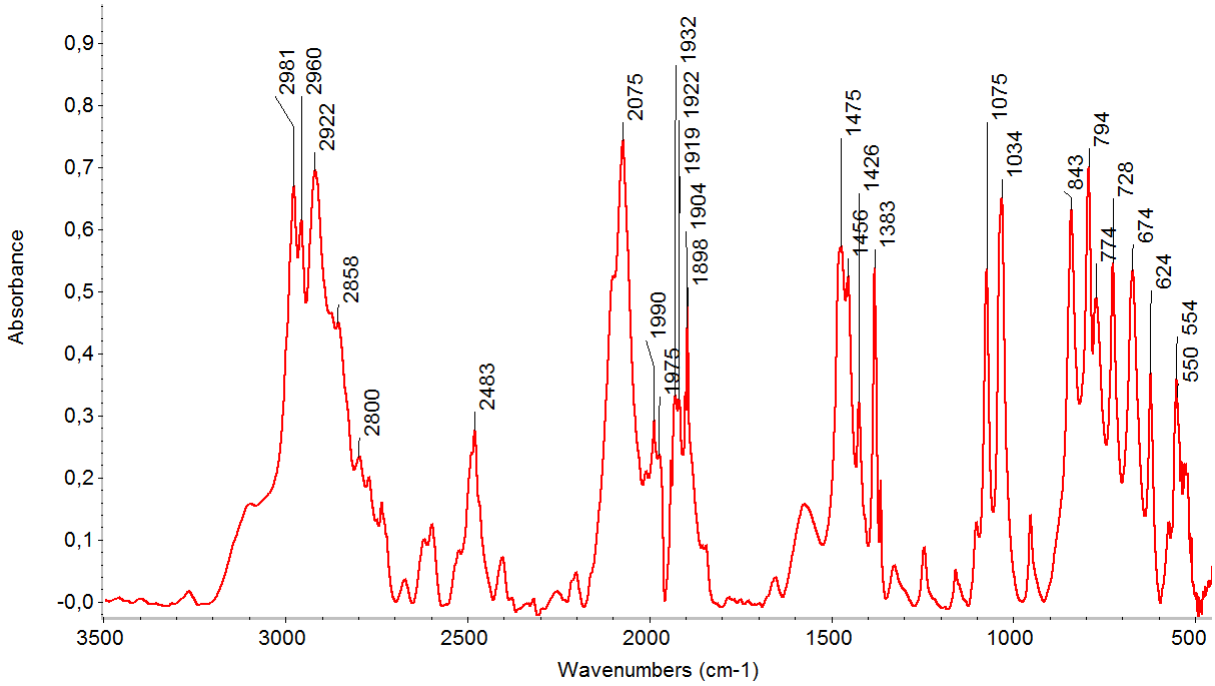

Figure S16. DRIFT (293 K, cm^{-1}) spectrum of compound **4**.

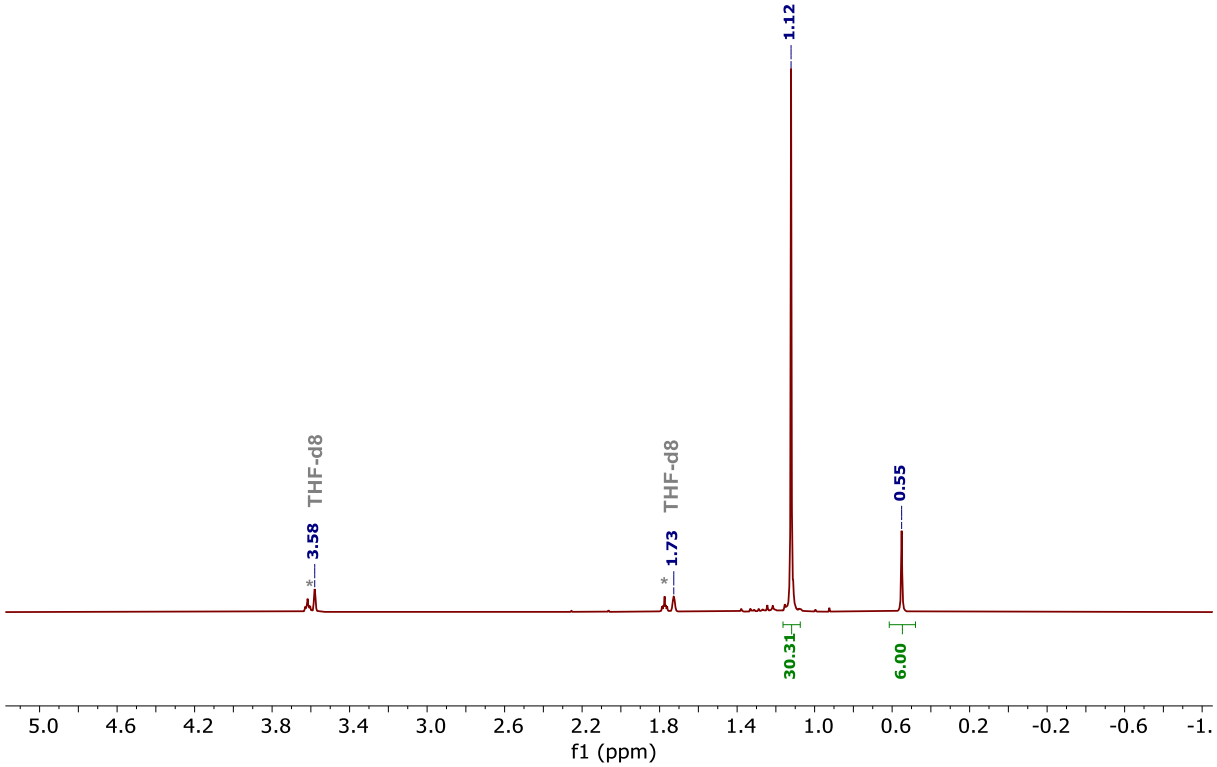

Figure S17. ^{1}H-NMR spectrum (500 MHz, THF-d_8, 298 K) of compound **5**. (* = THF)

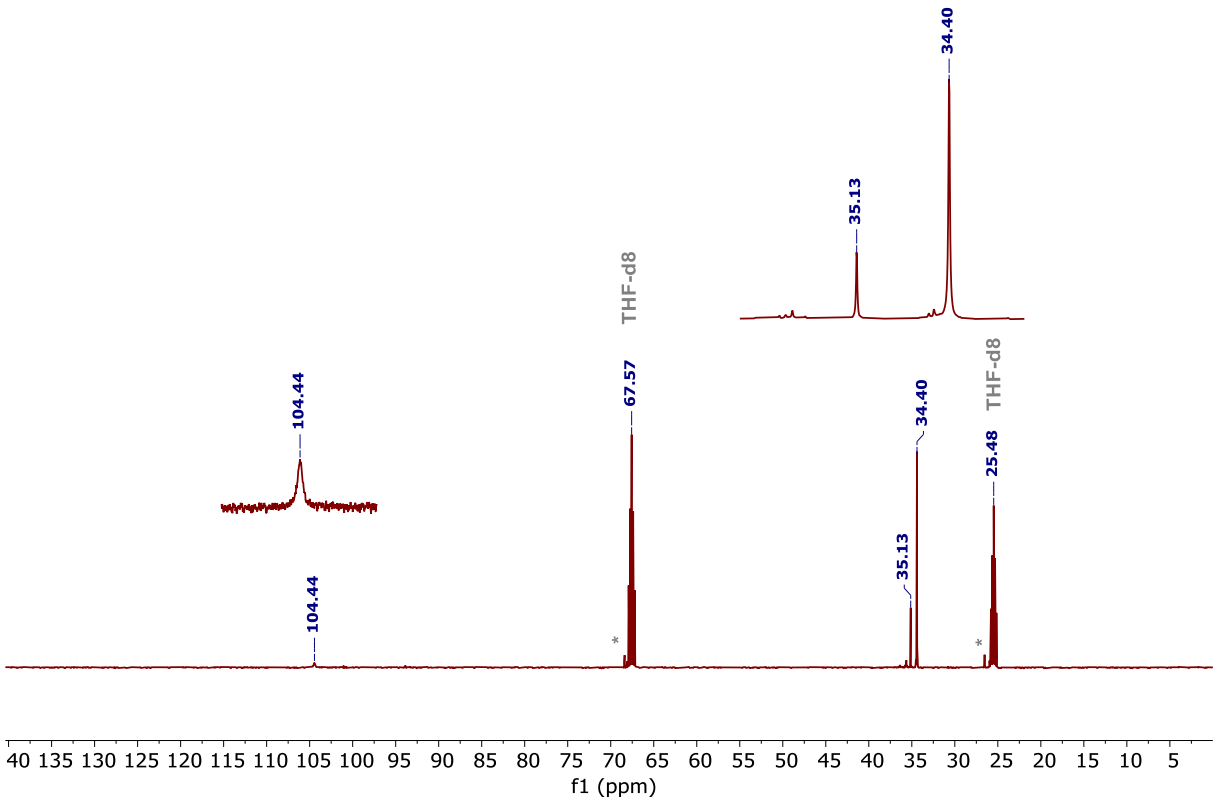

Figure S18. ^{13}C{^{1}H}-NMR spectrum (126 MHz, THF-d_8, 298 K) of compound **5**. (* = THF)

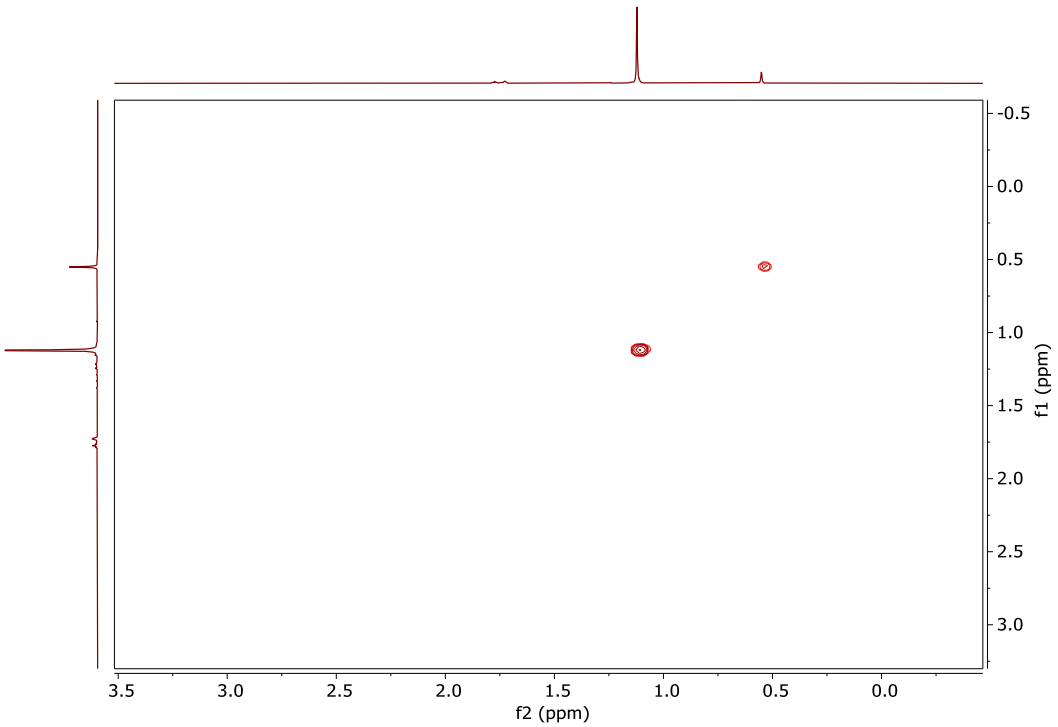

Figure S19. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, THF-d_8, 298 K) of compound **5**.

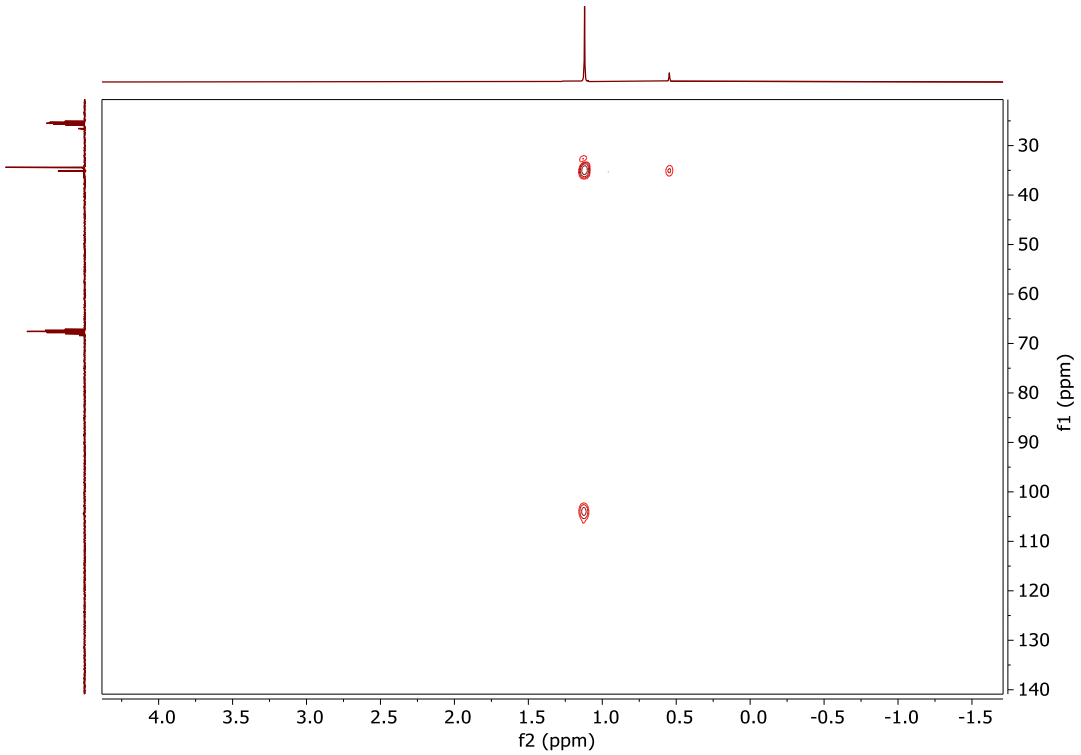

Figure S20. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz, THF-d_8, 298 K) of compound **5**.

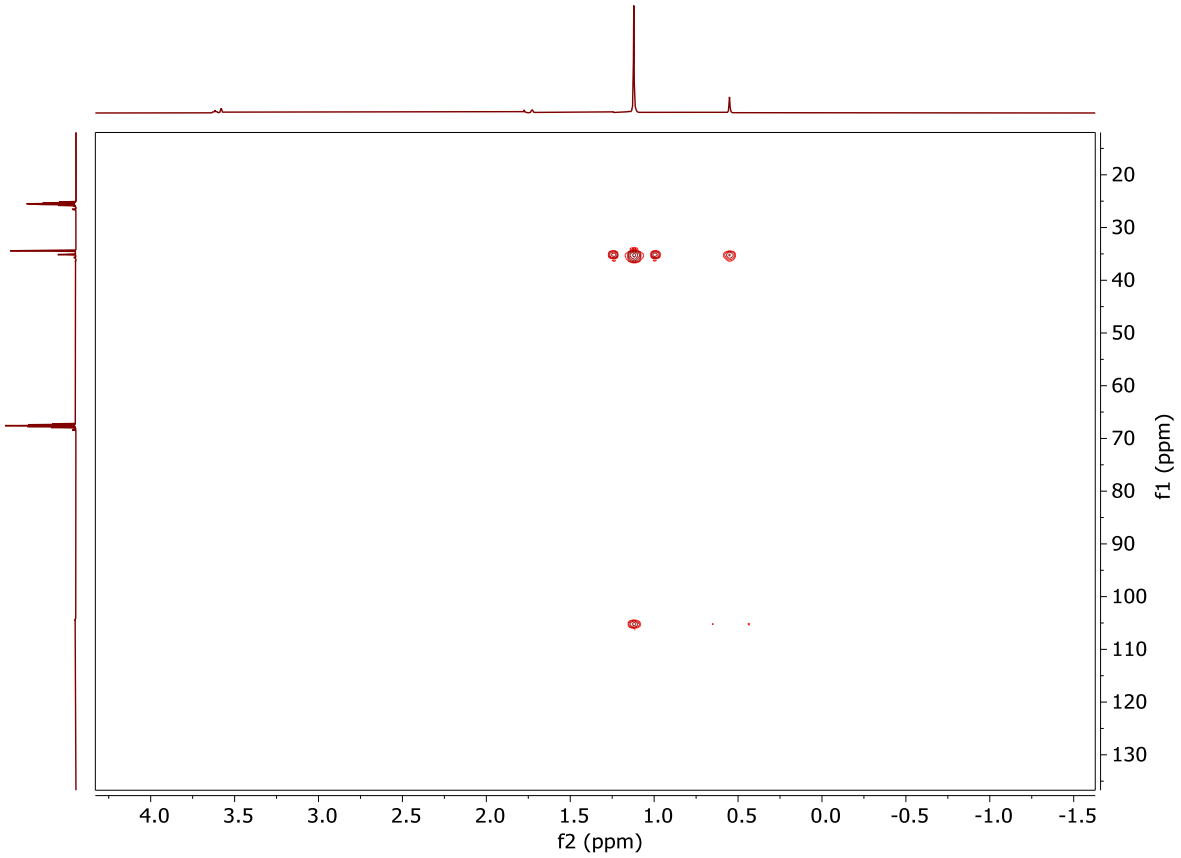

Figure S21. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz, THF-d_8, 298 K) of compound **5**.

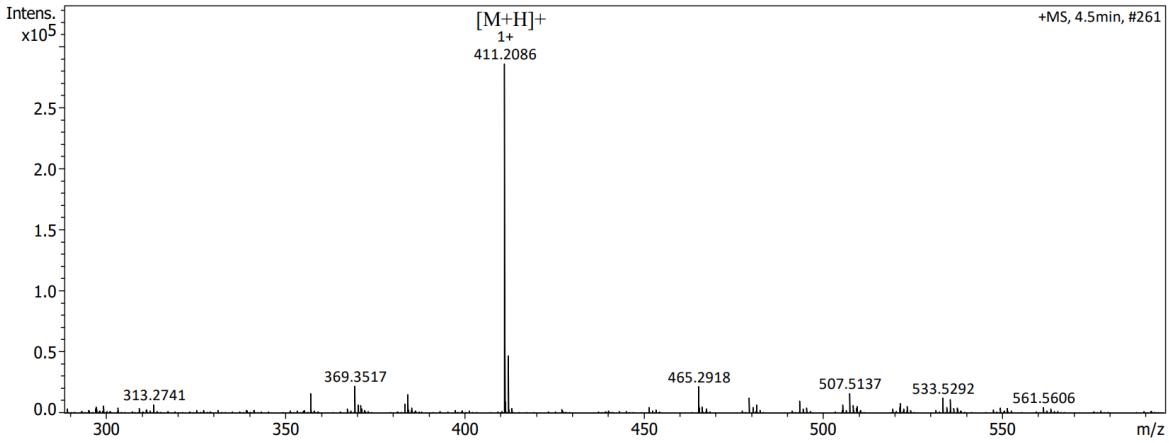

Figure S22. HRMS (APCI-SP^{+}) spectrum of complex $[Ta(O)(CH_2tBu)_3]_x$, **5.**

C. X-ray crystallography

Samples of single crystals for compound **1** were coated in Paratone-N oil for transport to the Advanced Light Source (ALS, Berkeley, CA, USA). Crystals were mounted on a MiTeGen 10 μm aperture Dual-Thickness MicroMount loop. X-ray diffraction data was collected at the ALS, Lawrence Berkeley National Lab, Berkeley, CA, station 12.2.1 using a silicon monochromated beam of 17 keV (λ = 0.7288 Å) synchrotron radiation. Data was collected at 100 K, with the crystals cooled by a stream of dry nitrogen. Bruker APEX3 software was used for the data collections, Bruker SAINT v8.37A or V8.38A software was used to conduct the cell refinement and data reduction procedures,[7] and absorption corrections were carried out by a multi-scan method utilizing the SADABS program.[7] Initial structure solutions were found using direct methods (SHELXT),[8] and refinements were carried out using SHELXL-2014,[9] as implemented by Olex2.[10] Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically. Thermal ellipsoid plots were made using Mercury.[11]

A suitable crystal of compound **2** was selected and mlouted on a MiTeGen Dual-Thickness MicroMount loop coated in Fomblin oil. The X-ray diffraxction data was collected at 100 K on a Rigaku-Oxford Diffraction XtaLAB Synergy diffractometer equipped with an HyPix-Arc 100 detector and a Molybdenum microsource (λ = 0.71073 Å). Data collection, unit-cell refinement, data reduction and absorption correction[12] were carried out with the CrysalisPro software.[13] The resulting set of *hkl* reflections were used to solve the structure with the ShelXT[8] structure solution program using the intrinsic phasing solution method and by using Olex2[10] as the graphical interface. Displacement parameters for all non-hydrogen atoms were refined anisotropically with version 2018/3 of ShelXL[9] using least-square minimization. Hydrogen atoms were place geometrically and their position was refined using riding restraints.

CCDC 2351192 and 2351850 contain supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

D. Computational data

Methods.

All DFT calculations were carried out with the Gaussian 09 suite of programs.[i] Geometries were fully optimized in gas phase without symmetry constraints, employing the B3PW91 functional. [ii] The nature of the extrema was verified by analytical frequency calculations. The calculation of electronic energies and enthalpies of the extrema of the potential energy surface (minima and transition states) were performed at the same level of theory as the geometry optimizations. IRC calculations were performed to confirm the connections of the optimized transition states. Iridium, Osmium, Rhenium and Tantalum atoms were treated with a small-core effective core potential (60 MWB), associated with its adapted basis set [iii] augmented with a polarization function (ζ_f = 0.938, 0.886, 0.869 and 0.790 respectively for Ir, Os, Re and Ta).[iv] For the other elements (H, C and O), Pople's double-ζ basis set 6-31G(d,p) was used. [v] The electronic charges (at the DFT level) were computed using the natural population analysis (NPA) technique.[vi]

[i] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[ii] (a) A. D. Becke, *J. Chem. Phys.* 1993, *98*, 5648-5652 ; (b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* 1992, *46*, 6671-6687.

[iii] (a) D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, Theoretica chimica acta 1990, 77, 123-141 ; (b) X. Cao and M. Dolg, Journal of Molecular Structure: THEOCHEM, 2004, 673, 203–209 ; (c) X. Cao, M. Dolg and H. Stoll, J. Chem. Phys., 2003, 118, 487–496.

[iv] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, Chemical Physics Letters, 1993, 208, 111–114.

[v] (a) J. A. Pople, *J. Chem. Phys.* 1971, *54*, 724-728 ; (b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* 1972, *56*, 2257-2261 ; (c) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* 1973, *28*, 213-222 ; (d) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* 1982, *77*, 3654-3665.

[vi] A. E. Reed, L. A. Curtiss, *Chem. Rev*. 1988, 88, 899 – 926.

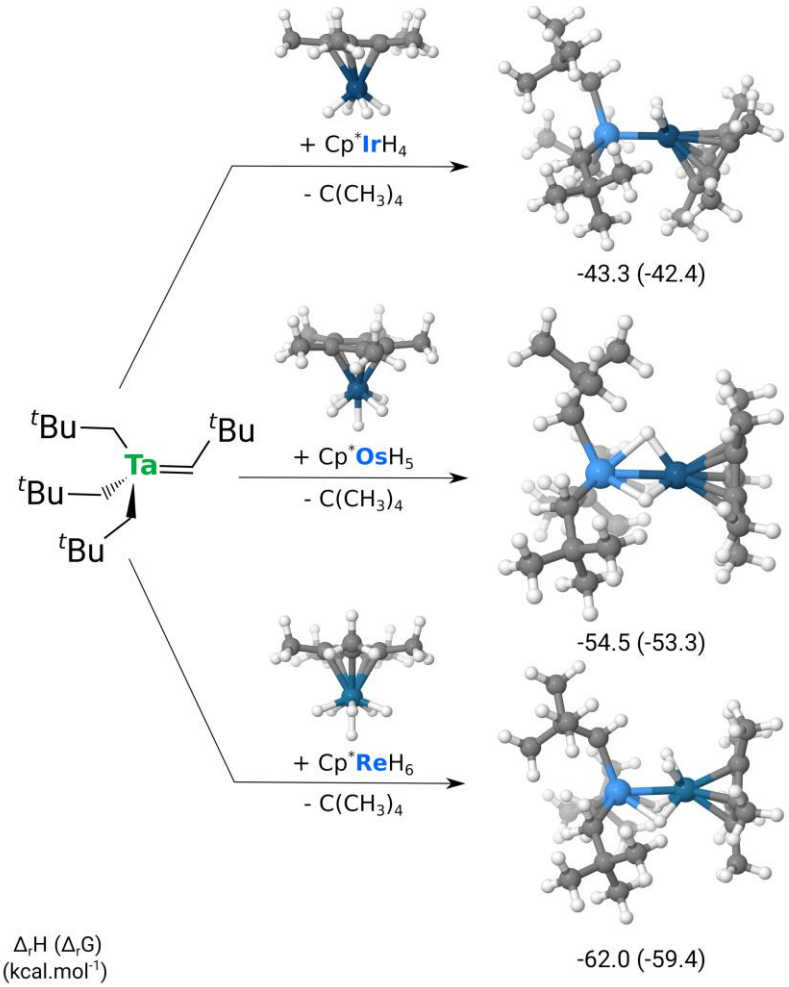

Figure S-DFT.1. Calculated enthalpy energy (Gibbs free energy) of the formation of $Ta(CH_2tBu)_3IrH_2Cp^*$, $Ta(CH_2tBu)_3(\mu\text{-}H)_3OsCp^*$ and $Ta(CH_2tBu)_3(\mu\text{-}H)_2Re(\eta\text{-}H)_2Cp^*$. The energies are given in kcal/mol.

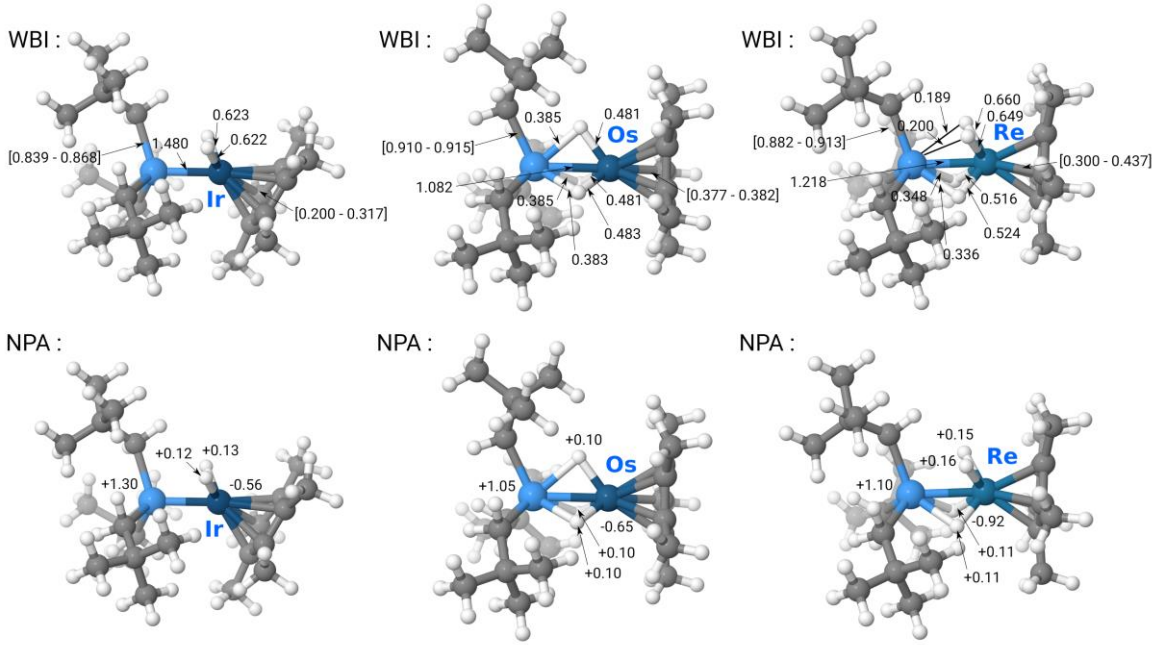

Figure S-DFT.2 Wiberg Bond Indexes and Natural Charges for Ta(CH_2*t*Bu)$_3$IrH_2Cp*, Ta(CH_2*t*Bu)$_3$(μ-H)$_3$OsCp* and Ta(CH_2*t*Bu)$_3$(μ-H)$_2$Re(η-H)$_2$Cp*.

Table S-DFT.1 NBO Analysis of $Ta(CH_2tBu)_3IrH_2Cp^*$, $Ta(CH_2tBu)_3(\mu\text{-}H)_3OsCp^*$ and $Ta(CH_2tBu)_3(\mu\text{-}H)_2Re(\eta\text{-}H)_2Cp^*$.

Bonding							
(1.84086) BD Ta - Ir (39.02%) Ta 2 s(27.03%) p 0.15(4.16%) d 2.54(68.74%) f 0.00(0.06%) (60.98%) Ir 4 s(30.11%) p 0.26(7.69%) d 2.07(62.19%) f 0.00(0.01%)							
2nd order pertubation analysis					M = Ir	M = Os	M = Re
BD	$C_{CH2\text{-}neo}$ -Ta	→	LP*	M	~404	~101	~501
BD	$C_{CH2\text{-}neo}$ -Ta	→	BD*	Ta - M	~265	-	-
BD	$C_{CH2\text{-}neo}$ -Ta	→	BD*	M - H	~405	~70	~205
BD	$C_{CH2\text{-}neo}$ -Ta	→	BD*	M - C_{Cp^*}	-	~80	~49
BD	M - C_{Cp^*}	→	BD*	Ta	-	~1621	-
BD	M - C_{Cp^*}	→	BD*	Ta - $C_{CH2\text{-}neo}$	-	~4070	~80
BD	Ta - M	→	LP*	Ta	~2071	-	-
BD	Ta - M	→	LP*	M	~295	-	-
BD	Ta - M	→	BD*	$C_{CH2\text{-}neo}$ -Ta	~80	-	-
BD	Ta - M	→	BD*	$C_{CH2\text{-}neo}$ - H	~4	-	-
BD	Ta - M	→	BD*	M - H	~510	-	-
BD	M - H	→	LP*	Ta	~9637	~6000	~6400
BD	M - H	→	BD*	$C_{CH2\text{-}neo}$ -Ta	~1800	-	-
BD	M - H	→	BD*	Ta - M	~1950	-	-
CR	Ta	→	LP*	M	~286	~201	~225
CR	Ta	→	BD*	Ta - M	~265	-	-
CR	Ta	→	BD*	M - H	~130	~260	~240
CR	Ta	→	BD*	M - C_{Cp^*}	-	~120	~2
CR	M	→	LP*	Ta	~513	~665	~1110
CR	M	→	BD*	$C_{CH2\text{-}neo}$ -Ta	~50	~75	~116
CR	M	→	BD*	Ta - M	~214	-	-
LP	M		LP*	Ta	~26	~488	~1475
LP	M		BD*	$C_{CH2\text{-}neo}$ -Ta	~10	~796	~1285

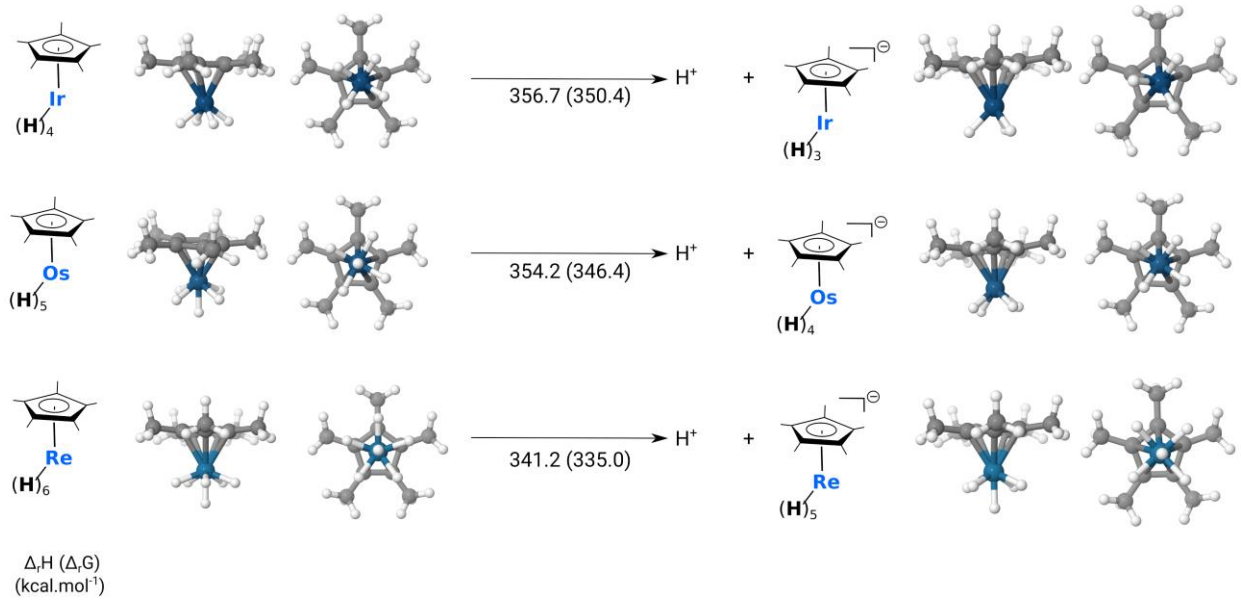

Figure S-DFT.3 Calculated enthalpy energy (*Gibbs-free* energy) for the Cp^*IrH_4, Cp^*OsH_5 and Cp^*ReH_6 deprotonation. The energies are given in kcal/mol.

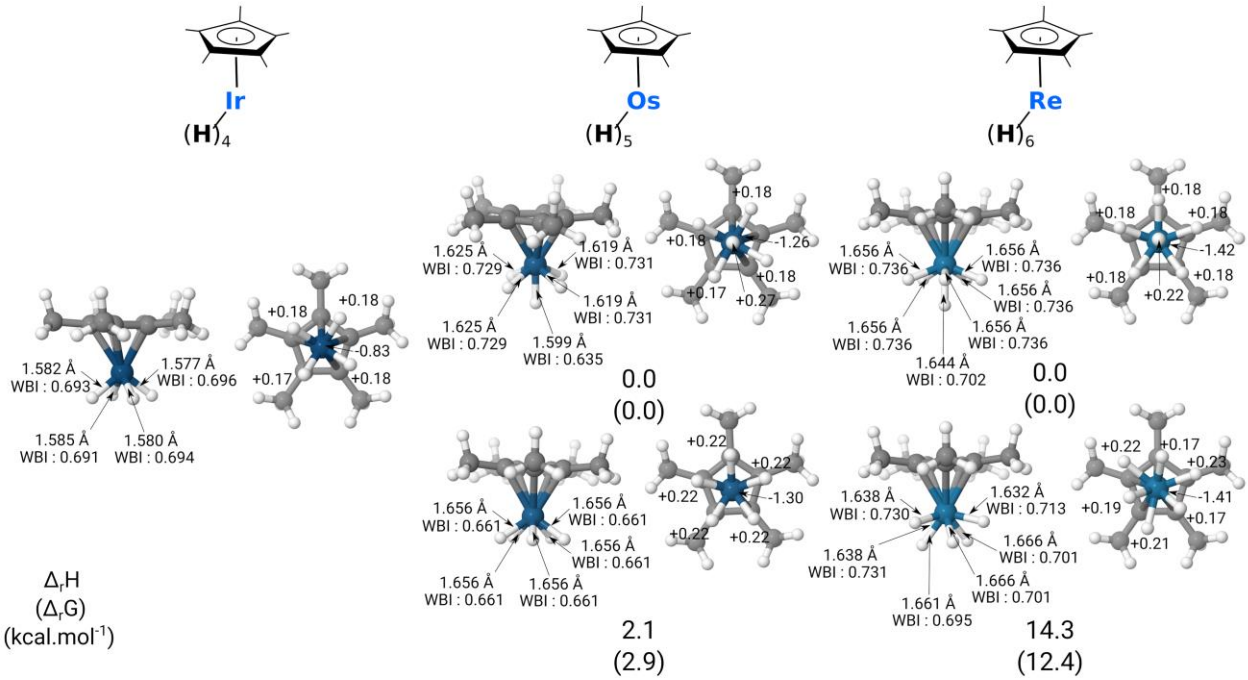

Figure S-DFT.4 Wiberg Bond Indexes and Natural Charges for Cp^*IrH_4, Cp^*OsH_5 and Cp^*ReH_6 and relative stability of the different isomers of Cp^*OsH_5 and Cp^*ReH_6. The energies are given in kcal/mol.

Discussion regarding the lack of reactivity between Cp*ReH_6 and Ta(CH*t*Bu)(CH_2*t*Bu)$_3$

According to the DFT calculations, the formation of the Ta/Re analogue should be thermodynamically favorable (see Figure DFT SI.1). The formation of this complex would even be the most favorable of the three. The bonding within the Ta/Re and the Ta/Os complexes is also similar both regarding the Wiberg Bond Indexes (see Figure S-DFT.2) and the second-order perturbation natural bond order (NBO) analysis (see Table S-DFT.1). Therefore, the observed lack of reactivity is surprising.

To assess if the reactivity difference is due to the precursors, we studied the deprotonation reaction of Cp^*IrH_4, Cp^*OsH_5 and Cp^*ReH_6 (see Figure S-DFT.3) and obtained similar energy values (enthalpy and/or *Gibbs-free* energy) for the three complexes. However, it is interesting to note that for Cp^*OsH_5 and Cp^*ReH_6 two isomers were obtained (see Figure S-DFT.4). In both cases, the pseudo-C_{4v} or -C_{5v} isomers with four or five equatorial hydrides and one axial hydride are the most stable ones for Cp^*OsH_5 and Cp^*ReH_6 respectively. For Cp^*OsH_5, although less stable, the C_{5V} "piano stool" isomer, less sterically hindered, is close in energy (ΔH = 2.1 kcal/mol) and could easily be formed to allow the interaction with the Ta complex. For Cp^*ReH_6, the stability difference between both isomers is higher (ΔH = 14.3 kcal/mol) which could indicate that this complex is less fluxional and therefore less likely to react with the Ta complex due to the lack of a coordination site.

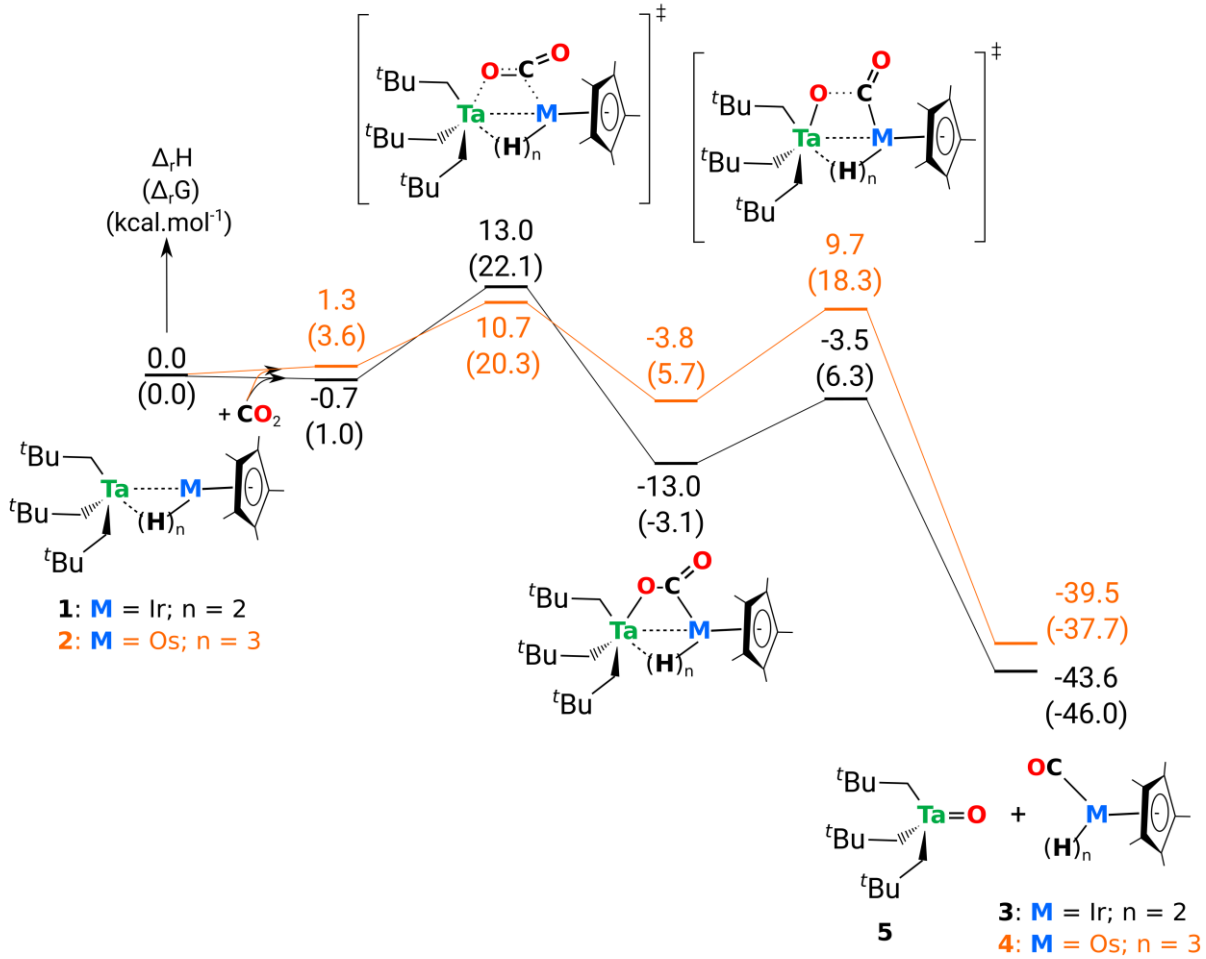

Figure DFT SI.5 - Computed reaction pathway for the reaction of CO_2 with $Ta(CH_2tBu)_3IrH_2Cp^*$ and $Ta(CH_2tBu)_3(\mu\text{-}H)_3OsCp^*$ at room temperature. The energies are given in kcal/mol.

Cartesian Coordinates :

17

C(CH3)4

C	-0.00009	-0.00000	-0.00031
C	-0.00026	0.00000	1.53482
C	1.44766	-0.00000	-0.51137
C	-0.72376	-1.25352	-0.51180
C	-0.72376	1.25352	-0.51180
H	-0.74119	1.28121	-1.60745
H	-1.76176	1.28175	-0.16055
H	-0.22800	2.16652	-0.16231
H	1.48075	0.00000	-1.60704
H	1.99091	0.88523	-0.16081
H	1.99091	-0.88523	-0.16081
H	-0.74119	-1.28121	-1.60745
H	-0.22800	-2.16652	-0.16231
H	-1.76176	-1.28175	-0.16055
H	-1.02270	0.00000	1.92994
H	0.51113	-0.88537	1.92991
H	0.51113	0.88537	1.92991

3

CO2

C	-0.26743	-2.29440	-0.31006
O	0.84053	-2.13018	-0.56225
O	-1.37540	-2.45840	-0.05771

64

Ta(CHtBu)(CH2tBu)3

C	1.54007	6.80730	-9.25112
Ta	-0.37778	6.32889	-10.13378
C	-0.07018	6.31711	-12.27971
C	-1.96878	7.60874	-9.36277
H	-2.60414	7.14190	-8.59881
H	-2.56576	7.53378	-10.30248
C	-1.78442	9.10582	-9.01291
C	2.57561	5.97841	-8.46630
H	1.23277	7.67279	-8.62458
H	2.05388	7.28491	-10.11320
H	0.75015	7.05457	-12.39479
C	-1.06340	6.49437	-13.44966
H	0.43209	5.33362	-12.37872
C	3.79732	6.85688	-8.13999
C	3.03456	4.78646	-9.31588
C	1.96736	5.47344	-7.15200

C	-2.21073	5.48060	-13.33630
C	-0.32698	6.26515	-14.78214
C	-1.64282	7.91574	-13.45265
H	2.70022	4.89063	-6.58157
H	1.09838	4.83621	-7.34058
H	1.64578	6.31036	-6.51977
H	4.55503	6.29210	-7.58320
H	3.51133	7.72219	-7.53053
H	4.26887	7.23350	-9.05539
H	2.18443	4.14228	-9.56094
H	3.78266	4.18668	-8.78397
H	3.48732	5.12452	-10.25631
H	-2.91187	5.58765	-14.17275
H	-2.77232	5.61486	-12.40492
H	-1.83120	4.45324	-13.34976
H	0.49673	6.97781	-14.90474
H	-1.00468	6.38574	-15.63610
H	0.09567	5.25516	-14.82943
H	-2.30033	8.06672	-14.31665
H	-0.84735	8.66846	-13.50487
H	-2.23501	8.10991	-12.55176
C	-3.14382	9.82171	-9.10783
C	-0.80336	9.78807	-9.97947
C	-1.26337	9.23936	-7.57470
H	0.20552	9.36172	-9.90664
H	-0.71160	10.85766	-9.75702
H	-1.13872	9.69644	-11.01856
H	-3.05752	10.87900	-8.82801
H	-3.87847	9.35651	-8.44120
H	-3.54273	9.77717	-10.12786
H	-1.13961	10.29323	-7.29963
H	-0.29409	8.74573	-7.44662
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C	-0.83392	4.56065	-9.59155
H	-1.19800	5.04569	-8.63822
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H	0.65437	2.64992	-10.89767
H	-0.84014	2.93901	-11.80486
H	0.59257	2.53856	-8.33890

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H -0.93662 2.77990 -7.47732
H -2.80295 1.72763 -9.72442
H -3.04951 3.27287 -10.56585
H -3.09508 3.20931 -8.79646
30
IrCp*H4
Ir -7.07526 2.85516 -7.52772
C -7.37592 1.10550 -8.91313
C -8.54617 1.17841 -8.07524
C -8.13761 0.96179 -6.71647
C -6.71581 0.75769 -6.70240
C -6.23761 0.84395 -8.06120
C -9.95865 1.32714 -8.55113
C -9.04892 0.86362 -5.53204
C -5.89687 0.37940 -5.50639
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H -6.41443 1.49648 -10.79892
H -7.52843 0.12196 -10.81751
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H -5.89698 -0.70927 -5.36656
H -4.85868 0.70074 -5.61557
H -6.28793 0.83230 -4.59232
H -7.94152 4.03319 -8.13033
H -7.60641 3.83830 -6.40417
H -6.21754 3.76761 -8.48589
H -5.89413 3.55634 -6.74696
29
IrCp*H3 -
Ir -7.07375 2.83918 -7.59210
C -7.37035 1.04394 -8.95770
C -8.52370 1.18437 -8.11966
C -8.12537 0.99570 -6.74394

C -6.69955 0.77789 -6.74641
C -6.22890 0.78650 -8.10100
C -9.93615 1.35636 -8.59206
C -9.04073 0.87719 -5.56458
C -5.87427 0.45218 -5.53768
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C -7.35822 1.01823 -10.45575
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H -7.46556 -0.00378 -10.85611
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H -8.03212 4.11390 -7.59263
H -6.24595 3.87769 -8.47347
H -6.39991 3.75642 -6.47482
31
OsCp*H5
Os -7.16759 2.85552 -7.50676
C -7.42094 1.11638 -8.90894
C -8.59615 1.12684 -8.07932
C -8.18990 0.93195 -6.72078
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C -6.27251 0.90623 -8.05126
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C -7.40900 1.14229 -10.40690
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H -4.64177 1.19551 -9.42360
H -4.72072 -0.42415 -8.71082
H -6.46208 1.52755 -10.79022
H -7.55063 0.13145 -10.81032

H -8.20531 1.77703 -10.80192
H -10.41783 0.22369 -8.74814
H -10.07507 1.79195 -9.49339
H -10.65099 1.71792 -7.82836
H -10.00811 1.39688 -5.66520
H -8.62026 1.09906 -4.61884
H -9.41808 -0.25531 -5.43158
H -5.93193 -0.64734 -5.33802
H -4.90514 0.77059 -5.60082
H -6.33589 0.90311 -4.58262
H -8.34210 3.79299 -8.12473
H -7.76036 3.51318 -6.14382
H -6.37256 3.57485 -8.71969
H -5.79890 3.30102 -6.76505
H -6.95961 4.43291 -7.34639
31
OsCp*H5 less stable isomer
C -6.26826 0.80927 -8.08159
C -7.42060 1.05202 -8.90866
C -8.56564 1.18378 -8.04724
C -8.12149 1.02046 -6.68832
C -6.70152 0.78883 -6.70970
Os -7.10336 2.87955 -7.55999
C -7.44843 1.01855 -10.40690
C -9.99084 1.31192 -8.49385
C -9.00433 0.94587 -5.47914
C -5.85168 0.43247 -5.52744
C -4.89076 0.47834 -8.57173
H -4.12610 0.78245 -7.85324
H -4.67177 0.97854 -9.51778
H -4.78758 -0.60251 -8.73296
H -6.50747 1.37436 -10.83257
H -7.61326 -0.00506 -10.76734
H -8.24911 1.64520 -10.80621
H -10.44014 0.32149 -8.64182
H -10.06707 1.85718 -9.43726
H -10.59433 1.84505 -7.75579
H -9.89156 1.57296 -5.59185
H -8.47940 1.27596 -4.57993
H -9.34204 -0.08481 -5.31038
H -5.84431 -0.65390 -5.37061
H -4.81765 0.75623 -5.66602
H -6.22330 0.89873 -4.61218

H -6.95460 3.85606 -8.83965
H -7.73944 3.82093 -6.41034
H -6.18380 3.56252 -6.41991
H -8.22302 3.99195 -7.90663
H -5.69488 3.58323 -7.92576
30
OsCp*H4 -
Os -7.05512 2.87785 -7.50019
C -7.35848 1.18838 -8.90056
C -8.53503 1.21317 -8.06144
C -8.13798 0.95438 -6.71337
C -6.71655 0.78331 -6.68822
C -6.21659 0.91723 -8.04265
C -9.94676 1.36263 -8.54441
C -9.05659 0.82577 -5.53626
C -5.90622 0.37630 -5.49384
C -4.83135 0.57632 -8.50640
C -7.34991 1.19635 -10.40037
H -4.08610 0.84494 -7.75149
H -4.57786 1.13015 -9.41521
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H -8.14940 1.83083 -10.79503
H -10.39706 0.38973 -8.79912
H -9.99109 1.99269 -9.43713
H -10.57967 1.83348 -7.78632
H -9.93982 1.46050 -5.65120
H -8.55823 1.13001 -4.61145
H -9.40488 -0.21082 -5.40278
H -5.87175 -0.71877 -5.37307
H -4.87619 0.73324 -5.58055
H -6.31674 0.80017 -4.57244
H -7.98092 4.04827 -8.16134
H -7.59365 3.90193 -6.33739
H -5.80126 3.50595 -6.67229
H -6.16106 3.83061 -8.46108
32
ReCp*H6
C -6.26175 0.85723 -8.07757
C -7.41269 1.09982 -8.90344
C -8.55664 1.23042 -8.04345
C -8.11301 1.06703 -6.68634

C	-6.69479	0.83621	-6.70762
Re	-7.09150	2.95414	-7.55435
C	-7.44199	1.05872	-10.40136
C	-9.98178	1.35159	-8.49117
C	-8.99634	0.98656	-5.47813
C	-5.84621	0.47261	-5.52690
C	-4.88630	0.51935	-8.56797
H	-4.12020	0.82186	-7.85118
H	-4.66657	1.01572	-9.51530
H	-4.79511	-0.56297	-8.72411
H	-6.50097	1.40893	-10.83029
H	-7.61034	0.03148	-10.74861
H	-8.24118	1.68491	-10.80295
H	-10.42002	0.35611	-8.63582
H	-10.05864	1.89451	-9.43528
H	-10.58791	1.88314	-7.75488
H	-9.88517	1.61056	-5.59030
H	-8.47335	1.31621	-4.57824
H	-9.32663	-0.04757	-5.31823
H	-5.84484	-0.61512	-5.38216
H	-4.81220	0.79548	-5.66361
H	-6.21759	0.93377	-4.60953
H	-6.99011	3.65299	-9.05220
H	-7.89349	3.61114	-6.26309
H	-6.82625	4.57305	-7.44425
H	-6.10271	3.31592	-6.27635
H	-8.44141	3.81382	-7.97860
H	-5.54628	3.34307	-8.00376

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ReCp*H6 less stable isomer

Re	-7.08967	2.93065	-7.51944
C	-7.37308	1.09119	-8.91800
C	-8.55137	1.17431	-8.08312
C	-8.14862	0.98524	-6.73171
C	-6.71618	0.77832	-6.71595
C	-6.25677	0.78733	-8.07206
C	-9.96219	1.29333	-8.57385
C	-9.06013	0.86711	-5.54815
C	-5.90201	0.40882	-5.51201
C	-4.87571	0.43633	-8.53429
C	-7.36385	1.11037	-10.41752
H	-4.12065	0.70789	-7.79350
H	-4.62338	0.93990	-9.46990

H	-4.80428	-0.64513	-8.70552
H	-6.40643	1.46344	-10.80751
H	-7.54140	0.10581	-10.82243
H	-8.13884	1.77197	-10.81118
H	-10.38596	0.29729	-8.75441
H	-10.01575	1.85459	-9.50915
H	-10.59967	1.80102	-7.84668
H	-9.95089	1.48856	-5.66295
H	-8.56138	1.17221	-4.62580
H	-9.38950	-0.17243	-5.42479
H	-5.91896	-0.67625	-5.34783
H	-4.85892	0.71318	-5.62540
H	-6.28478	0.89010	-4.60923
H	-8.22167	3.59653	-8.49778
H	-7.41831	3.22754	-5.94264
H	-6.63925	4.14173	-8.57167
H	-6.03357	3.86879	-6.63609
H	-7.84769	4.34063	-7.07828
H	-5.53370	3.10403	-7.98124

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ReCp*H5 -

C	-6.25765	0.81921	-8.05560
C	-7.40783	1.11081	-8.89937
C	-8.56559	1.23577	-8.01496
C	-8.10720	1.00688	-6.66514
C	-6.70826	0.74866	-6.69843
Re	-7.12045	2.86874	-7.63792
C	-7.44903	1.00747	-10.39344
C	-9.99766	1.32727	-8.44661
C	-8.97656	0.96380	-5.44538
C	-5.85071	0.42498	-5.51323
C	-4.88234	0.47326	-8.53982
H	-4.11975	0.77023	-7.81387
H	-4.65685	0.99675	-9.47243
H	-4.77301	-0.60809	-8.72250
H	-6.50871	1.35059	-10.83468
H	-7.62761	-0.02553	-10.73681
H	-8.24126	1.64020	-10.80338
H	-10.45163	0.33290	-8.59201
H	-10.08384	1.87729	-9.38752
H	-10.59747	1.86630	-7.70737
H	-9.83134	1.63638	-5.55160
H	-8.42624	1.27945	-4.55466

H -9.36295 -0.05117 -5.26355
H -5.81945 -0.66003 -5.33165
H -4.82524 0.77188 -5.66375
H -6.22735 0.90781 -4.60756
H -6.86530 4.50234 -7.59221
H -8.18091 3.68190 -6.60392
H -5.98916 3.33334 -6.46543
H -8.01556 3.72269 -8.77298
H -5.89083 3.38558 -8.66503
77
Complex 1
C -4.12684 4.09326 -6.99414
Ta -6.08270 4.82313 -7.58346
C -5.78299 5.58100 -9.57118
Ir -7.62451 3.00166 -7.42176
C -8.12494 1.21964 -8.78789
C -9.28439 1.31839 -7.92669
C -8.86901 1.11929 -6.59191
C -7.43611 0.89639 -6.59117
C -6.98945 0.90686 -7.95881
C -10.68341 1.56733 -8.39853
C -9.74200 1.10805 -5.37528
C -6.63492 0.45216 -5.40539
C -5.64370 0.46183 -8.44447
C -8.17228 1.14295 -10.28276
C -6.81907 6.41234 -6.30056
H -4.85534 0.68997 -7.72275
H -5.37535 0.93711 -9.39100
H -5.63520 -0.62455 -8.60707
H -7.21308 1.40648 -10.73356
H -8.42432 0.12507 -10.61084
H -8.92596 1.81653 -10.69866
H -11.16858 0.62932 -8.69856
H -10.70027 2.23701 -9.26227
H -11.29770 2.02151 -7.61698
H -10.63730 1.71890 -5.51604
H -9.21337 1.49512 -4.50032
H -10.07061 0.08785 -5.13735
H -6.75881 -0.62542 -5.23130
H -5.56845 0.64055 -5.54942
H -6.94094 0.97120 -4.49329
H -8.41728 4.26824 -8.02327
H -7.71646 3.82065 -6.05155

H	-6.07715	6.22024	-5.49031
H	-7.78207	6.09948	-5.87525
C	-6.87236	7.93668	-6.56420
C	-3.34817	4.22379	-5.66418
H	-3.50328	4.51891	-7.80596
H	-4.22643	3.02289	-7.24602
H	-6.44773	6.46507	-9.45727
C	-5.91137	5.04578	-11.00847
H	-4.76112	5.99446	-9.43310
C	-2.06020	3.38445	-5.75154
C	-4.19358	3.70866	-4.49138
C	-2.95502	5.68568	-5.41043
C	-5.05152	3.78483	-11.16792
C	-5.41400	6.11237	-12.00127
C	-7.37863	4.72586	-11.31682
H	-2.36779	5.77741	-4.48921
H	-3.83571	6.32736	-5.30467
H	-2.34800	6.08081	-6.23366
H	-1.47263	3.46290	-4.82860
H	-1.42717	3.71828	-6.58179
H	-2.29147	2.32537	-5.91279
H	-5.10238	4.30537	-4.35639
H	-3.62484	3.74690	-3.55449
H	-4.50389	2.67191	-4.65564
H	-5.10294	3.40034	-12.19359
H	-5.38993	2.99596	-10.48901
H	-3.99824	3.99357	-10.94413
H	-5.99331	7.03812	-11.90807
H	-5.50791	5.76178	-13.03627
H	-4.35967	6.35706	-11.82571
H	-7.48380	4.30990	-12.32587
H	-7.99370	5.63231	-11.26432
H	-7.77805	4.00974	-10.59434
C	-7.14668	8.65921	-5.23171
C	-8.02286	8.25379	-7.53108
C	-5.55038	8.46641	-7.13869
H	-7.87727	7.77822	-8.50682
H	-8.10724	9.33423	-7.69709
H	-8.97903	7.89903	-7.13048
H	-7.22273	9.74388	-5.37775
H	-6.34320	8.47381	-4.50948
H	-8.08509	8.31336	-4.78412
H	-5.59342	9.55362	-7.27396

H -5.32282 8.02542 -8.11493
H -4.71150 8.25096 -6.46714
78
Complex 2
C -4.47954 5.18226 -6.30847
Ta -5.97107 4.81434 -7.83124
C -4.81416 5.07204 -9.63982
Os -7.30579 2.67635 -7.62305
C -9.08155 1.52507 -8.32121
C -9.18030 1.72984 -6.88934
C -8.06236 1.08309 -6.26798
C -7.25694 0.47037 -7.30358
C -7.89493 0.75017 -8.56417
C -10.31899 2.39714 -6.18153
C -7.82346 0.95531 -4.79536
C -6.07545 -0.42340 -7.08561
C -7.45524 0.22653 -9.89640
C -10.10768 1.91706 -9.33868
C -7.10211 6.66129 -7.78634
H -6.37124 0.09548 -9.93705
H -7.73961 0.90233 -10.70676
H -7.91722 -0.74885 -10.09648
H -9.65481 2.07520 -10.32082
H -10.87563 1.13882 -9.44645
H -10.61427 2.84447 -9.05903
H -11.12231 1.67877 -5.97079
H -10.74535 3.20372 -6.78323
H -9.99928 2.83022 -5.23054
H -8.25420 1.79527 -4.24491
H -6.75542 0.92238 -4.56527
H -8.27646 0.03327 -4.40788
H -6.38915 -1.46627 -6.93962
H -5.39257 -0.39925 -7.93877
H -5.50479 -0.12330 -6.20277
H -7.91263 4.25224 -7.66583
H -6.11868 3.23855 -6.55896
H -6.31351 7.32085 -8.21083
H -7.10161 6.89116 -6.70312
C -8.45946 7.07372 -8.39715
C -4.42246 4.91086 -4.78989
H -4.38032 6.27804 -6.47215
H -3.58168 4.74954 -6.79240
H -5.54737 5.60171 -10.27905

C	-3.97117	4.11582	-10.51007
H	-4.14714	5.87651	-9.25781
C	-3.29059	5.74975	-4.16890
C	-4.13447	3.42833	-4.51894
C	-5.75370	5.30792	-4.13494
C	-3.09948	3.22243	-9.61515
C	-3.05799	4.94591	-11.43062
C	-4.87900	3.24087	-11.38386
H	-5.71423	5.16484	-3.04843
H	-6.57878	4.70355	-4.52769
H	-5.98401	6.36445	-4.31995
H	-3.20947	5.56614	-3.09061
H	-3.46802	6.82227	-4.31232
H	-2.32354	5.50577	-4.62365
H	-4.90754	2.78721	-4.95186
H	-4.09276	3.23644	-3.44032
H	-3.17030	3.13162	-4.94883
H	-2.46472	2.56252	-10.21860
H	-3.71985	2.59558	-8.96469
H	-2.43783	3.82479	-8.98032
H	-3.64671	5.60571	-12.07850
H	-2.45153	4.29787	-12.07474
H	-2.37276	5.57302	-10.84791
H	-4.27871	2.57237	-12.01224
H	-5.49690	3.85674	-12.04812
H	-5.54824	2.62767	-10.77419
C	-8.55960	8.60994	-8.41612
C	-9.61792	6.52058	-7.55713
C	-8.57033	6.55014	-9.83703
H	-9.58530	5.42879	-7.50452
H	-10.58106	6.81540	-7.99012
H	-9.57975	6.90881	-6.53231
H	-9.51994	8.93732	-8.83259
H	-7.76309	9.05064	-9.02748
H	-8.47419	9.02360	-7.40469
H	-9.51695	6.86142	-10.29473
H	-8.52513	5.45546	-9.86094
H	-7.75841	6.94101	-10.46270
H	-6.27331	3.10410	-8.89156

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Dimer complex with Re

C	-7.73388	0.59657	-6.72206
C	-8.62889	0.93546	-7.81153

C	-9.52567	1.95559	-7.34756
C	-9.19587	2.26495	-5.99439
C	-8.09068	1.43857	-5.59171
Re	-7.29943	2.68976	-7.29254
Ta	-5.49296	4.36232	-7.91112
C	-5.65223	6.36326	-7.10254
C	-6.85099	7.26383	-6.73150
C	-7.91576	7.21902	-7.83708
C	-8.72305	0.21657	-9.12363
C	-10.66036	2.54157	-8.13077
C	-9.92618	3.23192	-5.11301
C	-7.54267	1.32122	-4.20016
C	-6.80430	-0.57976	-6.68693
C	-3.46488	3.88308	-7.37399
C	-2.78656	2.96378	-6.33824
C	-3.29430	3.30868	-4.93052
C	-5.59336	4.69139	-10.06049
C	-4.45207	5.02491	-11.05138
C	-3.64320	3.75961	-11.37237
C	-6.35416	8.71318	-6.57532
C	-7.47105	6.81680	-5.40123
C	-1.26404	3.18915	-6.38790
C	-3.07296	1.48984	-6.65175
C	-3.51857	6.11022	-10.49579
C	-5.07446	5.54320	-12.36170
H	-5.98539	-0.42134	-5.98046
H	-6.35783	-0.76295	-7.66761
H	-7.33326	-1.49294	-6.38189
H	-7.75004	-0.17336	-9.43191
H	-9.41924	-0.63011	-9.05746
H	-9.07602	0.87904	-9.91803
H	-11.57698	1.95885	-7.97194
H	-10.44670	2.54175	-9.20211
H	-10.86486	3.57324	-7.83457
H	-10.36775	4.04963	-5.68806
H	-9.26324	3.67189	-4.36381
H	-10.73899	2.72401	-4.57771
H	-8.11655	0.59338	-3.61075
H	-6.50099	0.99093	-4.20926
H	-7.57774	2.27865	-3.67381
H	-7.80263	3.70445	-8.53307
H	-7.08951	4.28345	-6.64268
H	-5.05487	6.87554	-7.88718

H -4.96780 6.29898 -6.23485
H -3.05703 4.90724 -7.25718
H -3.14842 3.57639 -8.39524
H -6.22549 3.90422 -10.49018
H -6.26837 5.57330 -9.98894
H -2.79671 2.69028 -4.17411
H -4.37395 3.14425 -4.85021
H -3.09183 4.35862 -4.68516
H -0.74715 2.54682 -5.66484
H -1.00872 4.22928 -6.15327
H -0.86430 2.96129 -7.38288
H -4.14702 1.28406 -6.64878
H -2.59314 0.83891 -5.91149
H -2.68145 1.21583 -7.63882
H -2.73985 6.36607 -11.22388
H -3.01414 5.78318 -9.57948
H -4.07233 7.02913 -10.26913
H -5.74835 4.79751 -12.79795
H -4.30021 5.77342 -13.10418
H -5.65418 6.45709 -12.18834
H -2.86325 3.97379 -12.11256
H -4.28944 2.97551 -11.78258
H -3.15023 3.35193 -10.48362
H -7.84790 5.79183 -5.46306
H -8.30624 7.47184 -5.12665
H -6.73371 6.85877 -4.59043
H -7.17575 9.38362 -6.29556
H -5.92277 9.08663 -7.51164
H -5.58364 8.78500 -5.79896
H -8.74954 7.89213 -7.60384
H -8.31731 6.20668 -7.95459
H -7.49817 7.53523 -8.80097
H -6.36393 2.23341 -8.61104
H -5.67738 2.73874 -6.70679
80
CO2 reaction - Complex 1 - nucleophilic attack adduct
Ta -0.67822 0.90491 0.77723
C 0.57893 2.38443 1.70401
Ir 0.53507 -0.98277 -0.11634
C -2.15539 0.31223 2.24056
C -1.83631 2.07999 -0.62616
H 1.20971 0.45586 -0.41579
H 0.80904 -0.70282 1.45270

O	1.39248	3.62959	-3.67102
C	2.18743	2.78158	-3.78219
O	2.98488	1.93639	-3.90050
C	-2.76156	1.69450	-1.79593
C	-3.56200	2.92543	-2.25634
C	-2.06731	-0.41033	3.60339
C	-1.74636	-1.89335	3.39045
C	0.24978	-3.23736	-0.20270
C	-0.24250	-2.64243	-1.41765
C	0.87846	-2.04767	-2.09629
C	2.07323	-2.35188	-1.33295
C	1.68914	-3.07561	-0.18291
C	-0.53218	-4.12881	0.71182
C	-1.62571	-2.80341	-1.96814
C	0.88066	-1.48726	-3.48581
C	3.46694	-1.98092	-1.73370
C	2.60029	-3.60723	0.87955
C	2.07704	2.75160	1.66967
C	2.93754	1.57605	2.15080
C	2.48567	3.13881	0.24098
C	2.32135	3.95790	2.59511
C	-3.74427	0.60363	-1.34774
C	-1.91386	1.18396	-2.96579
C	-0.98069	0.22319	4.48365
C	-3.41989	-0.29258	4.32929
H	-0.01076	3.29983	1.48751
H	3.89973	-2.74199	-2.39638
H	4.12463	-1.88763	-0.86560
H	3.48954	-1.02894	-2.26993
H	2.11509	-3.60755	1.85892
H	3.51217	-3.01047	0.96271
H	2.89747	-4.64042	0.65785
H	-1.58584	-3.84345	0.74896
H	-0.14848	-4.10135	1.73456
H	-0.48214	-5.17151	0.36938
H	-1.70002	-3.73225	-2.55019
H	-1.89789	-1.97740	-2.62828
H	-2.37274	-2.85309	-1.17199
H	1.59111	-0.66357	-3.59083
H	-0.10426	-1.11598	-3.77512
H	1.16504	-2.26220	-4.21043
H	-2.43332	2.64709	0.12211
H	-1.08594	2.81266	-0.98253

H	-4.19810	3.30892	-1.44964
H	-4.21189	2.67879	-3.10494
H	-2.89338	3.73507	-2.56982
H	-1.26746	1.97949	-3.35422
H	-2.54600	0.83387	-3.79086
H	-1.27023	0.36443	-2.63363
H	-4.43778	0.34168	-2.15583
H	-3.21214	-0.30700	-1.05128
H	-4.34348	0.94040	-0.49307
H	-2.61926	1.30858	2.40863
H	-2.87252	-0.22973	1.59371
H	-1.65871	-2.41431	4.35140
H	-2.53962	-2.38460	2.81516
H	-0.81049	-2.01229	2.83793
H	-0.97112	-0.23431	5.48009
H	0.01450	0.08604	4.04584
H	-1.15194	1.29856	4.61655
H	-3.40035	-0.82320	5.28913
H	-3.67146	0.75532	4.53196
H	-4.22869	-0.72052	3.72597
H	0.29582	2.12625	2.74890
H	3.37915	4.24829	2.59331
H	1.73503	4.82796	2.27615
H	2.04067	3.72513	3.62896
H	3.53378	3.45969	0.20994
H	2.37158	2.28939	-0.44043
H	1.87209	3.96675	-0.13475
H	3.99961	1.84926	2.14405
H	2.67486	1.29207	3.17718
H	2.79930	0.69913	1.51254

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CO2 reaction - Complex 1 - nucleophilic attack TS

Ta	-0.22497	12.99215	8.67763
C	1.05056	14.45935	9.63125
Ir	0.87845	10.90625	7.88234
C	-1.42674	12.62039	10.47636
C	-1.95277	13.86721	7.64605
H	1.77985	12.07055	8.58468
H	-0.14274	11.02831	9.15214
O	0.73670	14.14601	6.65356
C	1.02141	13.29360	5.87452
O	1.34942	12.76990	4.88071
C	-2.99216	13.18012	6.73035

C	-4.11339	14.17818	6.39090
C	-1.21477	11.70975	11.71366
C	-1.58955	10.25916	11.38056
C	0.29479	8.86280	7.15987
C	0.90581	9.56118	6.06612
C	2.27298	9.84560	6.43863
C	2.51708	9.23886	7.72672
C	1.31144	8.64327	8.17265
C	-1.07804	8.26396	7.17127
C	0.30000	9.74808	4.71154
C	3.34879	10.38539	5.54687
C	3.83396	9.21829	8.43721
C	1.12550	7.85534	9.43072
C	2.39193	15.20157	9.43285
C	3.49998	14.25330	8.95803
C	2.22863	16.35192	8.42769
C	2.81803	15.80836	10.78470
C	-3.60846	11.96438	7.43635
C	-2.33010	12.71774	5.42607
C	0.23722	11.75847	12.20870
C	-2.13798	12.19482	12.84687
H	0.27118	15.22422	9.83966
H	4.44588	8.37343	8.09523
H	3.70683	9.11860	9.51809
H	4.40298	10.13261	8.25215
H	0.09969	7.92033	9.80097
H	1.78874	8.20217	10.22703
H	1.34286	6.79393	9.25416
H	-1.76330	8.82584	6.53296
H	-1.50209	8.25292	8.17871
H	-1.05579	7.22778	6.80811
H	0.51611	8.87174	4.08539
H	0.69726	10.62763	4.20573
H	-0.78588	9.85280	4.76685
H	4.07037	10.98552	6.10826
H	2.94240	11.01011	4.75192
H	3.90131	9.56018	5.07788
H	-2.49251	14.26793	8.52714
H	-1.56269	14.75996	7.12919
H	-4.62484	14.52095	7.29803
H	-4.86544	13.72270	5.73457
H	-3.71324	15.06086	5.87897
H	-1.88577	13.56321	4.88683

H -3.06569 12.25290 4.75814
H -1.54139 11.98594 5.63175
H -4.35305 11.47681 6.79537
H -2.83944 11.22488 7.68635
H -4.11363 12.25813 8.36424
H -1.52826 13.66500 10.83387
H -2.41875 12.38525 10.05495
H -1.45769 9.61434 12.25764
H -2.63716 10.18699 11.06496
H -0.96628 9.86300 10.57366
H 0.36649 11.12955 13.09802
H 0.92999 11.40235 11.43816
H 0.52681 12.77922 12.48562
H -2.04635 11.55624 13.73420
H -1.88995 13.21996 13.14623
H -3.18782 12.18280 12.53178
H 1.11815 13.88118 10.57659
H 3.74516 16.38551 10.68241
H 2.04636 16.48144 11.17635
H 2.99164 15.02583 11.53267
H 3.16773 16.90925 8.32900
H 1.94502 15.98869 7.43791
H 1.45917 17.05821 8.76232
H 4.45795 14.78372 8.89454
H 3.62615 13.41399 9.65112
H 3.27405 13.83742 7.97240
80
CO2 reaction - Complex 1 - nucleophilic attack product
Ta -0.71761 0.91530 0.32955
C 0.67666 2.20947 1.35362
Ir 0.69904 -1.31919 -0.51991
C -2.09630 0.30577 1.91350
C -2.13559 2.54996 -0.08568
H 1.24044 0.04678 0.17755
H -0.75375 -1.11978 0.25051
O -0.82153 0.82831 -1.65736
C -0.00229 -0.17891 -2.05255
O 0.25697 -0.31808 -3.23351
C -3.37213 2.60310 -1.02474
C -4.30662 3.72928 -0.54494
C -1.97275 -0.82012 2.96831
C -2.37420 -2.17092 2.36488
C 0.70347 -3.59901 -0.52821

C	1.15529	-3.13596	-1.80461
C	2.35319	-2.35906	-1.59276
C	2.65334	-2.40144	-0.17715
C	1.64797	-3.17338	0.48475
C	-0.45621	-4.51635	-0.29825
C	0.55954	-3.44597	-3.13928
C	3.18899	-1.76300	-2.68039
C	3.87233	-1.81524	0.46294
C	1.65384	-3.60715	1.91694
C	1.83101	3.08560	0.81099
C	2.96581	2.21852	0.25048
C	1.32500	4.02569	-0.29226
C	2.38627	3.93370	1.96983
C	-4.15549	1.28135	-1.00961
C	-2.94524	2.91616	-2.46718
C	-0.54261	-0.89358	3.52107
C	-2.93361	-0.50548	4.13028
H	-0.04920	2.87187	1.86604
H	4.70399	-2.52924	0.41480
H	3.69813	-1.57513	1.51428
H	4.18802	-0.90078	-0.04330
H	0.64096	-3.71904	2.31138
H	2.17643	-2.88902	2.55378
H	2.15969	-4.57547	2.02835
H	-1.25945	-4.33753	-1.01625
H	-0.87070	-4.40217	0.70549
H	-0.13621	-5.56046	-0.40685
H	1.17942	-4.18049	-3.66838
H	0.49508	-2.53899	-3.74617
H	-0.44531	-3.86378	-3.04304
H	3.90287	-1.03599	-2.28559
H	2.54950	-1.25229	-3.40505
H	3.75889	-2.54116	-3.20391
H	-2.45667	2.84407	0.92984
H	-1.44239	3.35176	-0.39768
H	-4.67564	3.53574	0.46989
H	-5.17744	3.82600	-1.20524
H	-3.78605	4.69404	-0.53473
H	-2.42795	3.88219	-2.51695
H	-3.82534	2.97869	-3.11892
H	-2.27312	2.15095	-2.85870
H	-5.02928	1.34344	-1.66952
H	-3.53316	0.45097	-1.35917

H -4.52415 1.04383 -0.00471
H -2.04220 1.27006 2.46160
H -3.11036 0.29333 1.49045
H -2.31640 -2.96423 3.12003
H -3.40402 -2.14233 1.99020
H -1.72237 -2.44255 1.53046
H -0.46140 -1.65833 4.30277
H 0.17353 -1.14192 2.72950
H -0.24538 0.06376 3.96707
H -2.89458 -1.29081 4.89512
H -2.67495 0.44423 4.61308
H -3.96864 -0.43147 3.77799
H 1.06455 1.54436 2.14889
H 3.20963 4.57232 1.62859
H 1.61114 4.58431 2.39107
H 2.76773 3.29933 2.77838
H 2.13535 4.67509 -0.64280
H 0.94955 3.46697 -1.15657
H 0.51845 4.67180 0.07301
H 3.80562 2.84917 -0.06372
H 3.33863 1.51782 1.00668
H 2.63789 1.63733 -0.61645
80
CO2 reaction - Complex 1 - C - O activation TS
Ta 0.36336 13.22613 8.92100
C -1.74552 13.56059 8.47902
C 0.59660 15.30224 9.63109
C 0.65639 12.73174 11.05820
Ir 0.95988 10.49674 7.50528
H -0.23393 11.58334 7.37983
H 1.07465 11.09783 9.01948
C 2.17686 8.63803 7.06952
C 3.66178 8.48511 7.18335
C 1.19888 8.29099 8.05962
C -0.11366 8.49815 7.50919
C 0.05938 8.95285 6.14378
C 1.46368 9.03856 5.87390
C -1.03978 9.16407 5.15039
C 2.10377 9.37575 4.56365
C 1.48901 7.69219 9.39848
C -1.40701 8.08548 8.14170
C 2.18469 11.91793 6.94897
O 3.12361 12.10903 6.26407

O	1.72246	13.37088	7.72398
C	-2.74010	13.13542	7.37472
C	-3.13375	11.66285	7.54642
C	0.44477	11.42523	11.86215
C	1.67779	10.52151	11.73986
C	0.97127	16.51176	8.72918
C	0.11577	16.56431	7.45543
C	-2.13063	13.36107	5.98384
C	-4.01487	13.99133	7.49857
C	0.26297	11.78761	13.34807
C	-0.81313	10.68502	11.38556
C	0.73799	17.80569	9.52982
C	2.45403	16.43891	8.33747
H	1.50499	6.59781	9.31733
H	0.72995	7.95975	10.13610
H	2.45962	8.00986	9.78479
H	-2.24594	8.67326	7.76253
H	-1.38240	8.20984	9.22690
H	-1.62258	7.02925	7.93307
H	-0.75045	9.88157	4.37960
H	-1.94752	9.53844	5.62793
H	-1.28885	8.21803	4.65310
H	2.42086	8.46031	4.04902
H	2.98132	10.01134	4.70206
H	1.41266	9.90684	3.90560
H	3.99283	8.55906	8.22190
H	4.18405	9.25869	6.61522
H	3.98384	7.50949	6.79704
H	-2.15110	13.24315	9.46566
H	-1.76014	14.66177	8.53149
H	-4.47011	13.88194	8.48986
H	-4.76228	13.69561	6.75220
H	-3.79347	15.05404	7.34653
H	-1.83811	14.40834	5.84971
H	-2.85515	13.11497	5.19808
H	-1.24156	12.74003	5.83275
H	-3.82786	11.35252	6.75602
H	-2.25366	11.01494	7.51033
H	-3.63325	11.50129	8.50938
H	1.64921	13.13402	11.31610
H	-0.05390	13.47999	11.46119
H	-0.99365	9.78529	11.98701
H	-1.70069	11.32328	11.47912

H -0.72214 10.38117 10.33694
H 1.53492 9.58857 12.29840
H 1.88868 10.26969 10.69712
H 2.56375 11.02155 12.14878
H 0.14758 10.88674 13.96370
H 1.12857 12.34349 13.72565
H -0.62658 12.41071 13.49780
H -0.33425 15.53806 10.17678
H 1.36606 15.23670 10.41749
H 1.02785 18.68864 8.94654
H -0.31790 17.91745 9.80497
H 1.32688 17.80726 10.45441
H 0.37032 17.44668 6.85597
H 0.28179 15.68102 6.82923
H -0.95327 16.62800 7.69154
H 2.72777 17.29479 7.70874
H 3.09273 16.46425 9.22895
H 2.67460 15.52133 7.78664
80
CO2 reaction - Complex 1 - C - O activation product
Ta -2.76707 5.50946 3.61092
C -4.82622 6.12644 3.36198
C -1.44400 7.09246 2.95498
C -2.37919 5.03020 5.68496
Ir 3.60150 -7.07974 -5.36843
H 2.38882 -6.07638 -5.55278
H 3.78253 -6.07532 -4.15612
C 4.66422 -9.13785 -5.40332
C 6.11975 -9.40804 -5.63079
C 4.02597 -8.95320 -4.14013
C 2.60380 -8.80485 -4.37037
C 2.37453 -8.95423 -5.79256
C 3.63820 -9.13849 -6.42998
C 1.03373 -9.00242 -6.45796
C 3.86671 -9.40948 -7.88520
C 4.69058 -9.00032 -2.79889
C 1.54410 -8.75080 -3.31138
C 4.57600 -5.85496 -6.34179
O 5.18342 -5.07367 -6.94847
O -2.47717 4.10705 2.65273
C -5.74357 5.72934 2.18384
C -6.00574 4.21735 2.20502
C -2.37170 3.60698 6.28577

C	-1.23444	2.78039	5.67040
C	-0.10927	6.88552	2.20386
C	-0.36908	6.26621	0.82409
C	-5.07582	6.11495	0.85520
C	-7.08385	6.47419	2.30724
C	-2.16402	3.69572	7.80729
C	-3.71606	2.92017	6.00174
C	0.58867	8.24426	2.02308
C	0.80445	5.95649	3.01783
H	4.69310	-10.02610	-2.40879
H	4.17227	-8.36902	-2.07397
H	5.72724	-8.66017	-2.85210
H	0.65303	-8.22733	-3.66548
H	1.89717	-8.22619	-2.42055
H	1.24083	-9.76097	-3.00738
H	1.08741	-8.66299	-7.49483
H	0.30820	-8.37109	-5.94054
H	0.64412	-10.02839	-6.45999
H	3.87340	-10.48915	-8.08280
H	4.82475	-9.00743	-8.22410
H	3.08437	-8.96347	-8.50359
H	6.73741	-8.96093	-4.84851
H	6.45890	-9.00663	-6.58901
H	6.31807	-10.48759	-5.63643
H	-5.29952	5.81797	4.31547
H	-4.77323	7.23258	3.42194
H	-7.58842	6.22578	3.24814
H	-7.75974	6.20907	1.48544
H	-6.93765	7.56055	2.28185
H	-4.84732	7.18745	0.82343
H	-5.73383	5.89234	0.00729
H	-4.14363	5.55836	0.70563
H	-6.66401	3.92733	1.37803
H	-5.07298	3.65260	2.11067
H	-6.49573	3.91718	3.13913
H	-1.39725	5.51140	5.86656
H	-3.10558	5.65602	6.24176
H	-3.75223	1.92579	6.46135
H	-4.55245	3.50264	6.40742
H	-3.87419	2.79261	4.92481
H	-1.21795	1.76939	6.09355
H	-1.35126	2.69406	4.58561
H	-0.26019	3.24051	5.87492

H -2.15140 2.69844 8.26316
H -1.21279 4.18441 8.04790
H -2.96661 4.27091 8.28398
H -2.10870 7.73842 2.34761
H -1.25313 7.67724 3.87764
H 1.53901 8.13242 1.48768
H -0.03884 8.93600 1.44929
H 0.80364 8.71107 2.99160
H 0.57265 6.11895 0.28282
H -0.86563 5.29515 0.91401
H -1.00296 6.92030 0.21338
H 1.77825 5.83930 2.52851
H 0.98575 6.35856 4.02233
H 0.36469 4.95759 3.11984
81
CO2 reaction - Complex 2 - nucleophilic attack adduct
C -0.50377 -3.38047 0.66813
C -1.86602 -2.97679 0.45550
C -2.04596 -2.66802 -0.94104
C -0.77361 -2.88418 -1.59546
C 0.17329 -3.32217 -0.61297
Os -0.54078 -1.27335 -0.06568
Ta 0.03607 1.13315 0.43639
C 2.04729 1.46917 1.15250
C 2.94567 0.72300 2.16512
C 2.13218 0.31026 3.40039
C -2.94588 -2.96867 1.49354
C -3.34342 -2.34753 -1.61672
C -0.53188 -2.78187 -3.06998
C 1.57621 -3.77584 -0.87451
C 0.07475 -3.91125 1.94319
C 3.41495 -0.23048 -2.93509
O 3.60032 0.80656 -2.43050
O 3.24276 -1.26468 -3.44847
C -1.23894 1.89934 2.05214
C -1.49189 3.37849 2.44959
C -2.07674 3.40023 3.87514
C -0.05337 2.51542 -1.21411
C -0.79390 2.54685 -2.56712
C -2.26473 2.14836 -2.37810
C -0.20725 4.21869 2.44702
C -2.52022 4.01008 1.50058
C -0.12130 1.58939 -3.55984

C	-0.73133	3.97336	-3.14339
C	3.56506	-0.52402	1.52011
C	4.08504	1.65955	2.60748
H	-0.03812	-5.00235	2.00351
H	-0.41987	-3.47732	2.81604
H	1.14096	-3.68418	2.02410
H	-3.70787	-2.21797	1.26964
H	-2.54399	-2.74742	2.48534
H	-3.44222	-3.94648	1.54145
H	-3.18996	-1.73346	-2.50804
H	-4.01359	-1.79587	-0.95224
H	-3.86402	-3.26290	-1.93040
H	-0.79602	-3.72300	-3.56988
H	0.51596	-2.56910	-3.29345
H	-1.13560	-1.98845	-3.51803
H	2.00610	-3.27476	-1.74461
H	1.60556	-4.85728	-1.06382
H	2.22767	-3.57370	-0.02010
H	-0.42227	3.36274	-0.59168
H	1.01634	2.74801	-1.38001
H	-2.34846	1.12800	-1.98983
H	-2.80636	2.20060	-3.33018
H	-2.76833	2.82171	-1.67452
H	-1.21984	4.69227	-2.47514
H	-1.23454	4.02763	-4.11632
H	0.30640	4.29779	-3.28390
H	0.91142	-0.70430	0.57926
H	-1.38012	-0.26966	0.97074
H	-0.44590	-0.01383	-1.18368
H	-0.63614	1.61290	-4.52746
H	0.92296	1.87667	-3.73139
H	-0.13731	0.56012	-3.18909
H	2.60603	1.60647	0.20783
H	1.87493	2.50097	1.52951
H	2.77134	-0.18232	4.14293
H	1.67831	1.18360	3.88447
H	1.33145	-0.38627	3.12766
H	4.21431	-1.04288	2.23508
H	2.79346	-1.22423	1.18762
H	4.17523	-0.25234	0.65089
H	4.75591	1.15706	3.31482
H	4.68431	1.98394	1.74895
H	3.69212	2.55677	3.10010

H -2.20807 1.38430 2.05733
H -0.67222 1.40447 2.87121
H -2.75206 5.03777 1.80424
H -2.15610 4.04407 0.46888
H -3.45659 3.44063 1.50338
H -0.41092 5.23876 2.79352
H 0.54922 3.78891 3.11376
H 0.23019 4.30013 1.44481
H -2.31009 4.42416 4.19285
H -3.00035 2.81306 3.92893
H -1.36962 2.97741 4.59799
81
CO2 reaction - Complex 2 - nucleophilic attack TS
C -0.24293 8.25252 8.92950
C -1.57441 8.72331 8.67943
C -1.72738 8.94538 7.26861
C -0.47201 8.60648 6.63491
C 0.44343 8.17917 7.65852
Os -0.12544 10.32472 8.04301
Ta 0.47867 12.75354 8.49958
C 2.32144 13.19187 9.55674
C 3.25991 12.36240 10.46049
C 2.45715 11.67171 11.57230
C -2.65207 8.88314 9.70751
C -2.99522 9.32087 6.56556
C -0.24375 8.53210 5.15684
C 1.79185 7.56493 7.44349
C 0.29949 7.78649 10.24521
C 2.16336 11.18175 6.44294
O 2.31242 12.31239 6.81766
O 2.43473 10.24115 5.78831
C -0.88915 13.51041 10.05695
C -1.18723 14.95520 10.55643
C -1.81703 14.85360 11.95919
C 0.17247 14.23919 6.96173
C -0.64860 14.29722 5.65591
C -2.10135 13.87166 5.91513
C 0.06324 15.83912 10.66025
C -2.20779 15.63558 9.63196
C -0.03401 13.38638 4.58447
C -0.64194 15.74437 5.12809
C 4.02162 11.30926 9.64481
C 4.28683 13.31056 11.10820

H	0.11164	6.71386	10.38718
H	-0.16217	8.31735	11.08155
H	1.37875	7.94440	10.31021
H	-3.35713	9.67009	9.42941
H	-2.23851	9.13632	10.68646
H	-3.21738	7.94868	9.81336
H	-2.79245	9.88098	5.64944
H	-3.63357	9.94474	7.19642
H	-3.57031	8.42716	6.28886
H	-0.52348	7.53973	4.77939
H	0.80153	8.71077	4.90222
H	-0.84777	9.27015	4.62299
H	2.25547	7.92663	6.52560
H	1.70219	6.47279	7.37351
H	2.47076	7.78853	8.27057
H	-0.23441	15.00286	7.65625
H	1.20811	14.56417	6.75289
H	-2.15070	12.84092	6.28174
H	-2.69228	13.93467	4.99359
H	-2.57807	14.51896	6.65968
H	-1.08538	16.43387	5.85604
H	-1.21642	15.82669	4.19742
H	0.37941	16.08503	4.92251
H	1.25479	10.79999	8.85602
H	-0.89495	11.36199	9.08540
H	-0.34928	11.54592	6.92514
H	-0.58362	13.48170	3.64052
H	1.01188	13.64990	4.39161
H	-0.06911	12.33572	4.88813
H	2.92323	13.69102	8.77682
H	1.90654	14.01453	10.17110
H	3.12092	11.10483	12.23615
H	1.92277	12.40534	12.18810
H	1.72016	10.97787	11.15428
H	4.72819	10.76656	10.28386
H	3.33882	10.57875	9.20057
H	4.59271	11.77522	8.83398
H	4.97579	12.76022	11.76049
H	4.88487	13.82352	10.34617
H	3.79100	14.07606	11.71637
H	-1.86493	13.02247	9.91581
H	-0.43822	12.94012	10.89750
H	-2.48263	16.62310	10.02115

H -1.81749 15.78029 8.62019
H -3.12453 15.03994 9.55367
H -0.20297 16.83667 11.02973
H 0.79446 15.41905 11.36015
H 0.55733 15.97299 9.69103
H -2.08800 15.84392 12.34583
H -2.72585 14.24155 11.93847
H -1.12099 14.39482 12.67104
81
CO2 reaction - Complex 2 - nucleophilic attack product
C -0.95650 -3.18920 -1.33686
C -0.03179 -3.58676 -0.30036
C -0.70840 -3.44358 0.96886
C -2.04164 -2.98194 0.71611
C -2.19451 -2.80640 -0.69725
Os -0.51140 -1.40475 -0.03838
Ta 0.19462 1.10428 0.26573
C -0.43796 2.60701 -1.18683
C -0.21757 2.72220 -2.71517
C 1.26342 2.93911 -3.05617
C 1.31106 -4.20371 -0.52974
C -0.16384 -3.84794 2.30451
C -3.10952 -2.77682 1.74596
C -3.46304 -2.42698 -1.39749
C -0.71931 -3.32616 -2.80704
C 1.13960 -0.75458 -1.25077
O 1.70122 -1.49978 -2.03458
O 1.54146 0.52136 -1.11916
C 1.86256 1.56172 1.59993
C 3.36025 1.17636 1.52817
C 4.03737 1.81955 0.30966
C -1.08776 2.19254 1.69477
C -1.38981 3.58944 2.28538
C -0.10135 4.31903 2.68850
C 4.04181 1.71576 2.80166
C 3.55133 -0.34574 1.48928
C -2.15662 4.45466 1.27416
C -2.27097 3.42740 3.53919
C -1.00899 3.95098 -3.20697
C -0.74822 1.48423 -3.45107
H -0.40908 -4.89710 2.51171
H -0.58244 -3.24151 3.11106
H 0.92240 -3.74583 2.33989

H	-3.82135	-2.00658	1.44085
H	-2.68980	-2.48173	2.71021
H	-3.67037	-3.70759	1.89740
H	-3.26082	-1.93934	-2.35300
H	-4.06656	-1.74371	-0.79555
H	-4.06699	-3.32081	-1.59743
H	-0.84329	-4.37141	-3.11662
H	0.29264	-3.00162	-3.05567
H	-1.42150	-2.71959	-3.38350
H	1.83866	-3.67244	-1.32431
H	1.20058	-5.25619	-0.81916
H	1.92725	-4.16620	0.37151
H	-1.51697	2.71625	-0.99168
H	0.01415	3.49741	-0.70434
H	-0.17157	0.59020	-3.20167
H	-0.68831	1.62661	-4.53677
H	-1.79989	1.29865	-3.19894
H	-2.08298	3.83615	-3.01673
H	-0.87347	4.09881	-4.28537
H	-0.67502	4.86440	-2.70072
H	0.67324	-1.09186	1.05504
H	-1.23308	-0.37466	1.02952
H	-1.20271	-0.28351	-1.02393
H	1.38876	3.08365	-4.13596
H	1.64967	3.83681	-2.55717
H	1.87264	2.08655	-2.75150
H	1.79531	2.66452	1.61886
H	1.47973	1.25295	2.58890
H	4.61633	-0.60077	1.54759
H	3.04910	-0.82671	2.33796
H	3.15815	-0.77856	0.56626
H	5.11052	1.59443	0.30510
H	3.60718	1.45346	-0.62460
H	3.93005	2.91121	0.33652
H	5.11569	1.49259	2.79572
H	3.92687	2.80314	2.88129
H	3.61134	1.26606	3.70467
H	-2.05044	1.78786	1.30857
H	-0.85080	1.51240	2.54464
H	-2.42619	5.41750	1.72418
H	-1.56358	4.65921	0.37929
H	-3.08596	3.96524	0.95846
H	-0.33619	5.27988	3.16221

H 0.48723 3.73168 3.40154
H 0.52817 4.52437 1.81605
H -2.52850 4.40160 3.97340
H -3.20711 2.91040 3.29767
H -1.75506 2.84328 4.31053
81
CO2 reaction - Complex 2 - C - O activation TS
C -0.89912 8.42310 7.05791
C 0.01584 8.02898 8.11099
C -0.63314 8.28270 9.37343
C -1.93652 8.82812 9.10863
C -2.10252 8.91301 7.68347
Os -0.33949 10.24130 8.24938
Ta 0.51600 12.90206 8.46094
C -0.28966 14.45375 7.12679
C -0.11079 14.55944 5.59429
C 1.34641 14.86753 5.22525
C 1.32508 7.33063 7.91154
C -0.09919 7.92464 10.72588
C -2.98424 9.13523 10.13393
C -3.35788 9.32359 6.97766
C -0.68912 8.19919 5.59246
C 1.20893 10.67411 7.07861
O 1.94698 10.23068 6.28967
O 1.79929 12.53026 7.22894
C 2.06837 13.42174 9.93040
C 3.55906 13.01229 9.90694
C 4.29484 13.67338 8.73347
C -0.84682 13.91833 9.97277
C -1.24639 15.23286 10.67593
C -0.01326 15.95155 11.24284
C 4.20601 13.49273 11.22097
C 3.71909 11.48791 9.82157
C -1.96293 16.18009 9.70190
C -2.21061 14.93249 11.84047
C -0.99697 15.71436 5.08775
C -0.55675 13.26744 4.89484
H -0.42631 6.91466 11.00181
H -0.45575 8.61418 11.49378
H 0.99196 7.94027 10.74319
H -3.66151 9.92138 9.79419
H -2.54191 9.46187 11.07718
H -3.58470 8.23988 10.33695

H	-3.14756	9.72209	5.98353
H	-3.90073	10.08866	7.53645
H	-4.02107	8.45773	6.86109
H	-0.95294	7.16915	5.32369
H	0.35230	8.36712	5.30948
H	-1.30713	8.87165	4.99391
H	1.84630	7.70866	7.02984
H	1.16435	6.25412	7.77728
H	1.98541	7.46794	8.77031
H	-1.36586	14.50342	7.35717
H	0.12795	15.36636	7.59055
H	0.09637	12.43339	5.16571
H	-0.52275	13.37958	3.80401
H	-1.58783	13.00793	5.16902
H	-2.05675	15.52427	5.29759
H	-0.88853	15.85186	4.00439
H	-0.72575	16.65906	5.57337
H	0.75661	10.56141	9.42011
H	-1.00139	11.35232	9.24837
H	-1.08534	11.35332	7.30877
H	1.45916	14.96472	4.13823
H	1.66777	15.81433	5.67716
H	2.01185	14.07669	5.57746
H	2.01095	14.52341	9.93669
H	1.64394	13.12693	10.90508
H	4.77395	11.19924	9.90850
H	3.17181	10.98898	10.63224
H	3.34764	11.10948	8.86566
H	5.35940	13.40832	8.74413
H	3.86564	13.36052	7.77908
H	4.22564	14.76640	8.80053
H	5.27563	13.24872	11.24843
H	4.10744	14.57885	11.33300
H	3.73249	13.02341	12.09224
H	-1.77611	13.51045	9.50768
H	-0.60959	13.18089	10.77418
H	-2.28516	17.09207	10.21946
H	-1.31343	16.47623	8.87413
H	-2.85614	15.70783	9.27479
H	-0.30839	16.85476	11.79153
H	0.54358	15.30806	11.93275
H	0.66944	16.25519	10.44250
H	-2.52679	15.85180	12.35068

H -3.11227 14.42362 11.47897
H -1.73584 14.28278 12.58555
81
CO2 reaction - Complex 2 - C - O activation product
C -0.61647 -4.55011 -0.34673
C -1.76758 -4.84521 0.47518
C -2.56851 -3.64984 0.54749
C -1.92232 -2.62004 -0.21754
C -0.71905 -3.17749 -0.76990
Os -0.53301 -3.25241 1.51921
Ta 0.59231 2.55140 -0.04692
C -0.39654 4.26551 -0.92793
C -0.92847 4.33268 -2.37740
C 0.20871 4.02177 -3.36191
C -2.14556 -6.19488 1.00677
C -3.91529 -3.53530 1.19452
C -2.46956 -1.25572 -0.50724
C 0.19558 -2.47926 -1.72967
C 0.40652 -5.54080 -0.81396
C 0.56971 -4.17533 2.69626
O 1.25665 -4.78022 3.41646
O 0.31441 1.18706 -1.06688
C 2.72249 2.91464 0.04525
C 3.82869 1.88580 -0.27793
C 3.76780 1.49485 -1.76054
C -0.11260 1.95012 1.91301
C -0.67472 2.94143 2.95809
C 0.16887 4.22620 2.98976
C 5.20339 2.50774 0.02186
C 3.64407 0.63365 0.59207
C -2.13127 3.29065 2.62006
C -0.63586 2.28871 4.35087
C -1.46743 5.74549 -2.65945
C -2.06176 3.31524 -2.56829
H -4.70401 -3.77456 0.47009
H -4.09709 -2.52405 1.56482
H -4.01588 -4.22197 2.03767
H -1.66980 -0.53309 -0.68454
H -3.08013 -0.88709 0.32078
H -3.10474 -1.28024 -1.40236
H 1.20973 -2.88154 -1.67948
H 0.24744 -1.40617 -1.53224
H -0.16745 -2.61623 -2.75641

H	0.08138	-6.02426	-1.74417
H	0.57270	-6.32585	-0.07244
H	1.36881	-5.06096	-1.00646
H	-1.26203	-6.79214	1.24414
H	-2.73707	-6.75231	0.26905
H	-2.74088	-6.11360	1.91923
H	-1.22807	4.47619	-0.22610
H	0.31896	5.09663	-0.76645
H	-1.70888	2.29586	-2.38296
H	-2.45391	3.35920	-3.59087
H	-2.89456	3.52133	-1.88482
H	-2.27879	6.00382	-1.96910
H	-1.86006	5.82164	-3.68047
H	-0.67928	6.49936	-2.54762
H	-1.40586	-3.05950	2.87040
H	-0.41968	-1.79856	2.23341
H	0.84233	-2.43877	1.25831
H	-0.13724	4.10542	-4.39871
H	1.04428	4.72118	-3.23511
H	0.58557	3.00324	-3.21679
H	2.84541	3.80178	-0.60775
H	2.87405	3.30120	1.07271
H	4.45223	-0.08607	0.41789
H	3.65305	0.88646	1.65935
H	2.69818	0.12812	0.36808
H	4.54864	0.76371	-1.99975
H	2.79844	1.05395	-2.01250
H	3.92458	2.36908	-2.40409
H	6.01280	1.80424	-0.20668
H	5.36680	3.41131	-0.57691
H	5.29051	2.78486	1.07896
H	-0.75833	1.06482	1.84112
H	0.85619	1.55096	2.28576
H	-2.55329	3.97529	3.36476
H	-2.21641	3.77431	1.64040
H	-2.75478	2.38998	2.60138
H	-0.19331	4.92129	3.75599
H	1.21919	4.00603	3.21576
H	0.12914	4.76478	2.03207
H	-1.05387	2.95712	5.11363
H	-1.21350	1.35828	4.36306
H	0.39154	2.04494	4.64386

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