Electronic Supplementary Information for Dalton Transactions

Supporting Information

A Tungsten-Mediated Closed Cycle of Reactivity for the Reduction of CO_2 to CO

Upul Jayarathne, Perumalreddy Chandrasekaran, Heiko Jacobsen, Joel T. Mague, and James P. Donahue*

Crystallography

Orange, block-shaped crystals of *trans*-[$W^{II}Cl_2(PMePh_2)_4$] (**1**) were obtained by diffusion of hexanes vapor into a toluene solution. Owing to their sensitivity to H_2O and O_2, these crystals were transferred to degassed paratone oil in the nitrogen box prior to screening under a microscope for a suitable specimen for X-ray diffraction. Block-shaped orange-red crystals of [$WCl_4(PMe_3)_2$] (**4a**) were obtained by cooling a pentane solution to –30 °C for 24 h. Crystals of **6** deposited from the reaction mixture upon standing undisturbed 12-18 h at ambient temperature. All other crystals were obtained by diffusion of alkane or ether vapors into benzene, THF, CH_2Cl_2 or 1,2-dichloroethane solutions.

Data were collected with a Bruker APEX CCD diffractometer equipped with a Kryoflex attachment supplying a nitrogen stream at 100 or 200 K. Full spheres of data were obtained by collecting either three sets of 606 frames in ω (0.3º/scan) with φ held constant at 0, 120, and then 240º (for **4c** and **4e**), or a combination of three sets of 400 scans in ω (0.5°/scan) at φ = 0, 90 and 180° and two sets of 800 scans in φ (0.45°/scan) at ω = –30 and 210° (for **1**, **2**, **3c**, **3e**, **4b**, **4a**, both polymorphs of [Cp^*_2Co][**4c**], [Cp^*_2Co][**5c**] and **6**). Data were collected under control of either the *SMART* software package[1] or the *APEX2* program suite[2]. The raw data were reduced to F^2 values using the SAINT+ software[3], and a global refinement of unit cell parameters was

*Department of Chemistry, Tulane University, 6400 Freret Street, New Orleans, LA 70118-5698.

performed using 2223–9958 selected reflections from the full data set. For $[W^{II}Cl_2(PMePh_2)_4]$, a face-indexed absorption correction was applied, while data for the remaining compounds were corrected for absorption on the basis of multiple measurements of symmetry equivalent reflections with the use of either *SADABS*[4] (for **3ce**, **4abce**, both polymorphs of $[Cp^*_2Co][\mathbf{4c}]$, $[Cp^*_2Co][\mathbf{5c}]$, **6**) or *TWINABS*[5] (for **2**). Structure solutions were obtained by direct methods for **2**, **3c, 4abc** and the $P2_1/n$ polymorph of $[Cp^*_2Co][\mathbf{4c}]$, while Patterson methods were employed for **1**, **3e**, **4e**, the $C2/c$ polymorph of$[Cp^*_2Co][\mathbf{4c}]$, $[Cp^*_2Co][\mathbf{5c}]$ and **6**. Refinements were accomplished by full-matrix least-squares procedures using the SHELXTL software suite[6,7]. In some instances, phenyl groups on the phosphine ligands displayed positional disorder; which was generally treated with a split atom model with distance and angle constraints. Interstitial solvent molecules were refined where possible, sometimes with partial site occupancies and appropriate constraints. Where refinement of interstitial solvent was not feasible, residual electron density was removed with the SQUEEZE option in PLATON. All hydrogen atoms were added in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the carbon atoms to which they were attached.

Other Physical Methods

UV-vis spectra (molar absorptivities reported in M^{-1} cm^{-1}) were obtained at ambient temperature with a Hewlett-Packard 8452A diode array spectrometer, while IR spectra were taken as pressed KBr pellets with a Thermo Nicolet Nexus 670 FTIR instrument in absorption mode. All NMR spectra were recorded at 25 °C either with a Varian Unity Inova spectrometer operating at 400 and 161.8 MHz for ^1H and ^{31}P, respectively, or with a Bruker AVANCE 300 spectrometer operating at 121.5 MHz for ^{31}P. Spectra were referenced to the solvent residual for

^{1}H and to external 85% H_3PO_4 for ^{31}P. Electrochemical measurements were made with a CHI620C electroanalyzer workstation using a Ag/AgCl reference electrode, a platinum disk working electrode, Pt wire as auxiliary electrode, and $[Bu_4N][PF_6]$ as the supporting electrolyte. The Cp_2Fe^+/Cp_2Fe couple occurred at +0.54 mV (by CV) in 0.10 *M* $[Bu_4N][PF_6]$ in CH_2Cl_2. Elemental analyses were performed by Midwest Microlab, LLC of Indianapolis, IN.

Table S1 Selected Bond Lengths (Å) and Angles (deg.) for $[Cp^*_2Co][W^{IV}Cl_5(PMePh_2)]$, $[Cp^*_2Co]$[**5c**]

W(1)–Cl(1)	2.370(1)	Cl(1)–W(1)–Cl(2)	89.21(5)	Cl(2)–W(1)–P(1)	89.53(4)
W(1)–C1(2)	2.340(1)	Cl(1)–W(1)–Cl(3)	175.86(4)	Cl(3)–W(1)–Cl(4)	91.91(5)
W(1)–Cl(3)	2.348(1)	Cl(1)–W(1)–Cl(4)	88.33(5)	Cl(3)–W(1)–Cl(5)	92.27(4)
W(1)–Cl(4)	2.346(1)	Cl(1)–W(1)–Cl(5)	91.86(4)	Cl(3)–W(1)–P(1)	87.03(4)
W(1)–Cl(5)	2.412(1)	Cl(1)–W(1)–P(1)	88.84(4)	Cl(4)–W(1)–Cl(5)	90.27(4)
W(1)–P(1)	2.563(1)	Cl(2)–W(1)–Cl(3)	90.45(5)	Cl(4)–W(1)–P(1)	89.17(4)
		Cl(2)–W(1)–Cl(4)	177.24(5)	Cl(5)–W(1)–P(1)	179.09(4)
		Cl(2)–W(1)–Cl(5)	91.06(4)		

Table S2 Selected Bond Lengths (Å) and Angles (deg.) for $[W^{IV}(O)Cl_2(dppe)(PMePh_2)_2]$, Compound **3e**

W(1)–O(1)	1.707(2)	O(1)–W(1)–Cl(1)	100.40(7)	Cl(1)–W(1)–P(3)	89.37(3)
W(1)–Cl(1)	2.4474(7)	O(1)–W(1)–Cl(2)	173.59(7)	Cl(2)–W(1)–P(1)	77.48(2)
W(1)–Cl(2)	2.4910(7)	O(1)–W(1)–P(1)	96.11(7)	Cl(2)–W(1)–P(2)	82.17(3)
W(1)–P(1)	2.4729(7)	O(1)–W(1)–P(2)	96.91(7)	Cl(2)–W(1)–P(3)	86.36(3)
W(1)–P(2)	2.5140(7)	O(1)–W(1)–P(3)	94.36(7)	P(1)–W(1)–P(2)	80.08(2)
W(1)–P(3)	2.5191(8)	Cl(1)–W(1)–Cl(2)	85.97(3)	P(1)–W(1)–P(3)	96.38(2)
		Cl(1)–W(1)–P(1)	162.05(2)	P(2)–W(1)–P(3)	168.47(2)
		Cl(1)–W(1)–P(2)	90.94(3)		

Table S3 Selected Bond Lengths (Å) and Angles (deg.) for $[W^{IV}Cl_4(dppe)]$, Compound **4e**

W(1)–Cl(1)	2.268(2)	Cl(1)–W(1)–Cl(2)	98.31(8)	Cl(2)–W(1)–P(2)	92.20(8)
W(1)–Cl(2)	2.330(2)	Cl(1)–W(1)–Cl(3)	93.64(8)	Cl(3)–W(1)–Cl(4)	94.74(7)
W(1)–Cl(3)	2.384(2)	Cl(1)–W(1)–Cl(4)	163.55(7)	Cl(3)–W(1)–P(1)	95.10(7)
W(1)–Cl(4)	2.331(2)	Cl(1)–W(1)–P(1)	86.95(7)	Cl(3)–W(1)–P(2)	175.45(6)
W(1)–P(1)	2.607(2)	Cl(1)–W(1)–P(2)	84.76(8)	Cl(4)–W(1)–P(1)	78.23(6)
W(1)–P(2)	2.539(2)	Cl(2)–W(1)–Cl(3)	92.25(8)	Cl(4)–W(1)–P(2)	85.80(6)
		Cl(2)–W(1)–Cl(4)	95.48(8)	P(1)–W(1)–P(2)	80.57(6)
		Cl(2)–W(1)–P(1)	170.69(8)		

Table S4 Selected Bond Lengths (Å) and Angles (deg.) for $[W^{IV}Cl_4(PMe_2Ph)_2]$, Compound **4b**

W(1)–Cl(1)	2.3486(5)	Cl(1)–W(1)–Cl(1A)	180.0	Cl(2)–W(1)–P(1A)	89.81(2)
W(1)–Cl(2)	2.3411(5)	Cl(1)–W(1)–Cl(2)	90.08(2)	Cl(1A)–W(1)–Cl(2A)	90.08(2)
W(1)–P(1)	2.5510(5)	Cl(1)–W(1)–Cl(2A)	89.92(2)	Cl(1A)–W(1)–P(1)	85.76(2)
		Cl(1)–W(1)–P(1)	94.24(2)	Cl(1A)–W(1)–P(1A)	94.24(2)
		Cl(1)–W(1)–P(1A)	85.76(2)	Cl(2A)–W(1)–P(1)	89.81(2)
		Cl(2)–W(1)–Cl(1A)	89.92(2)	Cl(2A)–W(1)–P(1A)	90.19(2)
		Cl(2)–W(1)–Cl(2A)	180.0	P(1)–W(1)–P(1A)	180.0
		Cl(2)–W(1)–P(1)	90.19(2)		

Table S5 Selected Bond Lengths (Å) and Angles (deg.) for $[W^{IV}Cl_4(PMe_3)_2]$, Compound **4a**

W(1)–Cl(1)	2.3140(8)	Cl(1)–W(1)–Cl(1A)	180.0	Cl(2)–W(1)–P(1A)	92.49(3)
W(1)–Cl(2)	2.3581(6)	Cl(1)–W(1)–Cl(2)	89.72(2)	Cl(1A)–W(1)–Cl(2A)	89.72(2)
W(1)–P(1)	2.5424(7)	Cl(1)–W(1)–Cl(2A)	90.28(2)	Cl(1A)–W(1)–P(1)	88.51(2)
		Cl(1)–W(1)–P(1)	91.49(2)	Cl(1A)–W(1)–P(1A)	91.49(2)
		Cl(1)–W(1)–P(1A)	88.51(2)	Cl(2A)–W(1)–P(1)	92.49(3)
		Cl(2)–W(1)–Cl(1A)	90.28(2)	Cl(2A)–W(1)–P(1A)	87.51(3)
		Cl(2)–W(1)–Cl(2A)	180.0	P(1)–W(1)–P(1A)	180.0
		Cl(2)–W(1)–P(1)	87.51(3)		

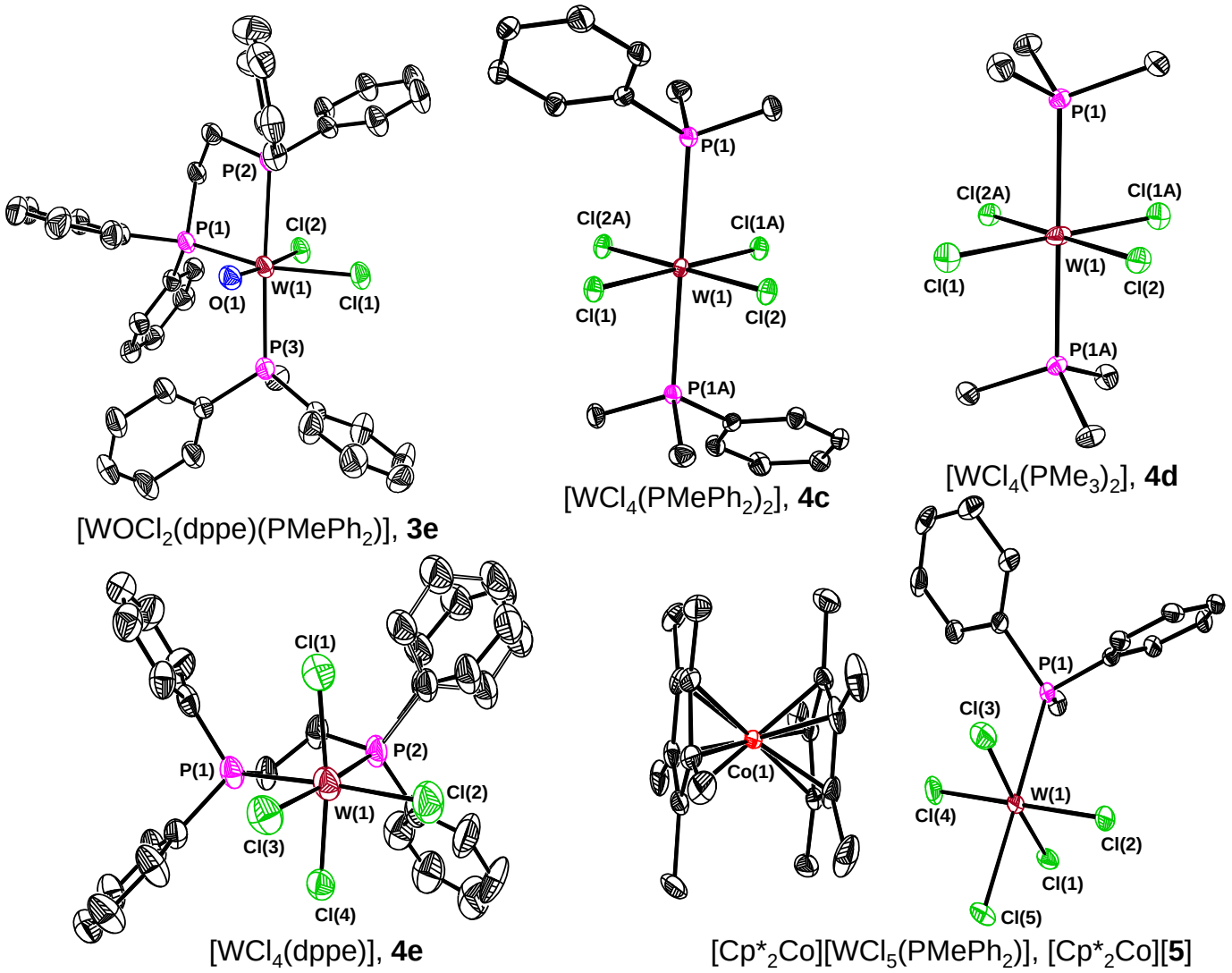

Fig. S1 Thermal ellipsoid plots of **3e**, **4c**, **4d**, **4e** and [Cp*$_2$Co][**5**] at the 50% probability level. Hydrogen atoms are omitted for clarity.

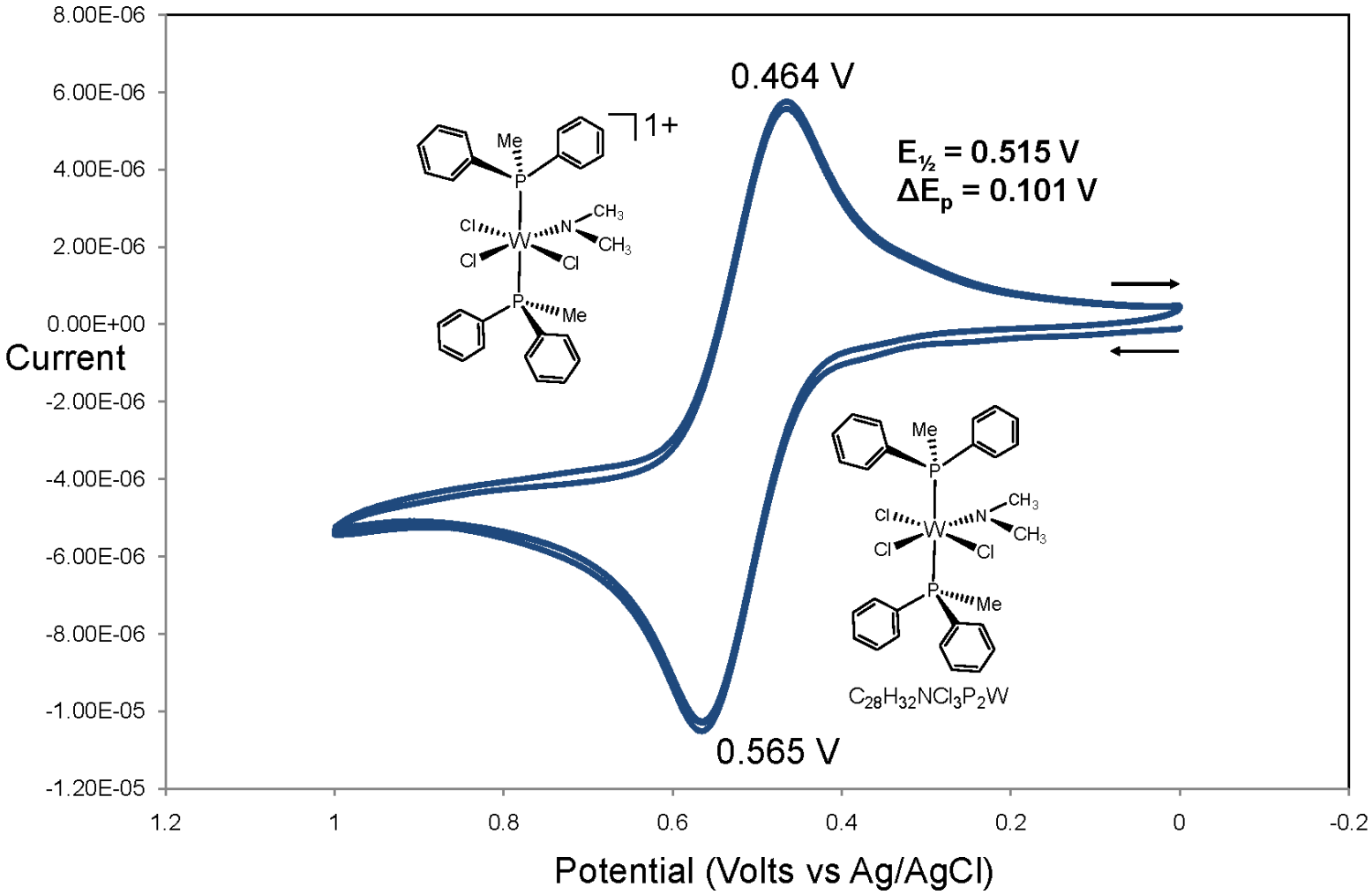

Fig. S2 Cyclic voltammogram of $[WCl_3(NMe_2)(PMePh_{2)2}]$ in CH_2Cl_2 with $[Bu_4N][PF_6]$ supporting electrolyte and scan speed 0.100 V/sec. The wave displayed corresponds to the $[WCl_3(NMe_2)(PMePh_2)_2] - e^- \rightarrow [WCl_3(NMe_2)(PMePh_2)_2]^{1+}$ oxidation.

	20 mV/sec	40 mV/sec	60 mV/sec	80 mV/sec	100 mV/sec	120 mV/sec	140 mV/sec	200 mV/sec	300 mV/sec	400 mV/sec	500 mV/sec
$E_{p,f}$	-0.513	-0.508	-0.519	-0.518	-0.525	-0.531	-0.531	-0.542	-0.551	-0.562	-0.562
i_{pf}	6.348×10^{-6}	7.858×10^{-6}	9.379×10^{-6}	9.884×10^{-6}	1.045×10^{-5}	1.379×10^{-5}	1.476×10^{-5}	1.741×10^{-5}	2.081×10^{-5}	2.327×10^{-5}	2.521×10^{-5}
E_{pr}	-0.41	-0.403	-0.401	-0.394	-0.391	-0.395	-0.393	-0.39	-0.382	-0.376	-0.374
i_{pr}	6.993×10^{-6}	9.203×10^{-6}	1.057×10^{-5}	1.097×10^{-5}	1.213×10^{-5}	1.354×10^{-5}	1.342×10^{-5}	1.541×10^{-5}	1.781×10^{-5}	1.901×10^{-5}	2.024×10^{-5}

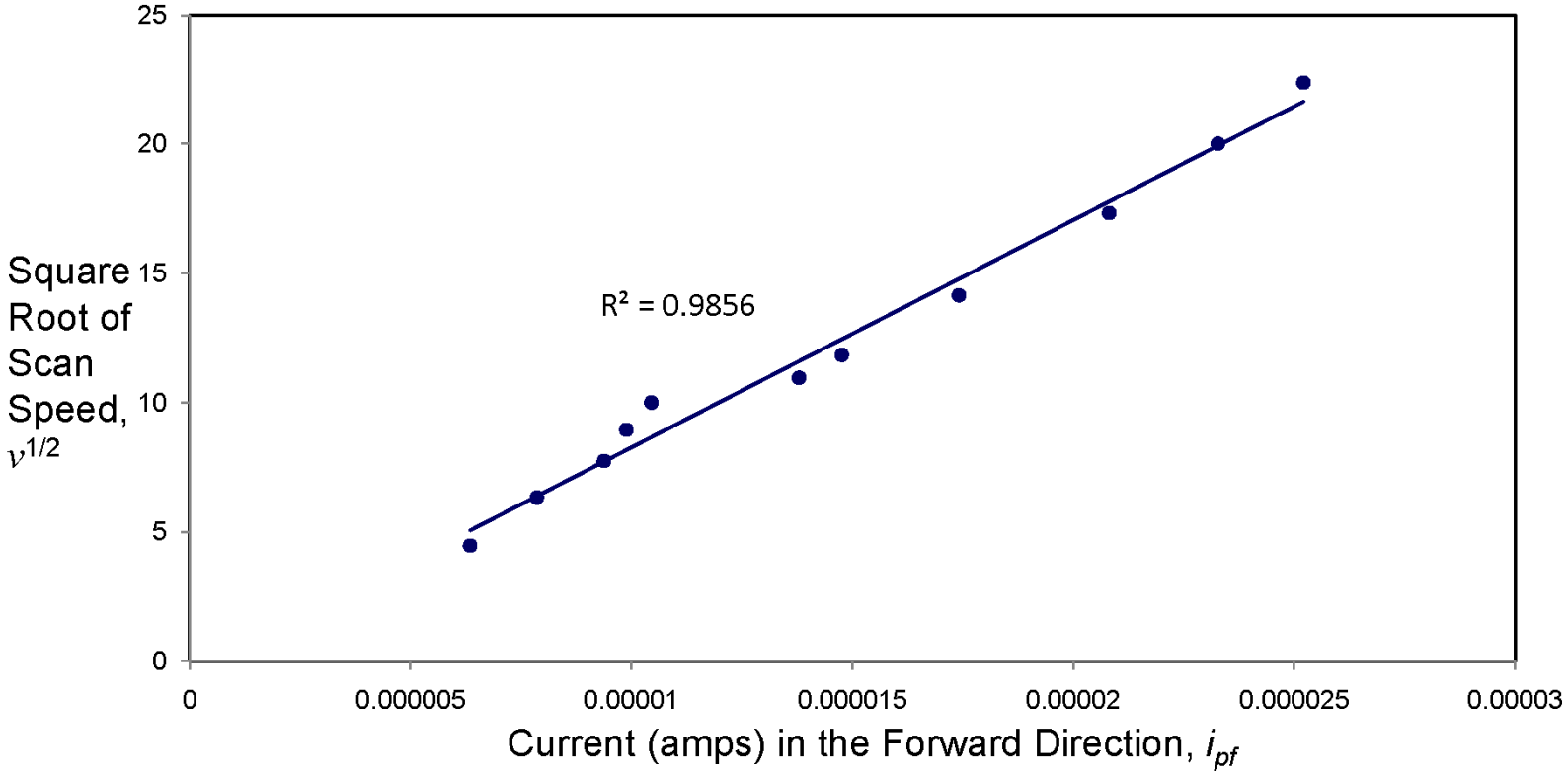

Fig.S3 Plot of i_{pf} vs square root of scan speed for the cyclic voltammetry of $[WCl_4(PMePh_2)_2]$. The wave in question corresponds to the $[WCl_4(PMePh_2)_2] + e^- \rightarrow [WCl_4(PMePh_2]^{1-}$ reduction.

Supporting Online Material - Computational Details

Geometries have been optimized and final energies have been evaluated in DFT calculations, using the PBE exchange-correlation functional as prescribed by Perdew, Burke and Ernzerhof.[8] For all calculations, tungsten was modeled by a small-core, quasi-relativistic effective core potential with an associated (8s7p6d)/[6s5p3d] valence basis set contracted according to a (311111/22111/411) scheme.[9] All main group elements except for those that are part of a phenyl group have been described by contracted Gaussian basis sets of triple zeta valence quality augmented by polarization functions (TZVP).[10] For phenyl groups, the C atom bonded to phosphorus has been described by a TZVP basis, whereas the remaining atoms were described by contracted Gaussian split-valence basis sets (SV).[11] The nature of stationary points located on the potential energy surface has been checked by harmonic frequency calculations, and all molecules considered in this work possess a harmonic spectrum without any imaginary frequencies. Enthalpies H have been evaluated at zero K from total energies E and zero-point energy correction terms (ZPE). The calculated frequency data provide thermodynamic corrections to calculate free energies G at 298 K. The *Gaussian 03* suite of programs constitutes the underlying computational engine of the present work.[12]

Optimized Geometries, Convergence Criteria, Final Energies, Thermodynamic Data

W(PH3) a

Route: #P PBEPBE/GenECP/Auto GFInput Opt(CalcFC) Nosymmetry Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.029871	0.001673	0.000965
Cl	2.451111	0.169922	0.020971
Cl	-2.421093	-0.159417	-0.020398
P	-0.162347	2.213696	1.075405
H	1.042539	2.923118	1.383417
H	-0.855894	3.295733	0.432749
H	-0.801726	2.372112	2.352673
P	0.149214	-2.214541	-1.075854
H	-0.442657	-2.449528	-2.364077
H	1.439991	-2.763868	-1.363419
H	-0.411057	-3.378336	-0.446191
P	0.048218	-1.075027	2.220183
H	1.309920	-1.279902	2.865525
H	-0.638467	-0.487836	3.337427
H	-0.473479	-2.400405	2.411822
P	-0.061085	1.073641	-2.218542
H	-0.646306	0.401279	-3.345487
H	-0.751873	2.317845	-2.419430
H	1.172041	1.445132	-2.844282

Energy E(UPBE-PBE)	-2359.26418650 a.u.
	-6194248.12 kJ/mol
SCF Convergence:	0.8914D-08
<S**2>:	2.0094
Charge:	0.0000
Maximum Force:	0.000003
ZPE-correction:	0.107927 a.u.
	283.36 kJ/mol
Energy (298K):	-2359.138991 a.u.
	-6193919.42 kJ/mol
Enthalpy (298K):	-2359.138047 a.u.
	-6193916.94 kJ/mol
Free Energy (298K):	-2359.204369 a.u.
	-6194091.07 kJ/mol
Lowest Frequency	67.0091 cm-1

W(PH3) b

Route: #P PBEPBE/GenECP/Auto GFInput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

W	-0.000408	-0.013007	-0.293931
O	-0.001894	-0.021057	-2.030631
Cl	0.001457	0.602531	2.145561
Cl	0.006926	-2.393382	0.265557
P	-2.497728	-0.168970	0.025855
H	-3.183532	0.833612	0.769255
H	-3.291119	-0.188084	-1.159110
H	-2.980995	-1.345125	0.670279
P	2.498097	-0.157242	0.022641
H	2.984308	-1.324222	0.681089
H	3.288615	-0.190832	-1.163932
H	3.184508	0.855973	0.751019
C	-0.005824	2.040339	-0.295724
O	-0.008694	3.198160	-0.311846

Energy E(RPBE-PBE)	-1861.78057367 a.u.
	-4888104.90 kJ/mol
SCF Convergence:	0.3475D-08
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000003
ZPE-correction:	0.066510 a.u.
	174.62 kJ/mol
Energy (298K):	-1861.699630 a.u.
	-4887892.38 kJ/mol
Enthalpy (298K):	-1861.698685 a.u.
	-4887889.90 kJ/mol
Free Energy (298K):	-1861.757556 a.u.
	-4888044.46 kJ/mol
Lowest Frequency	55.8431 cm-1

W(PH3) c

Route: #P PBEPBE/GenECP/Auto GFInput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.000132	-0.064617	-0.299810
O	0.000588	-0.041040	-2.033167
Cl	-0.000799	0.542870	2.176054
Cl	-0.000385	-2.447483	0.258581
P	0.000232	2.418757	-0.243447
H	1.068933	3.141411	0.380015

H	0.000772	3.090832	-1.507351
H	-1.069075	3.141387	0.379043
P	-2.470968	-0.214834	0.029191
H	-2.960729	-1.366034	0.717946
H	-3.196813	0.800192	0.725266
H	-3.258494	-0.291577	-1.158541
P	2.471049	-0.215237	0.030129
H	2.961148	-1.367858	0.716340
H	3.259185	-0.288692	-1.157399
H	3.196007	0.798446	0.729043

Energy E(RPBE-PBE)	-2091.50611765 a.u.
	-5491249.31 kJ/mol
SCF Convergence:	0.3285D-08
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000004
ZPE-correction:	0.085375 a.u.
	224.15 kJ/mol
Energy (298K):	-2091.405740 a.u.
	-5490985.77 kJ/mol
Enthalpy (298K):	-2091.404796 a.u.
	-5490983.29 kJ/mol
Free Energy (298K):	-2091.464234 a.u.
	-5491139.35 kJ/mol
Lowest Frequency	61.8091 cm-1

W(PH3) d

Route: #P UPBEPBE/GenECP/Auto GFInput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.000021	-0.000044	-0.000014
Cl	-0.228108	-1.619485	-1.725345
Cl	0.228073	1.619249	1.725504
P	-2.514989	0.001528	0.254739
H	-3.293935	0.065001	-0.936613
H	-3.126717	-1.118822	0.889649
H	-3.114611	1.059741	0.998566
P	2.514876	-0.001155	-0.254885
H	3.293936	-0.073462	0.935891
H	3.113834	-1.054515	-1.006114
H	3.127104	1.123303	-0.881989
Cl	-0.209927	1.740900	-1.605183
Cl	0.209996	-1.740875	1.605248

Energy E(UPBE-PBE)	-2593.40529231 a.u.
	-6808985.59 kJ/mol
SCF Convergence:	0.4068D-08
<S**2>:	2.0101
Charge:	0.0000
	Maximum Force: 0.000043
ZPE-correction:	0.057801 a.u.
	151.76 kJ/mol
Energy (298K):	-2593.332852 a.u.
	-6808795.40 kJ/mol
Enthalpy (298K):	-2593.331908 a.u.
	-6808792.92 kJ/mol
Free Energy (298K):	-2593.393206 a.u.
	-6808953.86 kJ/mol
Lowest Frequency	47.0814 cm-1

W(PMe3) a

Route: #P PBEPBE/GenECP/Auto GFInput Freq

Atom Coordinates (x,y,z) in Angstrom

W	-0.002284	-0.000175	-0.000401
Cl	0.002632	-0.000513	2.490920
Cl	-0.007827	-0.011542	-2.491291
P	-1.778916	-1.739712	0.347441
C	-3.242394	-1.239476	1.391588
C	-2.598594	-2.496272	-1.140857
C	-1.321252	-3.248021	1.347325
P	1.776592	1.738927	0.344965
C	2.587679	2.493214	-1.148616
C	1.318388	3.246350	1.346292
C	3.241904	1.241623	1.387512
P	1.748621	-1.770433	-0.346081
C	1.260785	-3.242975	-1.382596
C	3.249816	-1.301902	-1.350952
C	2.510590	-2.578175	1.145286
P	-1.741888	1.774349	-0.347918
C	-1.242672	3.237724	-1.391231
C	-3.251947	1.316018	-1.343196
C	-2.491243	2.591565	1.145083
H	-2.089850	3.921383	-1.548818
H	-0.416946	3.787796	-0.926056
H	-0.898358	2.846447	-2.358448
H	-3.926572	-2.087037	1.544648
H	-2.851084	-0.900695	2.360625
H	-3.792476	-0.411116	0.931017

H	3.353251	3.231008	-0.865980
H	3.042934	1.696759	-1.750615
H	1.818637	2.973815	-1.766840
H	3.908354	-2.169543	-1.504784
H	2.889788	-0.938371	-2.323207
H	3.820949	-0.499981	-0.869292
H	-3.865312	2.201726	-1.564939
H	-2.897919	0.870419	-2.282944
H	-3.869222	0.579780	-0.815894
H	-3.227581	3.358131	0.861712
H	-2.972304	1.825914	1.767036
H	-1.691731	3.047591	1.742831
H	-3.361994	-3.232855	-0.849694
H	-3.058766	-1.700833	-1.740839
H	-1.834634	-2.979494	-1.763373
H	-2.209607	-3.850848	1.585934
H	-0.600616	-3.875638	0.811100
H	-0.856814	-2.891714	2.277032
H	3.262184	-3.328960	0.859522
H	2.974762	-1.807232	1.773132
H	1.718505	-3.053391	1.738145
H	2.127426	-3.888926	-1.586290
H	0.483190	-3.834515	-0.886313
H	0.856807	-2.856286	-2.328087
H	2.207652	3.846974	1.587596
H	0.597262	3.878586	0.815532
H	0.855713	2.886410	2.275696
H	3.926966	2.089032	1.536989
H	2.850542	0.908146	2.358529
H	3.791682	0.410418	0.931401

Energy E(UPBE-PBE)	-2830.60174438 a.u.
	-7431744.88 kJ/mol
SCF Convergence:	0.9146D-08
<S**2>:	2.0107
Charge:	0.0000
Maximum Force:	0.000559
ZPE-correction:	0.448393 a.u.
	1177.26 kJ/mol
Energy (298K):	-2830.116501 a.u.
	-7430470.87 kJ/mol
Enthalpy (298K):	-2830.115556 a.u.
	-7430468.39 kJ/mol
Free Energy (298K):	-2830.220923 a.u.
	-7430745.03 kJ/mol
Lowest Frequency	30.3925 cm-1

W(PMe3) b

Route: #P PBEPBE/GenECP/Auto GFInput Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.000014	0.042054	-0.335519
O	0.000167	-0.038558	-2.071183
Cl	-0.000594	0.802791	2.105084
Cl	0.000617	-2.367651	0.253523
P	-2.509698	-0.116895	0.040735
C	-3.433260	1.465601	0.256090
C	-3.319350	-0.944400	-1.397357
C	-3.015806	-1.122188	1.497516
P	2.509784	-0.116465	0.040859
C	3.015655	-1.118504	1.499945
C	3.319126	-0.947623	-1.395295
C	3.433910	1.466235	0.252343
C	-0.000366	2.077389	-0.425917
O	-0.000558	3.237204	-0.506305
H	4.505295	1.281776	0.417076
H	3.300317	2.089369	-0.641729
H	3.015626	1.999849	1.116323
H	-4.405714	-1.025107	-1.249523
H	-3.106447	-0.370932	-2.308894
H	-2.881466	-1.945405	-1.507224
H	4.405312	-1.029386	-1.246720
H	2.880066	-1.948282	-1.503565
H	3.107449	-0.375532	-2.307984
H	4.111244	-1.186065	1.558618
H	2.615023	-0.641773	2.403884
H	2.570284	-2.116915	1.407344
H	-4.111454	-1.187727	1.557380
H	-2.572525	-2.121211	1.401656
H	-2.613119	-0.648747	2.402278
H	-4.504489	1.281039	0.421706
H	-3.013886	1.997607	1.120531
H	-3.300561	2.090246	-0.637059

Energy E(RPBE-PBE)	-2097.47686582 a.u.
	-5506925.51 kJ/mol
SCF Convergence:	0.7434D-08
<S**2>:	0.0000
Charge:	0.0000
	Maximum Force: 0.000197
ZPE-correction:	0.237332 a.u.
	623.12 kJ/mol
Energy (298K):	-2097.215558 a.u.

	-5506239.45 kJ/mol
Enthalpy (298K):	-2097.214614 a.u.
	-5506236.97 kJ/mol
Free Energy (298K):	-2097.293315 a.u.
	-5506443.60 kJ/mol
Lowest Frequency	32.3540 cm-1

W(PMe3) c

Route: #P PBEPBE/GenECP/Auto GFInput Opt(CalcFC) Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.000220	-0.199865	-0.219035
O	0.000227	-0.124756	-1.955557
Cl	0.000497	0.215864	2.298437
Cl	0.000658	-2.673828	0.226135
P	-0.001250	2.292614	-0.087175
C	1.414696	3.161236	0.748061
C	-0.003164	3.086420	-1.762894
C	-1.416643	3.159457	0.750822
P	-2.512844	-0.587554	-0.089693
C	-3.049575	-1.437227	1.456667
C	-3.820406	0.722979	-0.277117
C	-2.990603	-1.760687	-1.438845
P	2.513423	-0.585970	-0.089765
C	3.050638	-1.436629	1.455890
C	2.991614	-1.757883	-1.439832
C	3.820411	0.725250	-0.276169
H	4.117879	-1.695355	1.404091
H	2.858375	-0.774843	2.310233
H	2.439848	-2.340153	1.576434
H	-4.059309	-2.012989	-1.383345
H	-2.766589	-1.295484	-2.408189
H	-2.380250	-2.667157	-1.337302
H	-0.005463	4.182558	-1.679918
H	0.883906	2.758480	-2.319648
H	-0.888915	2.754709	-2.319486
H	4.814371	0.260268	-0.356550
H	3.628768	1.317590	-1.181171
H	3.809376	1.390548	0.596192
H	4.060652	-2.008983	-1.385286
H	2.382401	-2.665122	-1.338250
H	2.766252	-1.292515	-2.408781
H	-1.223275	4.239288	0.828034
H	-2.338542	2.998488	0.180087
H	-1.533976	2.733342	1.755652

H	1.221005	4.241089	0.824209
H	1.533416	2.736332	1.753254
H	2.335973	2.999913	0.176430
H	-4.813936	0.257431	-0.359504
H	-3.811234	1.387474	0.595886
H	-3.627737	1.316311	-1.181244
H	-4.117224	-1.694504	1.406100
H	-2.439873	-2.341555	1.576694
H	-2.855402	-0.775588	2.310693

Energy E(RPBE-PBE)	-2445.02996439 a.u.
	-6419426.17 kJ/mol
SCF Convergence:	0.2822D-08
<S**2>:	0.0000
Charge:	0.0000
	Maximum Force: 0.000004
ZPE-correction:	0.341519 a.u.
	896.66 kJ/mol
Energy (298K):	-2444.659151 a.u.
	-6418452.60 kJ/mol
Enthalpy (298K):	-2444.658207 a.u.
	-6418450.12 kJ/mol
Free Energy (298K):	-2444.746499 a.u.
	-6418681.93 kJ/mol
Lowest Frequency	38.3913 cm-1

W(PMe3) d

Route: #P PBEPBE/GenECP/Auto GFInput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.000004	-0.019808	-0.000461
Cl	-0.092561	-1.709376	-1.682020
Cl	0.114981	1.672449	1.685707
P	-2.560766	0.017665	0.047281
C	-3.342999	-0.135344	-1.617011
C	-3.354992	-1.321231	1.038828
C	-3.284070	1.574088	0.726369
P	2.560760	0.017714	-0.046109
C	3.341754	-0.132977	1.618935
C	3.355991	-1.322470	-1.035143
C	3.284206	1.573379	-0.726804
Cl	-0.115102	1.671500	-1.687326
Cl	0.092729	-1.708872	1.681830
H	-4.438469	-0.085699	-1.540502
H	-2.973930	0.679315	-2.253598

H	-3.039374	-1.089104	-2.067306
H	4.437259	-0.083292	1.542980
H	2.972190	0.682425	2.254262
H	3.037988	-1.086247	2.070166
H	-4.450764	-1.244136	0.996022
H	-3.032482	-2.293667	0.644375
H	-3.014121	-1.247479	2.079499
H	-4.382414	1.540329	0.697805
H	-2.937150	1.712575	1.758232
H	-2.920594	2.419961	0.128019
H	4.382539	1.540106	-0.697256
H	2.938106	1.710263	-1.759157
H	2.919880	2.419951	-0.129958
H	4.451731	-1.245456	-0.991229
H	3.032965	-2.294388	-0.639830
H	3.016285	-1.249948	-2.076283

Energy E(UPBE-PBE)	-2829.09970226 a.u.
	-7427801.27 kJ/mol
SCF Convergence:	0.3619D-08
<S**2>:	2.0112
	Maximum Force: 0.000042
ZPE-correction:	0.228382 a.u.
	599.62 kJ/mol
Energy (298K):	-2828.847032 a.u.
	-7427137.88 kJ/mol
Enthalpy (298K):	-2828.846088 a.u.
	-7427135.40 kJ/mol
Free Energy (298K):	-2828.927932 a.u.
	-7427350.29 kJ/mol
Lowest Frequency	17.6917 cm-1

W(PPh2Me) a

Route: #P PBEPBE/GenECP/Auto GFInput Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.192597	0.002879	-0.290540
Cl	-0.305435	-0.682532	-2.619660
P	-1.533607	-1.523554	0.867316
P	-1.486712	1.894551	-0.785442
Cl	0.703738	0.734157	2.011567
P	1.855910	-1.955633	-0.366848
P	2.046092	1.528406	-1.161628
C	-0.803733	-2.383412	2.351200
H	-0.284404	-1.620429	2.943307

H	-0.082175	-3.141304	2.023547
H	-1.586973	-2.843829	2.966934
C	-1.220085	2.650280	-2.469518
H	-0.301642	3.249723	-2.463198
H	-1.114725	1.825422	-3.185211
H	-2.075933	3.273161	-2.759955
C	2.828411	-1.992983	-1.958321
H	2.119288	-1.799321	-2.772943
H	3.299115	-2.971773	-2.115839
H	3.591157	-1.204194	-1.939291
C	2.222838	1.474694	-3.008943
H	2.482499	0.452673	-3.305146
H	1.254941	1.710626	-3.462685
H	2.987794	2.171664	-3.371892
C	-2.360414	-2.929219	-0.038085
C	-3.022716	-0.789998	1.751819
C	-1.575603	3.410381	0.301533
C	-3.321934	1.542487	-1.005340
C	1.221084	-3.726266	-0.446764
C	3.205061	-2.167133	0.910138
C	3.819183	1.255470	-0.601201
C	1.991203	3.375063	-0.821575
C	-2.802883	-2.731847	-1.363089
C	-3.505461	-3.743520	-2.052581
C	-3.768702	-4.977562	-1.420619
C	-2.628670	-4.168007	0.586396
C	-3.322403	-5.187945	-0.098330
H	-2.584579	-1.780810	-1.867524
H	-3.844106	-3.565799	-3.087768
H	-4.316055	-5.772875	-1.955888
H	-2.296667	-4.359222	1.617967
H	-3.515263	-6.150393	0.406021
C	-4.351024	-1.053927	1.357912
C	-5.440466	-0.537269	2.092971
C	-5.214838	0.255144	3.237695
C	-2.804612	0.011929	2.896988
C	-3.888613	0.532136	3.635634
H	-4.552346	-1.669843	0.467841
H	-6.470539	-0.758635	1.764653
H	-6.065392	0.654699	3.816835
H	-1.775603	0.233376	3.224905
H	-3.694939	1.150736	4.529387
C	-1.567501	3.257933	1.704614
C	-1.686816	4.375530	2.558400
C	-1.810756	5.671349	2.013527
C	-1.702593	4.711726	-0.234367

C	-1.814813	5.835318	0.611866
H	-1.451593	2.255878	2.138787
H	-1.678256	4.230205	3.652386
H	-1.900916	6.549445	2.676441
H	-1.710712	4.872133	-1.322973
H	-1.905725	6.843142	0.171452
C	-4.312016	2.122289	-0.185152
C	-5.683147	1.894860	-0.435684
C	-6.083105	1.081475	-1.516128
C	-3.731052	0.725058	-2.085040
C	-5.099232	0.493326	-2.341035
H	-4.022908	2.763194	0.662005
H	-6.439823	2.359540	0.219629
H	-7.154593	0.907968	-1.716999
H	-2.975424	0.271464	-2.747367
H	-5.396975	-0.142983	-3.192635
C	1.497956	-4.684398	0.552486
C	1.033753	-6.013609	0.429438
C	0.293714	-6.403988	-0.705719
C	0.467374	-4.124005	-1.575548
C	0.012770	-5.452159	-1.709929
H	2.099451	-4.407968	1.433416
H	1.264686	-6.747355	1.221285
H	-0.064899	-7.442857	-0.807075
H	0.214473	-3.387867	-2.355903
H	-0.574590	-5.739056	-2.598672
C	2.947254	-1.875253	2.267392
C	3.930074	-2.089295	3.258417
C	5.196532	-2.598389	2.900230
C	4.475949	-2.678750	0.563753
C	5.467069	-2.888460	1.545758
H	1.978980	-1.442068	2.557263
H	3.704363	-1.849313	4.311872
H	5.969786	-2.765306	3.670163
H	4.714173	-2.922183	-0.482839
H	6.454239	-3.282829	1.249097
C	4.079007	1.114358	0.780264
C	5.397502	0.969902	1.259331
C	6.482170	0.953037	0.356151
C	4.910837	1.236907	-1.497956
C	6.233529	1.080290	-1.026324
H	3.240349	1.102205	1.494684
H	5.574205	0.857489	2.342344
H	7.514821	0.834960	0.727141
H	4.751333	1.346289	-2.582091
H	7.070737	1.063516	-1.745459

C	1.847611	3.805508	0.516940
C	1.870781	5.176726	0.842818
C	2.023146	6.145336	-0.173036
C	2.137277	4.350958	-1.832005
C	2.147604	5.727968	-1.514012
H	1.696220	3.062642	1.316017
H	1.756117	5.488248	1.894822
H	2.038024	7.219677	0.079090
H	2.252117	4.057069	-2.887475
H	2.261316	6.473598	-2.320055

Energy E(UPBE-PBE)	-4361.11385999 a.u.
	-11450104.44 kJ/mol
SCF Convergence:	0.2947D-08
<S**2>:	2.0138
Charge:	0.0000
	Maximum Force: 0.000729
ZPE-correction:	0.873234 a.u.
	2292.68 kJ/mol
Energy (298K):	-4360.180497 a.u.
	-11447653.89 kJ/mol
Enthalpy (298K):	-4360.179553 a.u.
	-11447651.42 kJ/mol
Free Energy (298K):	-4360.337870 a.u.
	-11448067.08 kJ/mol
Lowest Frequency	-19.6879 cm-1

W(PPh2Me) b

Route: #P PBEPBE/GenECP/Auto GFInput Opt(Loose) Freq

Atom Coordinates (x,y,z) in Angstrom

W	-0.024571	-0.435185	-0.125035
O	-0.184366	-1.827234	-1.158513
Cl	0.375416	1.118068	1.819825
Cl	-0.524177	1.393277	-1.696733
P	2.430652	-0.098582	-0.818591
C	3.602855	-1.286056	-0.025779
C	2.547207	-0.421245	-2.634131
C	3.281695	1.534481	-0.618257
P	-2.469803	-0.259489	0.692369
C	-3.211168	1.429394	0.599638
C	-3.723739	-1.324178	-0.167958
C	-2.671004	-0.742347	2.467191
C	0.457640	-1.674167	1.422308
O	0.727158	-2.399998	2.287899

H	-3.689912	-0.539254	2.822386
H	-2.457316	-1.815801	2.549926
H	-1.939488	-0.190182	3.071040
H	3.582508	-0.340185	-2.990840
H	2.131478	-1.412596	-2.856257
H	1.919450	0.334511	-3.124348
C	2.545203	2.729798	-0.477817
C	3.215466	3.969612	-0.388653
C	4.624470	4.021861	-0.437850
C	4.694056	1.589333	-0.666469
C	5.364279	2.826978	-0.578178
H	1.445165	2.700357	-0.442684
H	2.628169	4.896775	-0.276618
H	5.147435	4.991158	-0.364224
H	5.283007	0.662259	-0.765521
H	6.466822	2.856872	-0.615034
C	4.176986	-2.368225	-0.725924
C	5.027938	-3.280454	-0.061697
C	5.312608	-3.112877	1.309340
C	3.886590	-1.126474	1.350962
C	4.738633	-2.031078	2.015029
H	3.967076	-2.518724	-1.797256
H	5.467990	-4.123778	-0.620934
H	5.976107	-3.824811	1.829564
H	3.436726	-0.290163	1.912782
H	4.951062	-1.894325	3.088862
C	-3.343585	-2.287054	-1.124877
C	-4.317442	-3.107722	-1.738192
C	-5.678733	-2.968259	-1.398062
C	-5.091582	-1.185319	0.168278
C	-6.064783	-2.002809	-0.441107
H	-2.282641	-2.401545	-1.400793
H	-4.005617	-3.855822	-2.486773
H	-6.440105	-3.606970	-1.878311
H	-5.408618	-0.424474	0.901313
H	-7.128120	-1.882980	-0.171459
C	-3.779417	1.878416	-0.613666
C	-4.306691	3.182000	-0.714619
C	-4.262854	4.053048	0.396013
C	-3.157419	2.306680	1.704064
C	-3.684280	3.612749	1.605349
H	-3.810670	1.211474	-1.490161
H	-4.746921	3.520408	-1.668027
H	-4.672583	5.074789	0.316431
H	-2.690149	1.987964	2.649050
H	-3.636268	4.288244	2.476504

Energy E(RPBE-PBE)	-2862.72945720 a.u.
	-7516096.19 kJ/mol
SCF Convergence:	0.9677D-08
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000088
ZPE-correction:	0.448138 a.u.
	1176.59 kJ/mol
Energy (298K):	-2862.244448 a.u.
	-7514822.80 kJ/mol
Enthalpy (298K):	-2862.243504 a.u.
	-7514820.32 kJ/mol
Free Energy (298K):	-2862.358331 a.u.
	-7515121.80 kJ/mol
Lowest Frequency	0.9871 cm-1

W(PPh2Me) c

Route: #P PBEPBE/GenECP/Auto GFInput Geom=check Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.255020	-0.669270	-0.193103
O	0.202025	-1.245271	-1.845012
Cl	0.062096	0.573160	1.966951
Cl	1.087000	-2.580849	1.140536
P	-0.563111	1.569882	-1.034559
C	0.501474	3.106999	-0.904762
C	-0.836149	1.444945	-2.865651
C	-2.174613	2.292876	-0.434043
P	-2.047196	-1.791449	0.192704
C	-2.882298	-1.558714	1.820559
C	-3.388854	-1.509447	-1.070327
C	-1.878431	-3.629900	0.010376
P	2.755571	-0.183470	-0.514715
C	3.173896	0.828003	-2.012912
C	3.690065	0.583778	0.880907
C	3.744091	-1.721079	-0.895751
H	2.808311	1.856648	-1.898006
H	4.254912	0.820985	-2.207512
H	2.658851	0.356354	-2.860621
H	-2.851954	-4.123693	0.128441
H	-1.493340	-3.821106	-0.999774
H	-1.142482	-4.003138	0.732423
H	-1.336430	2.333477	-3.269421
H	0.141079	1.310175	-3.345162

H	-1.441509	0.555770	-3.069031
C	1.406009	3.259928	0.167667
C	2.191555	4.427946	0.291209
C	2.087925	5.456080	-0.669655
C	0.394936	4.148449	-1.855688
C	1.187172	5.311399	-1.747378
H	1.489868	2.462264	0.922616
H	2.888664	4.525614	1.140741
H	2.704157	6.367294	-0.580177
H	-0.313652	4.071641	-2.695411
H	1.095457	6.108579	-2.505140
C	-2.202071	3.088506	0.734567
C	-3.416307	3.629085	1.208873
C	-4.622074	3.385235	0.514697
C	-3.385574	2.045730	-1.118667
C	-4.601988	2.590193	-0.651128
H	-1.270061	3.291279	1.285157
H	-3.416893	4.250264	2.121158
H	-5.571425	3.813536	0.879874
H	-3.400713	1.417290	-2.023006
H	-5.535818	2.386806	-1.202741
C	3.208673	-2.670891	-1.793715
C	3.954948	-3.810938	-2.158622
C	5.243308	-4.018064	-1.618781
C	5.032332	-1.930592	-0.360718
C	5.778967	-3.075391	-0.716373
H	2.191120	-2.534783	-2.196568
H	3.521587	-4.547337	-2.857144
H	5.824211	-4.915189	-1.894841
H	5.462795	-1.205250	0.348680
H	6.781769	-3.230422	-0.281932
C	3.512138	0.055380	2.180752
C	4.213982	0.602571	3.274985
C	5.097448	1.687361	3.081289
C	4.576859	1.666068	0.691224
C	5.277442	2.218731	1.786202
H	2.817700	-0.785559	2.341722
H	4.061785	0.182866	4.283691
H	5.642859	2.119140	3.938198
H	4.731796	2.096578	-0.310737
H	5.966437	3.065562	1.623787
C	-3.274182	-0.257784	2.209282
C	-3.917633	-0.040893	3.444610
C	-4.159490	-1.125114	4.316646
C	-3.120597	-2.637877	2.698557
C	-3.753662	-2.423253	3.942626

H	-3.067669	0.601973	1.552769
H	-4.217924	0.982031	3.728840
H	-4.654404	-0.957184	5.288846
H	-2.808011	-3.659133	2.431123
H	-3.926791	-3.276069	4.621098
C	-3.032003	-1.596998	-2.436398
C	-4.008247	-1.455916	-3.445842
C	-5.357358	-1.220830	-3.097035
C	-4.738497	-1.283168	-0.728519
C	-5.718577	-1.135182	-1.735352
H	-1.978587	-1.772945	-2.714988
H	-3.714641	-1.531515	-4.507217
H	-6.123512	-1.109551	-3.883730
H	-5.036227	-1.215082	0.329955
H	-6.770274	-0.957113	-1.451230

Energy E(RPBE-PBE)	-3592.91357097 a.u.
	-9433194.58 kJ/mol
SCF Convergence:	0.7291D-08
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000166
ZPE-correction:	0.658327 a.u.
	1728.44 kJ/mol
Energy (298K):	-3592.206842 a.u.
	-9431339.06 kJ/mol
Enthalpy (298K):	-3592.205898 a.u.
	-9431336.59 kJ/mol
Free Energy (298K):	-3592.341248 a.u.
	-9431691.95 kJ/mol
Lowest Frequency	15.7131 cm-1

W(PPh2Me) d

Route: #P PBEPBE/GenECP/Auto GFInput Opt(Loose) Freq

Atom Coordinates (x,y,z) in Angstrom

W	0.000116	-0.022899	-0.000238
Cl	-0.323417	-1.719716	1.637746
Cl	0.427466	1.644589	-1.657665
P	2.481073	-0.025141	0.747678
C	2.637165	-0.143060	2.586605
C	3.455910	-1.440358	0.079402
C	3.527067	1.465426	0.383989

P	-2.481257	-0.025366	-0.747610
C	-2.637495	-0.143751	-2.586486
C	-3.455916	-1.440457	-0.078917
C	-3.527044	1.465254	-0.383967
Cl	-0.427929	1.644989	1.656878
Cl	0.322899	-1.720501	-1.637462
H	3.693969	-0.180699	2.881758
H	2.165431	0.753904	3.007751
H	2.091129	-1.023059	2.947983
H	-3.694274	-0.181683	-2.881684
H	-2.165886	0.753203	-3.007809
H	-2.091254	-1.023705	-2.947683
C	-3.723809	-1.483424	1.309082
C	-4.436082	-2.564097	1.866354
C	-4.875684	-3.623480	1.041124
C	-3.891043	-2.503384	-0.897952
C	-4.597754	-3.592507	-0.341282
H	-3.371920	-0.669184	1.964648
H	-4.640185	-2.584000	2.950321
H	-5.427083	-4.474197	1.477130
H	-3.678916	-2.501451	-1.978811
H	-4.929185	-4.418931	-0.992869
C	-2.951763	2.751448	-0.487277
C	-3.742418	3.905233	-0.300363
C	-5.116908	3.782884	-0.003268
C	-4.904156	1.347522	-0.092569
C	-5.695980	2.500031	0.100096
H	-1.878015	2.860670	-0.709610
H	-3.277850	4.902796	-0.380566
H	-5.734792	4.684601	0.149541
H	-5.371444	0.352934	-0.009816
H	-6.769787	2.392583	0.331188
C	2.952402	2.751759	0.489278
C	3.743153	3.905412	0.302054
C	5.117157	3.782852	0.002746
C	4.903674	1.347497	0.090395
C	5.695610	2.499899	-0.102531
H	1.879125	2.861248	0.713705
H	3.279063	4.903069	0.383869
H	5.735110	4.684488	-0.150262
H	5.370564	0.352847	0.006164
H	6.769022	2.392248	-0.335360
C	3.721748	-1.484892	-1.308955
C	4.434246	-2.565579	-1.865910
C	4.876114	-3.623478	-1.039985
C	3.893224	-2.501869	0.899109

C	4.600169	-3.591019	0.342781
H	3.368071	-0.671863	-1.965062
H	4.636731	-2.586681	-2.950158
H	5.427699	-4.474212	-1.475722
H	3.682656	-2.498826	1.980267
H	4.933330	-4.416306	0.994925

Energy E(UPBE-PBE)	-3594.35246081 a.u.
	-9436972.39 kJ/mol
SCF Convergence:	0.9529D-08
<S**2>:	2.0118
Charge:	0.0000
Maximum Force:	0.000036
ZPE-correction:	0.439700 a.u.
	1154.43 kJ/mol
Energy (298K):	-3593.875942 a.u.
	-9435721.29 kJ/mol
Enthalpy (298K):	-3593.874998 a.u.
	-9435718.81 kJ/mol
Free Energy (298K):	-3593.987343 a.u.
	-9436013.77 kJ/mol
Lowest Frequency	12.2779 cm-1

PH3

Route: #P PBEPBE/TZVP/Auto GFinput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

P	0.000049	-0.000001	-0.132179
H	-0.607866	-1.034228	0.660731
H	1.199259	-0.009082	0.661218
H	-0.592130	1.043318	0.660730

Energy E(RPBE-PBE)	-342.97587704 a.u.
	-900483.17 kJ/mol
SCF Convergence:	0.6625D-09
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000013
ZPE-correction:	0.023149 a.u.
	60.78 kJ/mol
Energy (298K):	-342.949806 a.u.
	-900414.72 kJ/mol
Enthalpy (298K):	-342.948861 a.u.
	-900412.23 kJ/mol
Free Energy (298K):	-342.973803 a.u.

	-900477.72 kJ/mol
Lowest Frequency	983.5440 cm-1

PMe3

Route: #P PBEPBE/TZVP/Auto GFinput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

P	-0.001022	-0.000647	-0.609554
C	1.038427	-1.274614	0.283091
C	0.587185	1.535197	0.282638
C	-1.624295	-0.259872	0.283925
H	-2.332350	0.526823	-0.013314
H	-2.055872	-1.225224	-0.016951
H	-1.512786	-0.244328	1.379720
H	-0.033199	2.391802	-0.016997
H	0.545082	1.429482	1.378207
H	1.622664	1.755251	-0.013952
H	0.723279	-2.282375	-0.022679
H	2.091848	-1.153907	-0.007164
H	0.958769	-1.192080	1.378523

Energy E(RPBE-PBE)	-460.80226212 a.u.
	-1209836.34 kJ/mol
SCF Convergence:	0.6338D-09
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000336
ZPE-correction:	0.109338 a.u.
	287.07 kJ/mol
Energy (298K):	-460.686006 a.u.
	-1209531.11 kJ/mol
Enthalpy (298K):	-460.685061 a.u.
	-1209528.63 kJ/mol
Free Energy (298K):	-460.722489 a.u.
	-1209626.89 kJ/mol

PPh2Me

Route: #P PBEPBE/Gen/Auto GFinput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

P	0.035198	1.388965	-0.700841
C	-1.432453	0.324182	-0.294058
C	1.439830	0.270190	-0.191918
C	0.059808	2.585186	0.736530

H	1.000786	3.148988	0.680052
H	-0.767999	3.301124	0.637965
H	0.004132	2.084960	1.713954
C	1.373443	-0.618556	0.905387
C	2.485379	-1.411886	1.258297
C	3.683497	-1.322364	0.513843
C	2.639211	0.345731	-0.934804
C	3.759787	-0.440305	-0.584906
H	0.440354	-0.700893	1.488887
H	2.417868	-2.103382	2.116075
H	4.553691	-1.943696	0.788144
H	2.696526	1.024728	-1.803864
H	4.689247	-0.368635	-1.175813
C	-2.425263	0.678223	0.647226
C	-3.570376	-0.129572	0.833428
C	-3.735924	-1.309754	0.079692
C	-1.618153	-0.856727	-1.054778
C	-2.750637	-1.673359	-0.866601
H	-2.317940	1.592080	1.254697
H	-4.333236	0.165844	1.574672
H	-4.628119	-1.942810	0.225344
H	-0.862766	-1.145345	-1.806833
H	-2.869405	-2.593375	-1.464696

Energy E(RPBE-PBE)	-843.43656282 a.u.
	-2214442.70 kJ/mol
SCF Convergence:	0.8490D-08
<S**2>:	0.0000
Charge:	0.0000
	Maximum Force: 0.000047
ZPE-correction:	0.215489 a.u.
	565.77 kJ/mol
Energy (298K):	-843.208116 a.u.
	-2213842.91 kJ/mol
Enthalpy (298K):	-843.207172 a.u.
	-2213840.43 kJ/mol
Free Energy (298K):	-843.262143 a.u.
	-2213984.76 kJ/mol
Lowest Frequency	24.0487 cm-1

CO

Route: #P PBEPBE/TZVP/Auto GFinput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

C	0.000000	0.000000	-0.650424
O	0.000000	0.000000	0.487818

Energy E(RPBE-PBE)	-113.22899485 a.u.
	-297282.73 kJ/mol
SCF Convergence:	0.5482D-10
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000057
ZPE-correction:	0.004861 a.u.
	12.76 kJ/mol
Energy (298K):	-113.221773 a.u.
	-297263.77 kJ/mol
Enthalpy (298K):	-113.220829 a.u.
	-297261.29 kJ/mol
Free Energy (298K):	-113.243273 a.u.
	-297320.21 kJ/mol
Lowest Frequency	2133.8305 cm-1

CO2

Route: #P PBEPBE/TZVP/Auto GFinput Opt Freq

Atom Coordinates (x,y,z) in Angstrom

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.171989
O	0.000000	0.000000	-1.171989

Energy E(RPBE-PBE)	-188.46897017 a.u.
	-494825.28 kJ/mol
SCF Convergence:	0.3835D-08
<S**2>:	0.0000
Charge:	0.0000
	Maximum Force: 0.000331
ZPE-correction:	0.011355 a.u.
	29.81 kJ/mol
Energy (298K):	-188.454970 a.u.
	-494788.52 kJ/mol
Enthalpy (298K):	-188.454025 a.u.
	-494786.04 kJ/mol
Free Energy (298K):	-188.478338 a.u.
	-494849.88 kJ/mol
Lowest Frequency	643.2571 cm-1

H2O

Route: #P PBEPBE/TZVP/Auto GFinput Opt Freq
Atom Coordinates (x,y,z) in Angstrom

H	0.000000	0.765486	-0.477700
O	0.000000	0.000000	0.119425
H	0.000000	-0.765486	-0.477700

Energy E(RPBE-PBE)	-76.37435885 a.u.
	-200520.88 kJ/mol
SCF Convergence:	0.1529D-09
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000014
ZPE-correction:	0.020666 a.u.
	54.26 kJ/mol
Energy (298K):	-76.350857 a.u.
	-200459.18 kJ/mol
Enthalpy (298K):	-76.349913 a.u.
	-200456.70 kJ/mol
Free Energy (298K):	-76.371365 a.u.
	-200513.02 kJ/mol
Lowest Frequency	1570.3557 cm-1

HCl

Route: #P PBEPBE/TZVP/Auto GFinput Opt Freq
Atom Coordinates (x,y,z) in Angstrom

Cl	0.000000	0.000000	0.071989
H	0.000000	0.000000	-1.223821

Energy E(RPBE-PBE)	-460.62102476 a.u.
	-1209360.50 kJ/mol
SCF Convergence:	0.1943D-09
<S**2>:	0.0000
Charge:	0.0000
Maximum Force:	0.000002
ZPE-correction:	0.006538 a.u.
	17.17 kJ/mol
Energy (298K):	-460.612127 a.u.
	-1209337.14 kJ/mol
Enthalpy (298K):	-460.611182 a.u.
	-1209334.66 kJ/mol
Free Energy (298K):	-460.632389 a.u.
	-1209390.34 kJ/mol
Lowest Frequency	2869.6809 cm-1

Table S6 Relative energies, enthalpies and free energies (in kJ/mol) of tungsten complexes with reference to compound **a**.

		W(PH3)	**W(PMe3)**	**W(PMePh2)**
	ΔE			
a		0	0	0
b		2	-28	-52
c		58	25	10
d		39	14	-11
	ΔH (0 K)			
a		0	0	0
b		-15	-38	-66
c		43	14	-6
d		32	13	-15
	ΔG (298 K)			
a		0	0	0
b		-59	-102	-174
c		4	-34	-80
d		-21	-62	-119

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