Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Hydride, Gold(I) and Related Derivatives of the Unsaturated Ditungsten Anion $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$

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Structural characterization of compound 5.

The structure of **5** was reported in our preliminary work (see ref. 12 in the main text) and is not very different from that of its Mo_2 analogue, therefore only a brief comment is needed here. First we note that the short intermetallic separation of 2.5794(3) Å is comparable to that measured for its Mo_2 analogue [2.5743(7) Å], and itself consistent with the presence of a somewhat elongated metal–metal triple bond. The carbonyl ligands display distinct bending over the M–M vector [C1–W2–W1 = 72.0(2)º and C2–W1–W2 = 91.3(2)º], indicative of a distortion departing from the ideal *trans* dicarbonyl structure of C_2 symmetry (*i.e.* the structure of **2B**), which is accompanied by a significant puckering of the PW_2Sn ring (*ca.* 160.1º) and incipient semibridging interaction of one of the carbonyls (W2···C1 = 2.699(5) Å). This distortion might be derived from the steric pressure induced by the bulky $SnPh_3$ bridging group, however we note that isomer **T** of hydride **2** displays a comparable distortion, which in this case is unlikely to be due to steric factors. Perhaps to balance the distinct binding of carbonyls, the $SnPh_3$ group binds more tightly to the W1 atom, this resulting in W–Sn distances differing by *ca.* 0.06Å from each other, a difference much higher than that found in the Mo_2 analogue of **5** (*ca.* 0.01 Å).

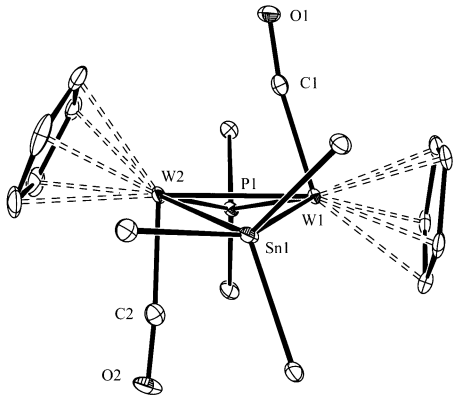
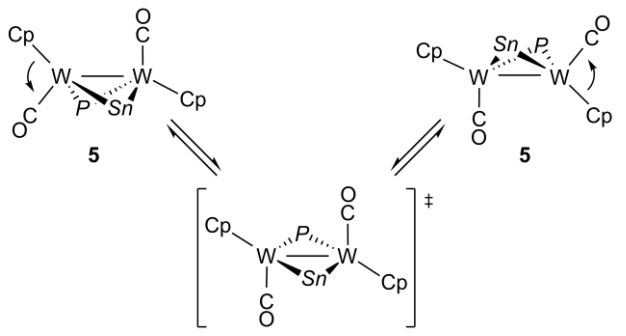


Figure 3: ORTEP diagram (30% probability) of compound **5** with H atoms and Cy groups (except their C^1 atoms) omitted for clarity.[12] Selected bond lengths (Å) and angles (deg): W1–W2 = 2.5794(3), W1–Sn1 = 2.8843(4), W2–Sn1 = 2.9451(4), W1–P1 = 2.387(1), W2–P1 = 2.379(1), W1–C1 = 1.920(5), W2–C2 = 1.958(6), W2···C1 = 2.699(5); C1–W1–W2 = 72.0(2), C2–W2–W1 = 91.3(2).

The IR spectrum of **5** in solution displays two C–O stretching bands with relative intensities (medium and strong in order of decreasing frequencies) differing significantly from those observed for the hydride **2B** and the carboxylates **4**, but itself consistent with the structural distortion discussed above, characterized by relative angles between CO ligands well below 180º (163º in the crystal). Its ^{31}P NMR spectrum displays a quite deshielded resonance (178.5 ppm) with relatively high one-bond P–W coupling (305 Hz), comparable to those measured for the H-bridged isomer **2B**, and consistent with the relatively low-coordination environments in these 30-electron complexes. The ^1H and ^{13}C NMR spectra, however, display a single resonance for each pair of inequivalent Cp and CO ligands down to 193 K, a circumstance also found for its Mo_2 analogue. To account for this, we propose the occurrence of a related fluxional rearrangement that would involve a concerted exchange of Cp and CO environments through a transition state having a C_2 structure analogous to that of the H-bridged isomer **2B** (see Scheme below; *P* = PCy_2; *Sn* = $SnPh_3$).



Scheme

Complete reference 44:

Gaussian 03, Revision B.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004

Table S1. Cartesian Coordinates for the Optimized Structure of **2B**.

C	-0.9217950	1.4262360	1.8343520
C	-1.3258030	-0.8601930	-1.9460270
C	1.9973800	-0.5365990	-1.5268730
H	1.2910840	-0.3945880	-2.3552510
C	2.5236180	-1.9862180	-1.6159900
H	3.1966140	-2.1910220	-0.7702330
H	1.6886590	-2.6922880	-1.5350510
C	3.2902310	-2.2291580	-2.9293470
H	3.6840200	-3.2538240	-2.9447710
H	2.5890210	-2.1505630	-3.7727790
C	4.4286240	-1.2162540	-3.1210650
H	4.9263310	-1.3813000	-4.0851390
H	5.1913870	-1.3751950	-2.3439500
C	3.9083010	0.2247710	-3.0293800
H	3.2309170	0.4204980	-3.8735900
H	4.7381010	0.9376230	-3.1215330
C	3.1544870	0.4679340	-1.7097280
H	3.8651080	0.3724140	-0.8766020
H	2.7723480	1.4955080	-1.6814660
O	-0.9663850	1.5221060	3.0033200
O	-1.3390840	-0.8241390	-3.1211700
P	0.9245090	-0.2252710	-0.0054330
W	-0.8546690	1.4249750	-0.1204360
W	-1.3647160	-1.0656780	-0.0113240
C	-2.9131460	-2.3206090	1.1948530
H	-3.7211120	-1.8245080	1.7166290
C	-1.6470150	-2.6738120	1.7543280
H	-1.3177860	-2.4641110	2.7633580
C	-0.8961480	-3.3533040	0.7523020
H	0.1083890	-3.7382950	0.8644620
C	-1.6848490	-3.4257300	-0.4248010
H	-1.3934930	-3.8912000	-1.3568360
C	-2.9445210	-2.7868130	-0.1609220
H	-3.7846400	-2.7299350	-0.8392430
C	-0.2227280	2.7807690	-1.9545990
H	0.2072240	2.3438380	-2.8460970
C	0.5017310	3.3435920	-0.8602450
H	1.5776000	3.3716770	-0.7556470
C	-0.4330510	3.8374680	0.0818080
H	-0.1910290	4.3019010	1.0290910
C	-1.7514680	3.5926380	-0.4141980
H	-2.6753850	3.8906050	0.0624640
C	-1.6216770	2.9409900	-1.6862090
H	-2.4319660	2.6652970	-2.3482120
H	-2.4471890	0.4544980	0.0235880
C	2.1468440	-0.3488590	1.4346720
C	1.5858880	-1.0886830	2.6652130
H	0.7195160	-0.5412410	3.0568600
H	1.2289850	-2.0823160	2.3734570
C	2.6439640	-1.2174800	3.7757350
H	2.2059000	-1.7222600	4.6466790
H	3.4645320	-1.8603310	3.4225750
C	3.2099570	0.1505620	4.1819960
H	3.9930760	0.0286430	4.9413430
H	2.4115170	0.7481190	4.6449490
C	3.7603470	0.9036660	2.9626850
H	4.6375650	0.3676520	2.5697150
H	4.1110660	1.9016640	3.2564870
C	2.7023130	1.0319430	1.8527440
H	1.8699790	1.6518770	2.2083130
H	3.1305250	1.5528370	0.9885310
H	2.9847810	-0.9454620	1.0445590

G = -1561.506771 a.u.

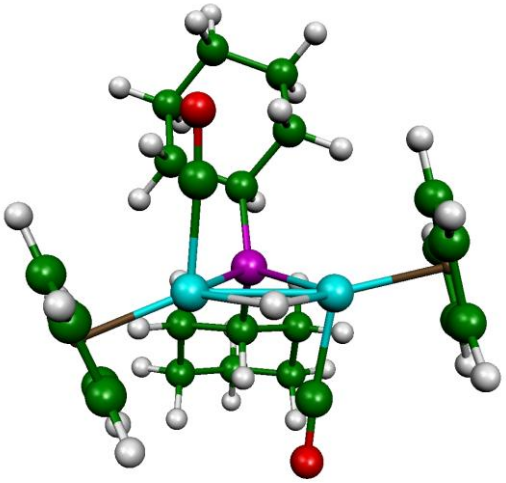


Table S2. Cartesian Coordinates for the Optimized Structure of **2T**.

W	1.1801960	-1.1543030	-0.4685570
W	1.0119430	1.2488630	0.3233750
P	-0.9794950	-0.0315890	-0.0678450
O	1.5906850	-0.2412850	3.0004820
C	1.3650390	0.2386520	1.9474680
H	0.4501370	-1.2062040	-2.0111850
C	2.2382910	0.1709030	-1.4871730
C	2.6593590	-2.9517060	-1.0336880
C	2.7857190	-2.6486020	0.3576720
C	1.5433750	-2.9718400	0.9892780
C	0.6574450	-3.4809050	-0.0062480
C	1.3491340	-3.4674780	-1.2510980
C	1.9603450	3.2754410	-0.3180020
C	0.5694790	3.4152950	-0.6155010
C	-0.1468680	3.3942410	0.6171400
C	0.7840960	3.2411130	1.6761610
C	2.0983400	3.1687160	1.1038520
C	-1.9996100	-0.6622430	1.3892100
C	-3.0562390	-1.7335290	1.0568340
C	-3.7002310	-2.2945010	2.3379380
C	-4.3049900	-1.1769240	3.2004630
C	-3.2620760	-0.0974110	3.5247140
C	-2.6093350	0.4665680	2.2498650
C	-2.0847710	0.4170300	-1.5279770
C	-2.5941150	-0.7902470	-2.3460420
C	-3.3179960	-0.3273770	-3.6228410
C	-4.4647270	0.6440590	-3.3073570
C	-3.9683780	1.8382480	-2.4795000
C	-3.2453210	1.3801260	-1.1994130
O	2.9555420	0.7276130	-2.2476170
H	-1.7510550	-1.4398150	-2.6034320
H	-1.2192380	-1.1403710	1.9987900
H	-1.3683950	0.9574050	-2.1639260
H	-3.3654370	1.0115260	1.6685100
H	-2.8773390	2.2534150	-0.6466090
H	2.7650810	3.2626510	-1.0415270
H	0.1388600	3.5279430	-1.6019700
H	-3.9690880	0.8767330	-0.5443930
H	-1.2204870	3.4605670	0.7285840
H	-4.9351370	0.9945270	-4.2348640
H	-2.6054220	-2.5464630	0.4737840
H	-2.5944000	0.1673850	-4.2872090
H	-1.8267680	1.1879750	2.5118880
H	-3.6973530	-1.1998720	-4.1704720
H	-3.2762110	2.4387020	-3.0880470
H	-2.9365580	-2.8301760	2.9210180
H	0.5466410	3.1941440	2.7304830
H	3.0274930	3.0934730	1.6527480
H	-4.4685890	-3.0331860	2.0752400
H	-3.2861950	-1.3880420	-1.7391480
H	-5.2450550	0.1126430	-2.7422270
H	-3.8449840	-1.2973300	0.4291910
H	-3.7225650	0.7178180	4.0978300
H	-5.1459470	-0.7180690	2.6589570
H	-4.7210820	-1.5945260	4.1260580
H	-2.4804370	-0.5281010	4.1673970
H	1.3243260	-2.8474920	2.0418260
H	-4.8062750	2.4971370	-2.2170840
H	0.9431330	-3.7753630	-2.2048150
H	-0.3553940	-3.8233790	0.1553120
H	3.4244780	-2.8229720	-1.7872720
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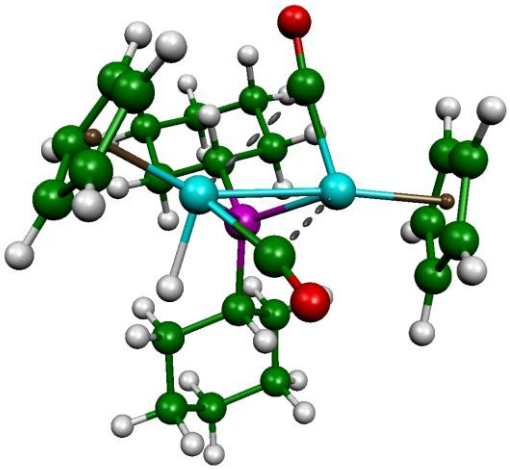

Table S3. Cartesian Coordinates for the Optimized Structure of **2C**.

W	-0.9925260	1.3637650	-0.0784610
W	-1.2013510	-1.1625880	-0.0889470
P	0.9541060	-0.1326590	0.0049270
O	-0.9965910	-2.1192290	2.8968500
C	-1.0474860	-1.7316100	1.7981350
H	-1.4968860	1.0326930	-1.6754860
C	-2.3809280	0.3909500	1.0377330
C	-1.9634700	3.4656840	-0.5947690
C	-1.9562130	3.3434480	0.8229400
C	-0.5967990	3.3248980	1.2558780
C	0.2368670	3.4583750	0.1069040
C	-0.6000440	3.5325230	-1.0381670
C	-2.7723380	-1.9010030	-1.7013120
C	-1.4953700	-2.0015110	-2.3250790
C	-0.7502590	-3.0084230	-1.6350430
C	-1.5706680	-3.5332950	-0.6041640
C	-2.8246300	-2.8434020	-0.6262900
C	2.0109190	-0.2169590	1.5691570
C	3.1265380	0.8407790	1.6848450
C	3.7665340	0.8160260	3.0852750
C	4.2936170	-0.5814380	3.4432370
C	3.1955910	-1.6462520	3.3013670
C	2.5564670	-1.6238640	1.9015330
C	2.0492260	-0.1073070	-1.5378770
C	2.6842600	1.2576630	-1.8781060
C	3.3990510	1.2145210	-3.2410390
C	4.4431670	0.0902140	-3.3024890
C	3.8170690	-1.2678330	-2.9541420
C	3.1089660	-1.2285730	-1.5878780
O	-3.3049300	0.4441700	1.7891780
H	1.9104990	2.0331620	-1.8896300
H	1.2566180	0.0192480	2.3336140
H	1.3047840	-0.3185940	-2.3182810
H	3.3085320	-1.9203080	1.1589280
H	2.6469580	-2.2005770	-1.3738850
H	-3.5657650	-1.2252960	-1.9908760
H	-1.1559530	-1.4253630	-3.1744540
H	3.8624660	-1.0595760	-0.8070580
H	0.2567300	-3.3262860	-1.8695890
H	4.9048200	0.0529120	-4.2973320
H	2.7272030	1.8406190	1.4743510
H	2.6515060	1.0580300	-4.0328880
H	1.7477700	-2.3605670	1.8473420
H	3.8704370	2.1848320	-3.4444270
H	3.0886850	-1.5424480	-3.7314340
H	3.0150930	1.1222090	3.8279200
H	-1.2869610	-4.3059470	0.0990140
H	-3.6715780	-3.0320680	0.0188180
H	4.5764620	1.5553140	3.1371770
H	3.4072300	1.5397760	-1.1014540
H	5.2529420	0.3081050	-2.5900760
H	3.9054270	0.6458260	0.9349420
H	3.6041340	-2.6440670	3.5070170
H	5.1311670	-0.8326740	2.7750610
H	4.6975810	-0.5838410	4.4635830
H	2.4134730	-1.4682590	4.0534580
H	-0.2605250	3.2335030	2.2807490
H	4.5837140	-2.0534380	-2.9526300
H	-0.2736010	3.6454150	-2.0630430
H	1.3175150	3.4940790	0.1085380
H	-2.8386130	3.5192900	-1.2277500
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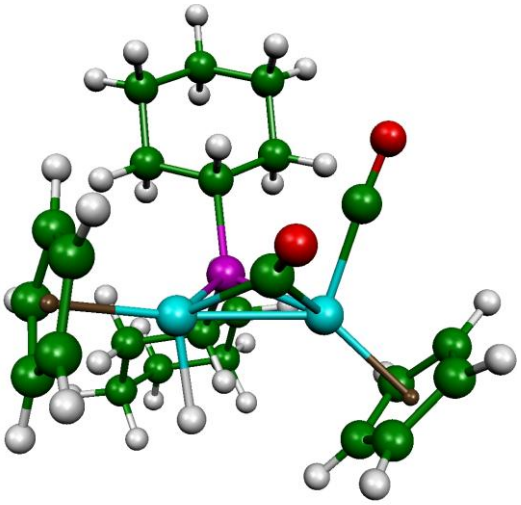

Table S4. Cartesian Coordinates for the Optimized Structure of **3B**.

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C	2.0459880	-0.4054900	-1.4995110
H	1.4022620	-0.0831360	-2.3288010
C	2.4026780	-1.8947890	-1.7340960
H	3.0136280	-2.2610170	-0.8960560
H	1.4913390	-2.5028940	-1.7539710
C	3.1823700	-2.0784920	-3.0490050
H	3.4507770	-3.1351760	-3.1662010
H	2.5225870	-1.8276950	-3.8917360
C	4.4372200	-1.1965840	-3.0990300
H	4.9368970	-1.3052790	-4.0683630
H	5.1541050	-1.5370480	-2.3379400
C	4.0898080	0.2763710	-2.8445970
H	3.4738070	0.6572790	-3.6720820
H	4.9998090	0.8875860	-2.8250690
C	3.3273340	0.4555050	-1.5184230
H	3.9852450	0.1577870	-0.6916530
H	3.0917880	1.5152530	-1.3633700
O	-2.5207560	1.2551370	2.6439450
O	-1.0720960	-1.2289310	-3.2153160
P	0.9415200	-0.2175450	0.0161030
W	-0.9043980	1.4723930	-0.0686090
W	-1.3083580	-1.0524970	-0.0905440
C	-2.8726440	-2.2632470	1.1075610
H	-3.7034410	-1.7544610	1.5804390
C	-1.6098150	-2.5567000	1.7196610
H	-1.3174940	-2.2899230	2.7263620
C	-0.8248050	-3.2897020	0.7851650
H	0.1761590	-3.6650380	0.9473770
C	-1.5848900	-3.4438320	-0.4035960
H	-1.2663370	-3.9693150	-1.2944900
C	-2.8621140	-2.8127190	-0.2127830
H	-3.6842690	-2.8129180	-0.9153820
C	-0.8344920	2.6228680	-2.1195160
H	-0.8659680	2.0860660	-3.0588550
C	0.3406540	3.0084590	-1.4054270
H	1.3605100	2.8292470	-1.7132250
C	-0.0681640	3.7353430	-0.2468130
H	0.5886590	4.1773210	0.4899900
C	-1.4944810	3.8065190	-0.2460230
H	-2.1066920	4.3030310	0.4955840
C	-1.9679210	3.1182000	-1.3970590
H	-3.0047800	3.0025060	-1.6854440
H	-2.3601030	0.4238730	-0.5765330
C	2.1076750	-0.3204960	1.4943910
C	1.4779720	-0.9859010	2.7334070
H	0.6295750	-0.3789390	3.0803740
H	1.0812860	-1.9721180	2.4714470
C	2.5035710	-1.1349000	3.8731960
H	2.0116620	-1.5764150	4.7481780
H	3.2822690	-1.8458950	3.5616930
C	3.1552530	0.2042700	4.2416990
H	3.9182750	0.0522950	5.0136120
H	2.3977940	0.8719470	4.6772400
C	3.7723280	0.8741470	3.0072050
H	4.6159990	0.2708140	2.6422720
H	4.1824880	1.8570510	3.2680520
C	2.7367370	1.0402280	1.8807770
H	1.9386860	1.7114390	2.2247810
H	3.1997390	1.5202760	1.0131590
H	2.9138960	-0.9758560	1.1324110
H	0.0720990	1.7237310	1.3210320

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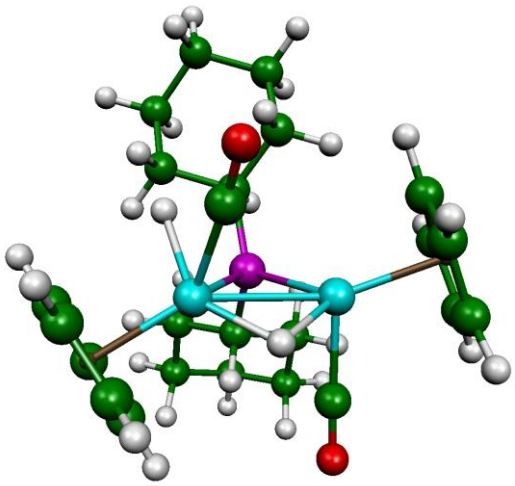


Table S5. Cartesian Coordinates for the Optimized Structure of **3T**.

C	-2.0396870	0.9611950	1.4521650
C	-2.1313570	-0.3094110	-1.7350800
C	2.0736380	-0.4685880	-1.5479970
H	1.3846660	-0.2340630	-2.3709950
C	2.5096620	-1.9461580	-1.6996150
H	3.1688700	-2.2218130	-0.8640680
H	1.6361800	-2.6060270	-1.6508900
C	3.2581590	-2.1657620	-3.0274520
H	3.5845200	-3.2106690	-3.0898490
H	2.5600270	-2.0056280	-3.8615120
C	4.4571230	-1.2188440	-3.1728770
H	4.9323320	-1.3586790	-4.1504850
H	5.2155290	-1.4713820	-2.4178470
C	4.0331030	0.2453510	-2.9949470
H	3.3718420	0.5407590	-3.8222990
H	4.9066600	0.9062170	-3.0412510
C	3.3008270	0.4622010	-1.6575670
H	3.9981630	0.2517720	-0.8363880
H	3.0039860	1.5132760	-1.5590190
O	-2.7313530	0.8776050	2.3830650
O	-2.6812590	-0.0096350	-2.7154620
P	1.0051730	-0.2120750	-0.0222600
W	-0.8475980	1.3891820	-0.0881920
W	-1.2906950	-1.1158230	-0.1200560
C	-3.0135010	-2.2283730	1.0267130
H	-3.8767130	-1.6698390	1.3657440
C	-1.8083590	-2.4389650	1.7700460
H	-1.6102740	-2.0704320	2.7678840
C	-0.9350110	-3.2359740	0.9746650
H	0.0434460	-3.5969400	1.2582060
C	-1.5999040	-3.5186420	-0.2575360
H	-1.2047410	-4.1124300	-1.0703680
C	-2.8849830	-2.8997530	-0.2241510
H	-3.6341420	-2.9472790	-1.0035070
C	-0.7406330	2.7056020	-2.0465930
H	-0.6471800	2.2380830	-3.0183220
C	0.3281080	3.1616790	-1.2227220
H	1.3816390	3.1158550	-1.4585570
C	-0.2404320	3.7378680	-0.0454290
H	0.3096130	4.1828030	0.7724280
C	-1.6608500	3.6437610	-0.1430980
H	-2.3741050	4.0093250	0.5838880
C	-1.9717200	3.0006810	-1.3765600
H	-2.9639970	2.7874810	-1.7533020
H	-0.4499470	-1.7021750	-1.4786320
C	2.1493770	-0.3557200	1.4656630
C	1.4776930	-0.9493110	2.7193780
H	0.6595260	-0.2887690	3.0386300
H	1.0333380	-1.9226870	2.4877950
C	2.4873670	-1.1079430	3.8718300
H	1.9700690	-1.5019830	4.7547250
H	3.2386610	-1.8592570	3.5891320
C	3.1890980	0.2149510	4.2061960
H	3.9397750	0.0562670	4.9887620
H	2.4552240	0.9243130	4.6152320
C	3.8420790	0.8231110	2.9583560
H	4.6658090	0.1779600	2.6206810
H	4.2862000	1.7977690	3.1931890
C	2.8255590	0.9939850	1.8148920
H	2.0488870	1.7053310	2.1250720
H	3.3182210	1.4265550	0.9386740
H	2.9296690	-1.0544890	1.1307970
H	0.0273560	1.6815930	1.3440000

G = -1561.88483 a.u.

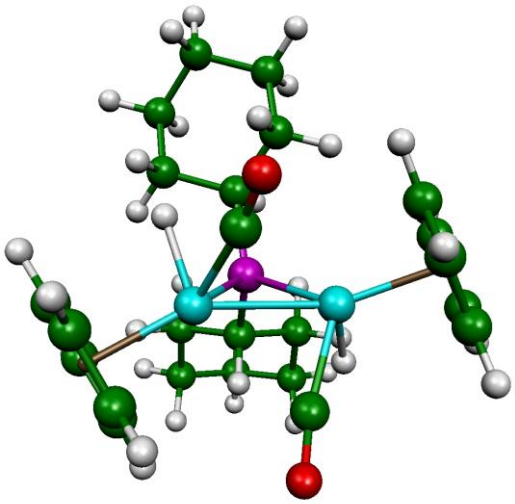
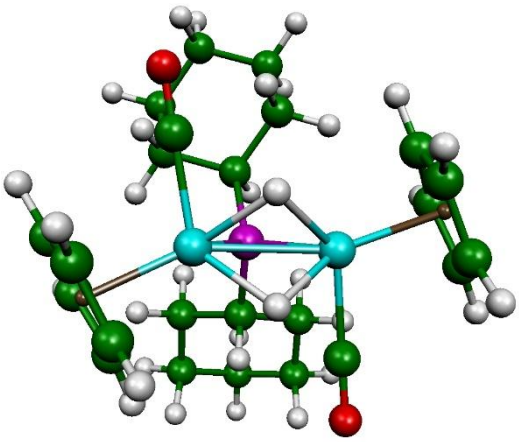


Table S6. Cartesian Coordinates for the Optimized Structure of **3HH**.

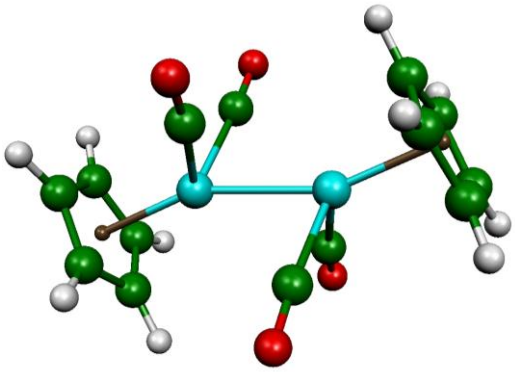
W	10.8887820	13.1664800	3.5002500
W	8.8319630	13.5436430	4.9940480
P	10.4790560	15.3014590	4.6340100
O	9.6351020	14.3888120	0.8755930
O	10.0310920	12.8105450	7.8218700
C	10.1103380	13.9720430	1.8437310
C	9.6019640	13.1241710	6.7955860
C	12.3446600	11.3588420	3.4293630
H	12.0545530	10.4099390	3.8615000
C	13.0334470	12.4202450	4.1137050
H	13.3440360	12.4102720	5.1496060
C	13.2806910	13.4615630	3.1762500
H	13.7933320	14.3925970	3.3723220
C	12.7367600	13.0613730	1.9267250
H	12.7834180	13.6309070	1.0072920
C	12.1542420	11.7547440	2.0748850
H	11.7081240	11.1625040	1.2877310
C	7.0281910	15.0517460	5.6172080
H	7.1850980	16.0867560	5.8842440
C	6.8270990	14.5410120	4.3031860
H	6.7782830	15.1255940	3.3938360
C	6.6290440	13.1198120	4.4079180
H	6.4068810	12.4492040	3.5880470
C	6.7229500	12.7561150	5.7832410
H	6.5816540	11.7678310	6.1988140
C	6.9666070	13.9596150	6.5241110
H	7.0677870	14.0287090	7.5998570
C	10.0619640	16.7730270	3.5341130
H	9.3214200	16.3655550	2.8330420
C	11.2827120	17.2447490	2.7090690
H	12.0602720	17.6243330	3.3876500
H	11.7222870	16.3996930	2.1659960
C	10.8911470	18.3566620	1.7188100
H	10.2066180	17.9397500	0.9662980
H	11.7833760	18.6929260	1.1772020
C	10.2159480	19.5388970	2.4272880
H	9.8989470	20.2884360	1.6931660
H	10.9442520	20.0345550	3.0854030
C	9.0144490	19.0729880	3.2607840
H	8.2305920	18.6891940	2.5917690
H	8.5748640	19.9169830	3.8054860
C	9.4125580	17.9711880	4.2606590
H	8.5309990	17.6486510	4.8280590
H	10.1193440	18.3930730	4.9871230
C	11.5212850	16.0385940	6.0260600
H	11.9588030	16.9404860	5.5742510
C	10.6614930	16.4845760	7.2339730
H	9.8499100	17.1448970	6.9107450
H	10.1904700	15.6010950	7.6826350
C	11.5191080	17.1908400	8.2994110
H	11.9145500	18.1292770	7.8847590
H	10.8846540	17.4690010	9.1495050
C	12.6817330	16.3038940	8.7636960
H	12.2818150	15.4241650	9.2882180
H	13.3048360	16.8425090	9.4868410
C	13.5331090	15.8441420	7.5728510
H	14.3277330	15.1666320	7.9078300
H	14.0336590	16.7144310	7.1244490
C	12.6851440	15.1429340	6.4948050
H	13.3232560	14.8795090	5.6447490
H	12.2878540	14.2035880	6.9017950
H	10.0702490	12.1383600	4.8750650
H	9.0918480	12.6465020	3.3248740



G = -1561.876617 a.u.

Table S7. Cartesian Coordinates for the Optimized Structure of $[W_2Cp_2(CO)_4]$.

O	0.2129080	3.1349540	0.3928230
O	-2.5440150	-0.0493450	1.8790780
C	2.6816830	0.2648200	2.0467670
C	1.8280050	0.8279310	3.0463910
C	0.9574450	-0.1892350	3.5134390
C	1.2588980	-1.3969880	2.8101080
C	2.3297450	-1.1153310	1.9027140
H	3.4720720	0.7814490	1.5186340
H	1.8336090	1.8583580	3.3769980
H	0.1842880	-0.0676680	4.2608400
H	0.7836350	-2.3573870	2.9595800
C	0.2741550	1.9871990	0.6085050
C	-1.4306960	0.0179920	1.5275650
H	2.8122380	-1.8294260	1.2474820
O	-0.2373280	-3.1318250	-0.4473310
O	2.5195590	0.0525020	-1.9335950
C	-2.7061360	-0.2617140	-2.1012640
C	-1.8524560	-0.8248140	-3.1008920
C	-0.9819080	0.1923610	-3.5679420
C	-1.2833710	1.4001100	-2.8646080
C	-2.3542110	1.1184400	-1.9572110
H	-3.4965180	-0.7783520	-1.5731300
H	-1.8580500	-1.8552420	-3.4315010
H	-0.2087520	0.0708030	-4.3153450
H	-0.8081170	2.3605140	-3.0140800
C	-0.2985860	-1.9840710	-0.6630100
C	1.4062420	-0.0148460	-1.5820780
H	-2.8367100	1.8325300	-1.3019760
W	0.4942950	0.0989880	1.1212860
W	-0.5187470	-0.0958610	-1.1757900



G = -975.993614 a.u.

Table S8. Relative Gibbs free energies (kcal/mol) at 298K of different isomers of the hydride complex **2**.

	2B	**2T**	**2C**
ΔG_{gas}	0.0	3.4	16.1

Table S9. Relative Gibbs free energies (kcal/mol) at 298K of different isomers of the cation in complex **3**.

	3B	**3T**	**3HH**
ΔG_{gas}	0.0	0.9	6.1

Table S10. AIM analysis for the DFT-optimized structures of compounds **2**. Values of the electron density at the bond critical points (ρ) are given in eÅ^{-3}; values of the laplacian of ρ at these points ($\nabla^2\rho$) are given in eÅ^{-5}.[a]

Bond	**2B**		Bond	**2T**		Bond	**2C**	
	ρ	$\nabla^2\rho$		ρ	$\nabla^2\rho$		ρ	$\nabla^2\rho$
W–W	0.644	1.200	W–W	0.629	1.422	W–W	0.655	1.094
W1–H$_{brid}$	0.522	3.627	W1–H	0.782	1.723	W1–H	0.780	1.767
W2–H$_{brid}$	0.518	3.424	W1–C	0.919	7.571	W1–C	0.862	4.489
W1–C	0.961	10.088	W2···C	Not located		W2···C	0.562	5.688
W2–C	0.36	10.153	W2–C	0.969	9.591	W2–C	0.882	10.276

[a] For comparison, the values computed for the W–W bcp in [$W_2Cp_2(CO)_4$] were $\rho = 0.652$ and $\nabla^2\rho = 1.667$; (W–W = 2.518 Å)

Table S11. AIM analysis for the DFT-optimized structures of compounds **3**. Values of the electron density at the bond critical points (ρ) are given in eÅ^{-3}; values of the laplacian of ρ at these points ($\nabla^2\rho$) are given in eÅ^{-5}.

Bond	**3B**		Bond	**3T**		Bond	**3HH**	
	ρ	$\nabla^2\rho$		ρ	$\nabla^2\rho$		ρ	$\nabla^2\rho$
W–W	0.615	1.470	W–W	0.614	1.566	W–W	0.652	1.667
W1–H$_{brid}$	0.537	3.582	W1–H$_{term}$	0.795	1.533	W1–H1$_{brid}$	0.516	2.889
W2–H$_{brid}$	0.522	3.031	W2–H$_{term}$	0.799	1.536	W2–H1$_{brid}$	0.521	3.066
W2–H$_{term}$	0.766	1.664	W1–C	0.897	7.902	W1–H2$_{brid}$	0.515	3.262
W1–C	0.879	11.945	W2–C	0.907	7.762	W2–H2$_{brid}$	0.512	2.717
W2–C	0.928	14.061						