Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Insertion, Coupling and Elimination Processes in the Reactions of the Unsaturated Alkyl-Bridged Complexes $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2R)(\mu\text{-}PCy_2)(CO)_2]$ (R = H, Ph) with Isocyanides and Secondary Phosphines.

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Structural Characterization of $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$

A few single black crystals of $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$ could be grown through the slow diffusion of a layer of petroleum ether into the toluene reaction mixture of compound **1a** with $HPEt_2$. The crystallographic analysis was performed as described for compound **8b**. The molecule of the complex was found to be placed on the symmetry operation –x+1,–y+1,–z+1. *Spectroscopic data*: ^{1}H NMR (toluene-d_8): δ 4.93 (s, 20H, Cp), 2.92-1.03 (m, 44H, Cy). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 163.0 (s, μ-PCy_2).

Crystals of this compound display centrosymmetric molecules made up from cisoid MoCp fragments bridged by symmetric PCy_2 and oxo ligands, with the resulting $Mo_2(\mu\text{-}P)(\mu\text{-}O)$ subunits being in turn connected to each other *via* almost linear (Mo–O–Mo = 168.6(1)^o) and essentially symmetrical oxygen bridges (Figure SX and Table SX), these defining and almost planar Mo_4O_2 ring. The corresponding Mo–O lengths are all similar and quite short (ca. 1.90 Å), significantly shorter than the reference values for Mo–O single bonds (ca. 2.20 Å),[1] and therefore indicative of multiple bonding, but still longer than the values of ca. 1.70 Å typically found for organometallic complexes with terminal oxo ligands.[2] Interestingly, the same comment applies to the lengths involving the angular O1 bridge within each Mo_2 subunit (1.921(2) Å). We have recently shown that angular O bridges between Mo atoms can be involved in π interactions with the metal centres, which is translated into relatively short Mo–O lengths below 1.9 Å,[3] whereby we might consider the angular O1 ligands in $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$ as contributing with four electrons to the dimetal centre. The multiplicity in the Mo–O bond of the almost linear O2 bridge is a more common finding, and it has been previously found in related molecules having a single linear O bridge such as the complexes $[Mo_2Cp^*_2(\mu\text{-}O)(O)_4]$,[4] and $[Mo_2Cp_4(\mu\text{-}CH_2PPh_2)(\mu\text{-}OPPh_2)(\mu\text{-}O)_3(CO)_2]$ (see ref. 30 in main text). Only two other organometallic complexes appear to have been characterized so far as having two O bridges defining an M_4O_2 ring: the carbyne cluster $[W_3(\mu\text{-}CEt)(\mu\text{-}O)_2(O^tBu)_5]_2$ (W–O–W = 156.0(5)^o), and the heterometallic hydride $[ReWCp^*(\mu\text{-}H)(\mu\text{-}C_2Ph)(CO)_2(\mu\text{-}O)]_2$ (W–O–Re = 173.0(4)^o).[5] The O bridge in the first complex displays W–O lengths of 1.755(8) and 2.119(8) Å, and its bonding has been described in terms of a W═O→W interaction,[5a] and a similar asymmetry was found in the WRe complex (W–O = 1.728(6), Re–O = 2.162(6) Å).[5b] The situation in $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$ is obviously different, since it displays symmetrical bridges with Mo–O distances of ca. 1.90 Å, midway between the above figures, thus denoting a fully delocalized π interaction along the Mo–O–Mo chain. In any case, this interaction allows for the antiferromagnetic coupling of both $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}O)(O)]$ subunits (which, if isolated, would have an odd number of electrons), thus yielding a diamagnetic molecule. By considering the bridging oxo ligands is this molecule as formal 4-electron donors, we then would have a total of 31 electrons per Mo_2 subunit, which leads in turn to a formal intermetallic bond order somewhere between 2 and 3. Indeed the intermetallic length of 2.6112(4) Å in $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$ is quite short,

only slightly shorter than the lengths determined for closely related molecules having double Mo=Mo bonds, such as $[Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2]$ (2.632(1) Å), and $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CPh)(CO)_2]$ (2.666(1) Å), (see refs. 15a and 12a in main text) but still longer than the intermetallic separations in related 30-electron complexes with only two bridging ligands connecting the metal centres, such as the cation $[Mo_2Cp_2(\mu\text{-}PCy_2)_2(H)(CO)]^+$ (2.534(2) Å),[6] and the hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (2.528(2) Å). All of this suggests that the actual intermetallic bond order in $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$ might be close to 2.

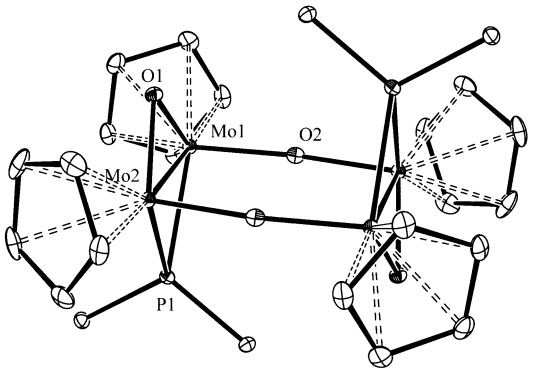

Figure SX. ORTEP drawing (30% probability) of the centrosymmetric molecule of $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$, with H atoms and cyclohexyl rings (except the C1 atoms) omitted for clarity.

Table SX. Selected Bond Lengths (Å) and Angles (deg) for $[Mo_4Cp_4(\mu\text{-}PCy_2)_2(\mu\text{-}O)_4]$.

Mo1–Mo2	2.6112(4)	Mo1–P1–Mo2	67.02(2)
Mo1–P1	2.3654(9)	Mo1–O1–Mo2	85.7(1)
Mo2–P1	2.3642(8)	O1–Mo1–P1	102.8(1)
Mo1–O1	1.921(2)	O1–Mo2–P1	102.8(1)
Mo2–O1	1.921(2)	Mo1–O2–Mo2´	168.6(1)
Mo1–O2	1.904(2)	O2–Mo1–Mo2	95.2(1)
Mo2–O2´	1.894(2)	O2–Mo1–P1	93.2(1)
		O2–Mo1–O1	102.5(1)

References

1. B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* 2008, 2832.
2. F. Bottomley, L. Sutin, *Adv. Organomet. Chem.* 1988, **28**, 339.
3. M. E. García, D. García-Vivó, S. Melón, M. A. Ruiz, C. Graiff, A. Tiripicchio, *Inorg. Chem.* 2009, **48**, 9282.
4. J. W. Faller, Y. Ma, *J. Organomet. Chem.* 1988, **340**, 59.
5. (a) F. A. Cotton, W. Schwotzer, E. S. Shamshoum, *Organometallics* 1983, **2**, 1340. (b) H. L. Wu, G. L. Lu, Y. Chi, L. J. Farrugia, S. M. Peng, G. H. Lee, *Inorg. Chem.* 1996, **35**, 6015.
6. M. A. Alvarez, M. E. García, M. E. Martínez, A. Ramos, M. A. Ruiz, D. Sáez, *Inorg. Chem.* 2006, **45**, 6965.

Computational Details

All the DFT computations were carried out using the GAUSSIAN03 package,[1] in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional[2] and the Lee−Yang−Parr correlation functional.[3] A accurate numerical integration grid (99,590) was used for all the calculations via the keyword Int=Ultrafine. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for the metal atoms.[4] The light elements (P, O, C, N and H) were described with the 6-31G* basis.[5] Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of related compounds, and frequency analyses were performed for all the stationary points to ensure that a minimum structure with no imaginary frequencies was achieved.

(1)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.
(2) Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
(3) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785.
(4) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.
(5) (a) Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta 1973, 28, 213. (b) Petersson, G. A.; Al-Laham, M. A. J. Chem. Phys. 1991, 94, 6081. (c) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley,W. A.; Mantzaris, J. J. Chem. Phys. 1988, 89, 2193.

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

P	-1.3082320	-0.1286260	-0.1120230
O	0.8227750	-2.5127490	2.7270500
C	0.6218160	0.9382980	-2.4532170
C	0.7889570	-2.0628120	1.6432330
C	1.4611400	0.2134790	0.9584130
C	0.6026710	-2.3935380	-2.4809920
H	0.3201300	-1.7758790	-3.3201060
C	1.9191340	-2.5766450	-1.9770940
H	2.8178090	-2.1199520	-2.3727130
C	1.8641290	-3.4454280	-0.8479350
H	2.7045830	-3.8158320	-0.2775770
C	0.4843680	-3.7741200	-0.6369600
H	0.0982830	-4.4302590	0.1317870
C	-0.2836720	-3.1219330	-1.6400030
H	-1.3558540	-3.1908270	-1.7543490
C	-0.1812220	3.5784670	-1.1444800
H	-0.7668980	3.7226130	-2.0422690
C	-0.6979840	3.3692480	0.1613950
H	-1.7450000	3.3219370	0.4219930
C	0.3930090	3.2487680	1.0641120
H	0.3223280	3.0874490	2.1312570
C	1.5967160	3.3810220	0.3101660
H	2.6033270	3.3333410	0.7059970
C	1.2496220	3.5949430	-1.0569130
H	1.9391920	3.7843430	-1.8678520
C	1.4988840	1.1029830	-4.8104060
C	2.9661800	1.2363520	-4.3661460
H	3.3172680	0.3085300	-3.9029670
H	3.0796360	2.0422330	-3.6340490
H	3.6055020	1.4563280	-5.2286510
C	1.3414830	-0.0482310	-5.8183790
H	1.6850530	-0.9947650	-5.3877230
H	1.9338220	0.1530070	-6.7177390
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H	-5.8520570	-0.0101740	-2.3198260
C	-4.0473190	0.7110160	-3.2708790
H	-4.5170680	1.6522850	-3.5858470
H	-3.3819660	0.4036210	-4.0913310
C	-3.2029880	0.9459380	-2.0053460
H	-3.8421800	1.3710820	-1.2196340
H	-2.4168820	1.6800540	-2.2100930
C	-2.2188050	-0.0154640	1.5467220
H	-1.4160520	0.3691550	2.1939820
C	-3.3899560	0.9881400	1.6134240
H	-3.0894470	1.9640720	1.2176960
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C	-3.9096050	1.1495260	3.0540160
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H	-4.7536440	1.8517830	3.0688570
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H	-5.1973850	-0.5858500	3.1130580
H	-4.6423790	-0.0662180	4.7017730
C	-3.1805150	-1.2198080	3.5735520
H	-3.5095830	-2.1944500	3.9567650
H	-2.3523290	-0.8952740	4.2205520
C	-2.6594990	-1.3765340	2.1336350
H	-3.4537370	-1.8097060	1.5117970
H	-1.8223820	-2.0795110	2.1172320
C	1.9988950	0.4464780	2.3408140
H	2.5201240	1.4110270	2.3889800
H	1.1887020	0.4540050	3.0756240
H	2.7103880	-0.3394640	2.6240610
Mo	0.7764960	-1.4483290	-0.1856290
Mo	0.5749170	1.4033860	-0.4991380
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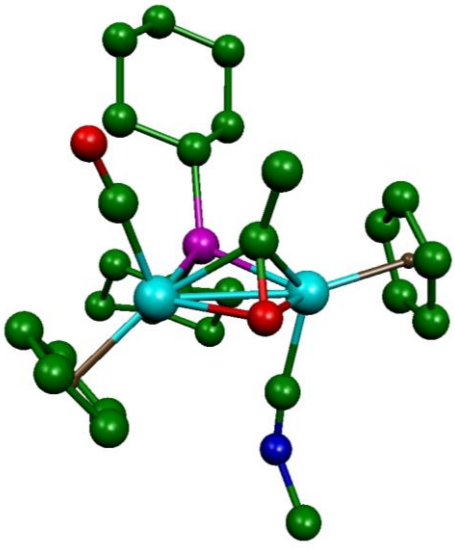

G (a.u.) = -1850.753955

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

P	-1.2179570	-0.1917840	-0.0741460
O	0.8414770	0.5496060	-3.4640690
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C	0.8037670	0.6942830	-2.3026060
C	1.4176270	0.0044840	1.1430120
C	0.8278460	-2.4740380	-2.3856660
H	0.6893270	-1.8375330	-3.2461800
C	2.0678590	-2.7591490	-1.7476130
H	3.0325600	-2.3627480	-2.0390410
C	1.8289990	-3.6490670	-0.6609390
H	2.5771090	-4.0966930	-0.0223180
C	0.4125880	-3.8775850	-0.6048080
H	-0.1019380	-4.5149700	0.1009510
C	-0.1920390	-3.1545220	-1.6687980
H	-1.2475900	-3.1420670	-1.8993870
C	0.1545170	3.4232760	-1.1864460
H	-0.3866670	3.5617940	-2.1126650
C	-0.4200310	3.3147220	0.1087630
H	-1.4769090	3.3390880	0.3318100
C	0.6305480	3.1920670	1.0598510
H	0.5119650	3.1014190	2.1310580
C	1.8639310	3.2145860	0.3471000
H	2.8510200	3.1219510	0.7826610
C	1.5813230	3.3633700	-1.0432030
H	2.3088170	3.4609060	-1.8374340
C	1.2723160	-3.6060140	3.8735680
C	2.7618330	-3.7318470	3.5072330
H	3.2175550	-2.7456390	3.3718690
H	2.8862850	-4.2945900	2.5759500
H	3.3056700	-4.2570240	4.3006990
C	1.1024940	-2.8129630	5.1822620
H	1.5470350	-1.8164190	5.0941450
H	1.5927830	-3.3381910	6.0096700
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H	-0.4279880	-4.9165650	4.2553450
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H	-2.9020340	2.0035440	1.1903880
H	-4.1063070	0.7565420	0.8964380
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H	-4.7367040	0.0739030	4.5950120
C	-3.3072480	-1.1718210	3.5234820
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H	-3.5317480	-1.7403890	1.4513210
H	-1.9454420	-2.1150380	2.1228610
C	1.7675250	0.2864340	2.5739170
H	2.2718280	1.2558010	2.6704680
H	0.8690850	0.2977100	3.1974990
H	2.4460510	-0.4842800	2.9634880
Mo	0.8357810	-1.5973000	-0.0511000
Mo	0.7544960	1.2551800	-0.4115140
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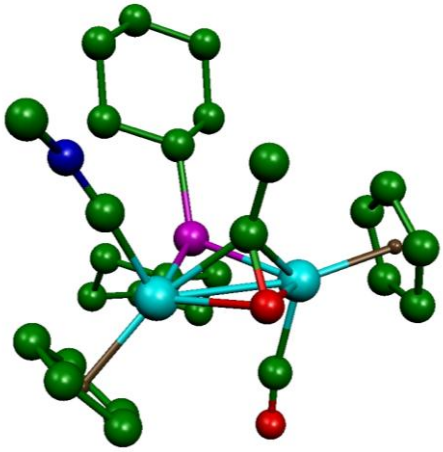
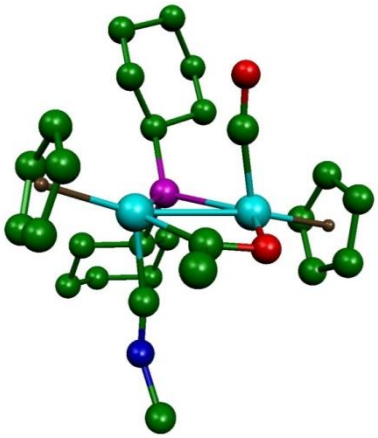
N	0.5327770	-2.9003560	2.8252070



G (a.u.) = -1850.751803

Table S3. Cartesian Coordinates for the Optimized Structure of **3A**

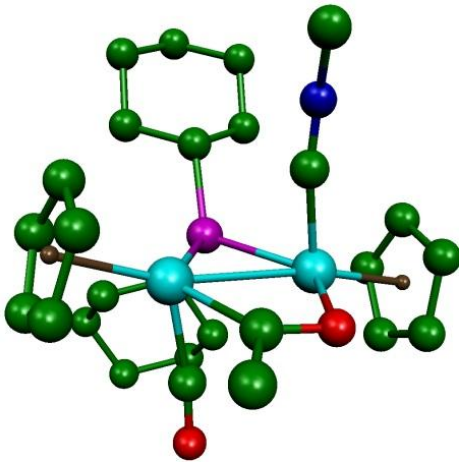
Mo	1.73892	4.90986	12.74858
Mo	4.15619	3.83667	13.51509
P	2.82631	2.95409	11.67163
C	1.10283	3.62051	14.13010
C	4.58413	5.30374	12.32240
N	0.54264	2.88928	14.90172
O	5.04064	6.14994	11.64314
O	3.58613	5.35384	14.97444
C	2.50814	5.82843	14.50426
C	1.95062	6.98290	15.32529
H	2.38411	6.96977	16.33211
H	0.85963	6.96246	15.39019
H	2.23591	7.92940	14.84649
C	-0.53178	5.10071	12.01528
H	-1.23827	4.30374	12.20492
C	0.24440	5.26838	10.83763
H	0.24355	4.60528	9.98390
C	1.02241	6.45028	10.98027
H	1.73072	6.83814	10.25965
C	0.72659	7.02289	12.24787
H	1.13585	7.94665	12.63251
C	-0.24042	6.18953	12.89385
H	-0.71329	6.37294	13.84844
C	5.53282	3.16682	15.36743
H	5.27874	3.52926	16.35504
C	5.09527	1.94972	14.78953
H	4.46620	1.20594	15.26151
C	5.59596	1.89680	13.45590
H	5.45271	1.08631	12.75678
C	6.36784	3.07042	13.21943
H	6.91888	3.29930	12.31793
C	6.32696	3.86747	14.40785
H	6.82668	4.81394	14.56193
C	1.92939	1.29383	11.84793
H	1.71973	1.24697	12.92473
C	0.56958	1.28346	11.11522
H	0.73280	1.39205	10.03208
H	-0.02427	2.14687	11.43384
C	-0.21342	-0.01614	11.37373
H	-0.48822	-0.06072	12.43817
H	-1.15494	-0.00401	10.80874
C	0.61093	-1.25951	11.01220
H	0.05121	-2.17309	11.25099
H	0.78658	-1.27515	9.92604
C	1.96184	-1.25472	11.74110
H	2.56199	-2.12372	11.44063
H	1.78952	-1.35274	12.82348
C	2.74770	0.04179	11.47077
H	3.69129	0.02080	12.02808
H	3.01195	0.07537	10.40453
C	3.45220	2.91271	9.87430
H	2.78796	2.19633	9.36692
C	3.34243	4.25371	9.12206
H	2.30919	4.61195	9.14231
H	3.94880	5.01162	9.63192
C	3.80998	4.12673	7.66011
H	3.12604	3.45596	7.11791
H	3.74360	5.10488	7.16594
C	5.23879	3.57550	7.56126
H	5.52956	3.45230	6.50991
H	5.93816	4.30303	7.99850
C	5.36289	2.24271	8.31135
H	6.39988	1.88237	8.28412
H	4.75446	1.48022	7.80165
C	4.89651	2.37332	9.77203
H	4.98320	1.40377	10.27536
H	5.56215	3.06426	10.30527
C	0.29544	2.44540	16.25997
C	1.36135	1.39491	16.62894
C	-1.10882	1.81773	16.31348
C	0.38394	3.65427	17.21155
H	2.36310	1.83458	16.58440
H	1.32266	0.54614	15.93811
H	1.19007	1.02277	17.64524
H	-1.32393	1.45508	17.32462
H	-1.18134	0.97442	15.61886
H	-1.87181	2.55400	16.03973
H	1.37436	4.11701	17.15375
H	0.20494	3.33765	18.24544
H	-0.36547	4.40795	16.94764



G (a.u.) = -1850.762121

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

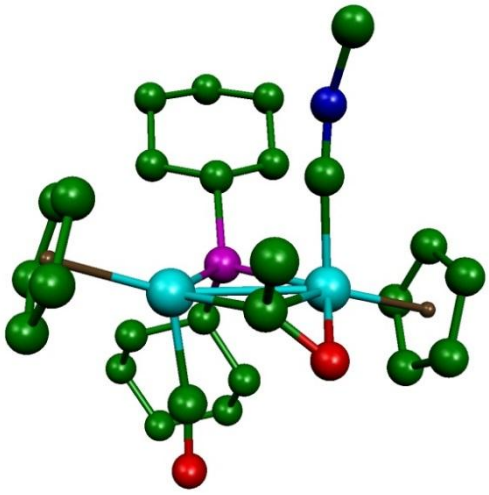
Mo	1.67064	4.86760	12.75453
Mo	4.10745	3.85912	13.54857
P	2.74750	2.96665	11.67988
C	1.13630	3.57207	14.15510
C	4.62708	5.30885	12.35186
N	0.58629	2.82478	14.91988
O	5.09257	6.16222	11.69005
O	2.41364	6.10054	14.39624
C	3.50832	5.54454	14.70290
C	4.27289	6.26420	15.80529
H	3.62921	7.01437	16.27875
H	5.14276	6.77331	15.36984
H	4.64898	5.57046	16.56375
C	-0.59259	4.82289	12.11971
H	-1.20453	3.95368	12.31780
C	0.11969	5.09148	10.91593
H	0.15081	4.44893	10.04756
C	0.74664	6.36501	11.04050
H	1.38209	6.83584	10.30142
C	0.44660	6.87429	12.32744
H	0.81525	7.80246	12.74408
C	-0.38779	5.92926	13.00616
H	-0.81430	6.04753	13.99257
C	5.17049	2.96915	15.50329
H	4.78611	3.17794	16.49260
C	4.84647	1.83641	14.70534
H	4.14915	1.05020	14.96473
C	5.60857	1.91209	13.50453
H	5.58943	1.19933	12.69301
C	6.40005	3.08748	13.55328
H	7.09174	3.42090	12.79096
C	6.13586	3.74790	14.78956
H	6.61604	4.65142	15.13786
C	1.92540	1.26811	11.84488
H	1.67000	1.22442	12.91148
C	0.60316	1.18027	11.05103
H	0.80925	1.28521	9.97504
H	-0.04931	2.01432	11.33037
C	-0.12396	-0.15530	11.28998
H	-0.44386	-0.20454	12.34153
H	-1.03833	-0.19644	10.68334
C	0.77821	-1.35783	10.98023
H	0.25500	-2.29662	11.20342
H	1.00442	-1.37407	9.90347
C	2.09169	-1.27701	11.77026
H	2.74860	-2.11670	11.50758
H	1.87446	-1.37409	12.84458
C	2.82237	0.05556	11.52122
H	3.73869	0.09003	12.12127
H	3.13334	0.09280	10.46771
C	3.41975	2.95519	9.89941
H	2.80332	2.21412	9.36766
C	3.26301	4.30081	9.16306
H	2.21305	4.60921	9.16170
H	3.81920	5.07913	9.69951
C	3.77493	4.22170	7.71281
H	3.14046	3.52679	7.14170
H	3.67304	5.20343	7.23189
C	5.23184	3.74418	7.64642
H	5.55760	3.65404	6.60198
H	5.88111	4.49778	8.11542
C	5.40156	2.40591	8.37775
H	6.45550	2.09755	8.37292
H	4.84552	1.62405	7.83835
C	4.89041	2.48578	9.82718
H	5.00547	1.50993	10.31235
H	5.51080	3.19207	10.39459
C	0.33709	2.37369	16.27555
C	0.80493	0.91073	16.39407
C	-1.17872	2.46409	16.53660
C	1.10660	3.26857	17.26623
H	1.88098	0.83239	16.20596
H	0.28167	0.27778	15.66992
H	0.60190	0.52800	17.40044
H	-1.41102	2.10967	17.54713
H	-1.73140	1.85063	15.81761
H	-1.52447	3.49892	16.44430
H	2.18258	3.21960	17.07069
H	0.92313	2.94140	18.29613
H	0.78969	4.31186	17.16935



G (a.u.) = -1850.761688

Table S5. Cartesian Coordinates for the Optimized Structure of **3** (isomer ***trans-syn***)

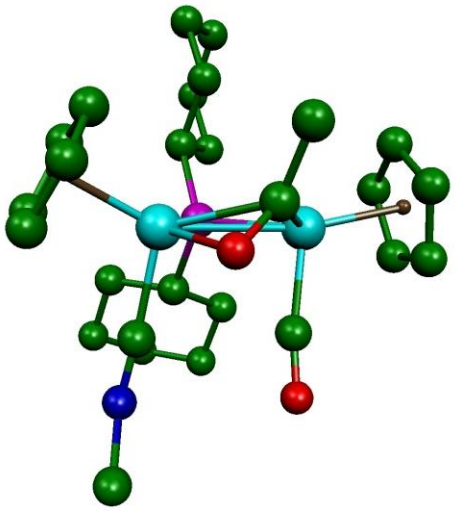
Mo	1.66497	4.75478	12.99594
Mo	4.16669	3.85097	13.75520
P	2.90636	2.96289	11.88569
C	0.97650	3.36028	14.21287
C	4.70620	5.34912	12.62257
N	0.42636	2.49171	14.84229
O	5.16256	6.22383	11.98815
O	2.52371	6.28888	14.28811
C	3.09660	5.29091	14.86698
C	2.90269	5.28850	16.38278
H	3.60110	6.02285	16.80807
H	3.10374	4.32269	16.85006
H	1.88859	5.62256	16.63376
C	-0.60080	4.62113	12.23970
H	-1.18118	3.72351	12.40207
C	0.17520	4.91103	11.08543
H	0.27588	4.27221	10.22020
C	0.75630	6.20112	11.25765
H	1.42341	6.69838	10.56614
C	0.34479	6.69893	12.52152
H	0.66347	7.63213	12.96491
C	-0.49986	5.73118	13.13896
H	-0.99515	5.83055	14.09453
C	5.79301	3.71743	15.54745
H	5.86752	4.50628	16.28349
C	4.96748	2.55895	15.63165
H	4.30806	2.30285	16.45061
C	5.17850	1.78196	14.45549
H	4.72134	0.82639	14.23830
C	6.14785	2.45524	13.64918
H	6.53606	2.11844	12.69833
C	6.51591	3.65127	14.32415
H	7.22436	4.38849	13.96893
C	2.17032	1.22065	11.97276
H	1.94926	1.10415	13.04126
C	0.83783	1.07765	11.20678
H	1.00754	1.24533	10.13230
H	0.13552	1.84829	11.54098
C	0.21174	-0.31514	11.40304
H	-0.07716	-0.42819	12.45850
H	-0.71279	-0.39531	10.81588
C	1.18544	-1.43918	11.02223
H	0.73410	-2.41965	11.22181
H	1.38036	-1.39913	9.94001
C	2.51417	-1.29759	11.77803
H	3.21910	-2.07731	11.46091
H	2.33879	-1.45232	12.85322
C	3.13982	0.09231	11.56125
H	4.07918	0.17180	12.12066
H	3.39957	0.19481	10.49852
C	3.54076	3.06296	10.09163
H	2.95137	2.31938	9.53359
C	3.33356	4.42834	9.40664
H	2.27426	4.69916	9.41410
H	3.86407	5.20508	9.97052
C	3.84007	4.42034	7.95208
H	3.22672	3.72434	7.35954
H	3.69929	5.41469	7.50832
C	5.31237	3.99867	7.85920
H	5.63216	3.95565	6.80994
H	5.93792	4.75885	8.34909
C	5.53523	2.64402	8.54438
H	6.59993	2.37596	8.52545
H	5.00616	1.85970	7.98183
C	5.03092	2.65891	9.99806
H	5.19396	1.67720	10.45620
H	5.62111	3.37694	10.58198
C	-0.16962	2.13528	16.12461
C	-1.23527	1.05622	15.86135
C	-0.81391	3.37893	16.76454
C	0.93963	1.57066	17.03228
H	-0.78613	0.17832	15.38553
H	-2.01980	1.43984	15.20045
H	-1.69955	0.74276	16.80281
H	-1.27003	3.11769	17.72615
H	-1.59573	3.78598	16.11421
H	-0.06598	4.15927	16.93547
H	1.42581	0.71176	16.55827
H	0.51437	1.24413	17.98790
H	1.69932	2.33236	17.23357



G (a.u.) = -1850.753282

Table S6. Cartesian Coordinates for the Optimized Structure of 3 (isomer ***cis-anti***)

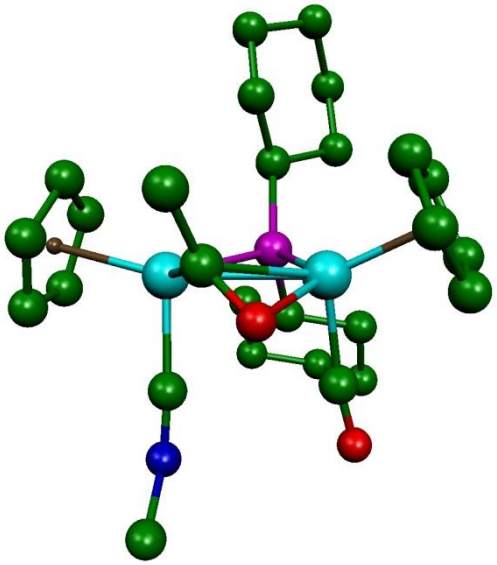
Mo	1.57466	4.87550	12.93493
Mo	4.15685	3.95781	13.49656
P	2.73842	3.07954	11.75296
C	0.50565	3.60388	14.07915
C	3.20614	3.02142	14.92017
N	-0.17627	2.85726	14.70372
O	2.79902	2.40040	15.82911
O	2.24115	5.90823	14.73565
C	3.35972	5.80038	14.08644
C	4.07359	7.13829	13.86034
H	3.35412	7.90397	13.54208
H	4.88143	7.08026	13.12576
H	4.49943	7.47436	14.81656
C	-0.39364	4.99854	11.62985
H	-0.98457	4.12263	11.40268
C	0.67508	5.51989	10.84068
H	1.03045	5.10640	9.90899
C	1.13354	6.72603	11.45185
H	1.94088	7.35441	11.09953
C	0.35418	6.94481	12.61993
H	0.50433	7.73563	13.34212
C	-0.58996	5.89444	12.73552
H	-1.32469	5.78962	13.52142
C	6.24957	3.03690	12.65083
H	6.29567	2.51066	11.70767
C	6.46679	4.43334	12.83915
H	6.68919	5.15345	12.06146
C	6.34070	4.71679	14.22783
H	6.45658	5.68485	14.69471
C	6.04306	3.50022	14.89841
H	5.91057	3.38111	15.96534
C	5.99541	2.45090	13.92046
H	5.82497	1.40210	14.12034
C	1.95617	1.36258	11.89852
H	1.43674	1.45529	12.86010
C	0.88257	1.05796	10.83385
H	1.34111	0.99071	9.83742
H	0.15674	1.88008	10.79053
C	0.15567	-0.26582	11.13400
H	-0.41830	-0.15521	12.06600
H	-0.57298	-0.48155	10.34120
C	1.14263	-1.43276	11.28579
H	0.60397	-2.35551	11.53780
H	1.63890	-1.61493	10.32046
C	2.20577	-1.12622	12.35138
H	2.92433	-1.95347	12.42212
H	1.71981	-1.04940	13.33533
C	2.94798	0.18893	12.05197
H	3.65490	0.41587	12.85827
H	3.54230	0.06014	11.13867
C	3.19486	3.30692	9.91789
H	2.24140	3.34048	9.36756
C	3.92727	4.64510	9.69211
H	3.35132	5.47698	10.10895
H	4.87344	4.62612	10.25088
C	4.22576	4.89991	8.20469
H	3.27823	5.01041	7.65582
H	4.76320	5.85066	8.09140
C	5.03622	3.75116	7.58915
H	5.19409	3.92328	6.51671
H	6.03396	3.72464	8.05225
C	4.33679	2.40508	7.81766
H	4.95104	1.58306	7.42730
H	3.39467	2.38609	7.24949
C	4.02896	2.15904	9.30671
H	3.50717	1.20372	9.40744
H	4.97249	2.05984	9.86152
C	-0.85280	2.41338	15.91170
C	-0.42322	0.95983	16.18231
C	-2.36919	2.49057	15.65722
C	-0.44010	3.33015	17.07851
H	0.66032	0.90389	16.31660
H	-0.70782	0.31001	15.34785
H	-0.91275	0.59228	17.09078
H	-2.91018	2.13630	16.54120
H	-2.65406	1.86674	14.80368
H	-2.67941	3.52118	15.45423
H	0.64299	3.29510	17.22249
H	-0.93316	3.00341	18.00117
H	-0.72881	4.36695	16.87713



G (a.u.) = -1850.751898

Table S7. Cartesian Coordinates for the Optimized Structure of 3 (isomer ***cis-anti-L***)

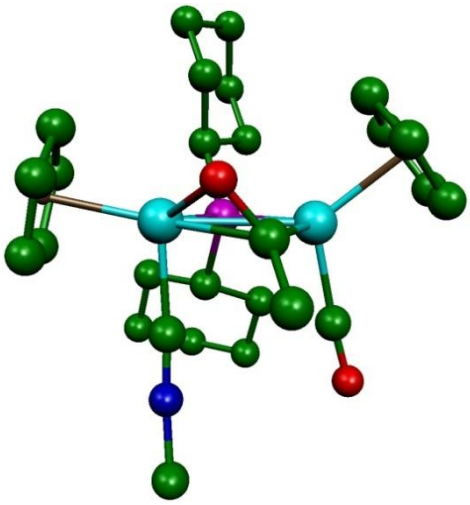
Mo	1.39031	4.63057	12.81174
Mo	3.84911	3.66704	13.75361
P	2.73258	2.91994	11.73388
C	0.43878	3.51213	14.14912
C	2.99464	2.16520	14.67749
N	-0.23570	2.82888	14.87871
O	2.63227	1.21121	15.24349
O	3.05761	5.04889	15.27737
C	2.61733	5.60144	14.19366
C	3.02913	7.07212	14.04351
H	2.43712	7.67432	14.74743
H	2.87394	7.46976	13.03687
H	4.08413	7.19693	14.31876
C	-0.77399	4.66936	11.68406
H	-1.35453	3.76621	11.55885
C	0.19689	5.18209	10.78435
H	0.48422	4.74430	9.83823
C	0.70282	6.40291	11.32842
H	1.45326	7.03808	10.87444
C	0.04285	6.64903	12.56410
H	0.20274	7.49585	13.21669
C	-0.85601	5.57735	12.79138
H	-1.51030	5.47458	13.64555
C	5.96443	3.41216	12.69810
H	6.06530	3.25976	11.63462
C	6.03989	4.66750	13.37257
H	6.14961	5.63815	12.90711
C	5.92351	4.41439	14.76482
H	5.86869	5.16401	15.54251
C	5.79646	3.01385	14.96533
H	5.70873	2.51644	15.92177
C	5.82320	2.38208	13.67771
H	5.80131	1.31864	13.48502
C	1.98828	1.18057	11.68014
H	1.37379	1.19202	12.58961
C	1.03344	0.94427	10.49218
H	1.59447	0.95243	9.54685
H	0.30134	1.75962	10.43350
C	0.30462	-0.40571	10.62266
H	-0.35792	-0.37112	11.49977
H	-0.34001	-0.56801	9.74858
C	1.29314	-1.57029	10.78162
H	0.74920	-2.51416	10.91634
H	1.87879	-1.67680	9.85576
C	2.24853	-1.33160	11.96043
H	2.97548	-2.15119	12.03421
H	1.67636	-1.33499	12.89937
C	2.98724	0.01276	11.83053
H	3.61670	0.17765	12.71151
H	3.65999	-0.03239	10.96419
C	3.32018	3.29171	9.96284
H	2.40229	3.24304	9.35663
C	3.87634	4.72403	9.84051
H	3.14896	5.44546	10.22840
H	4.76730	4.82545	10.47416
C	4.24433	5.07941	8.38950
H	3.33082	5.09580	7.77625
H	4.66398	6.09323	8.35069
C	5.23308	4.06779	7.79375
H	5.44818	4.31357	6.74598
H	6.18983	4.13496	8.33332
C	4.68672	2.63852	7.90605
H	5.41855	1.91632	7.52133
H	3.79260	2.54342	7.27191
C	4.31412	2.27667	9.35596
H	3.89084	1.26836	9.37502
H	5.22780	2.23810	9.96472
C	-0.73693	2.86606	16.26160
C	-0.35892	1.53341	16.92996
C	-2.26856	3.00151	16.18665
C	-0.11856	4.05426	17.01834
H	0.72643	1.40890	16.96147
H	-0.78296	0.69055	16.37428
H	-0.74839	1.50721	17.95403
H	-2.69471	2.99263	17.19613
H	-2.70438	2.17338	15.61834
H	-2.55594	3.94163	15.70264
H	0.97422	4.00894	16.98891
H	-0.44873	4.05001	18.06357
H	-0.42425	5.00343	16.56458



G (a.u.) = -1850.748314

Table S8. Cartesian Coordinates for the Optimized Structure of 3 (isomer ***cis-syn***)

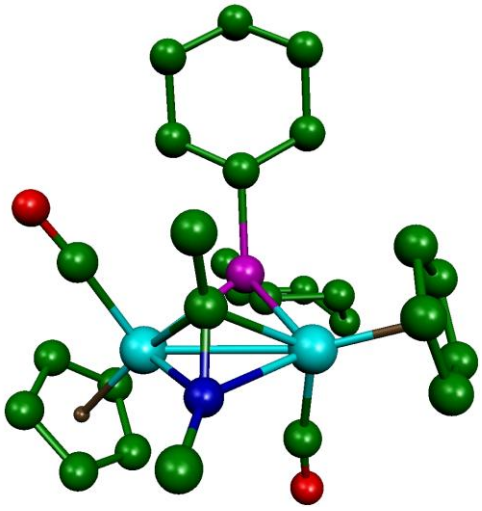
Mo	1.87649	4.85305	12.97763
Mo	4.38194	3.74509	13.67045
P	2.97352	2.94883	11.89181
C	1.09328	3.55056	14.31762
C	3.91537	2.29136	14.86804
N	0.55856	2.86044	15.11431
O	3.70644	1.41102	15.62591
O	3.02619	6.29839	14.00733
C	3.36724	5.26141	14.71353
C	3.13584	5.39456	16.20846
H	2.25255	6.01180	16.41950
H	4.00733	5.90042	16.64862
H	3.04110	4.42105	16.69283
C	-0.32373	4.68905	12.10391
H	-0.85759	3.74896	12.10908
C	0.50029	5.17515	11.04994
H	0.70684	4.67155	10.11653
C	0.96414	6.46842	11.42917
H	1.63567	7.09801	10.85909
C	0.40706	6.78940	12.69931
H	0.62019	7.68381	13.26938
C	-0.39295	5.70586	13.12363
H	-0.95670	5.64906	14.04440
C	6.45927	3.80246	12.43350
H	6.52793	3.37792	11.44147
C	6.18335	5.17194	12.74278
H	5.98415	5.96450	12.03467
C	6.21613	5.30405	14.15302
H	6.04414	6.22005	14.70254
C	6.51796	4.03266	14.72410
H	6.64773	3.82047	15.77686
C	6.68962	3.10311	13.64835
H	6.94974	2.05741	13.74423
C	2.06342	1.28410	11.98550
H	1.50677	1.38838	12.92472
C	1.03110	1.03985	10.86581
H	1.54055	0.95036	9.89644
H	0.34942	1.89635	10.78277
C	0.22459	-0.24822	11.11331
H	-0.38414	-0.12396	12.02180
H	-0.47923	-0.41378	10.28668
C	1.14508	-1.46533	11.28506
H	0.55163	-2.36358	11.49992
H	1.66909	-1.65696	10.33650
C	2.17869	-1.22680	12.39567
H	2.85774	-2.08578	12.47537
H	1.65963	-1.15074	13.36243
C	2.99042	0.05928	12.15708
H	3.67344	0.23278	12.99444
H	3.61379	-0.07667	11.26387
C	3.35976	3.17130	10.04128
H	2.39032	3.07560	9.52814
C	3.91131	4.57554	9.72900
H	3.23905	5.34562	10.12258
H	4.86581	4.71290	10.25077
C	4.12679	4.78595	8.22021
H	3.15595	4.74790	7.70299
H	4.53710	5.78825	8.03954
C	5.05529	3.71482	7.63117
H	5.16222	3.85287	6.54751
H	6.06073	3.83209	8.06235
C	4.53232	2.30615	7.94152
H	5.23091	1.54677	7.56636
H	3.58395	2.14773	7.40622
C	4.29848	2.09634	9.44932
H	3.88933	1.09463	9.61036
H	5.26177	2.12484	9.97724
C	0.00047	2.05834	16.17499
C	0.16806	0.57100	15.80838
C	-1.49115	2.42156	16.30917
C	0.75777	2.37362	17.48014
H	1.22718	0.32884	15.68341
H	-0.36146	0.33763	14.87863
H	-0.24442	-0.05477	16.60734
H	-1.94690	1.82146	17.10376
H	-2.02685	2.22166	15.37525
H	-1.61300	3.47995	16.56230
H	1.81732	2.12647	17.37220
H	0.33884	1.77840	18.29901
H	0.66396	3.43347	17.73746



G (a.u.) = -1850.746731

Table S9. Cartesian Coordinates for the Optimized Structure of 4

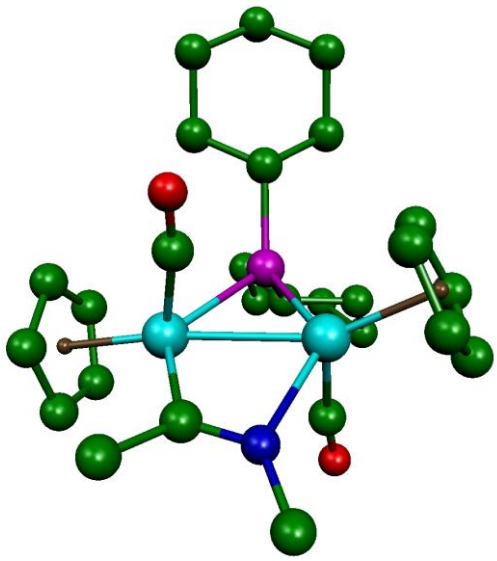
P	-1.2331430	-0.0471380	0.0899540
N	2.3594820	0.1375920	0.2813850
O	0.6995300	-2.6349630	2.8600290
O	0.8126920	0.8709260	-3.2663380
C	0.7377890	-2.1299350	1.7998740
C	0.7598950	0.9860910	-2.1016610
C	1.4597320	0.1772400	1.3003840
C	0.8734790	-2.2790310	-2.3493250
H	0.8418050	-1.6224810	-3.2065450
C	2.0441770	-2.7189570	-1.6722570
H	3.0602290	-2.4738860	-1.9483730
C	1.6633750	-3.5673550	-0.5972790
H	2.3270180	-4.1021160	0.0683120
C	0.2297560	-3.6338270	-0.5939570
H	-0.3783320	-4.2263380	0.0761980
C	-0.2448390	-2.8362620	-1.6740810
H	-1.2800890	-2.7133500	-1.9546340
C	0.1258190	3.7076470	-0.9587150
H	-0.1763710	3.8789760	-1.9838480
C	-0.7415550	3.4449360	0.1294230
H	-1.8189960	3.3881740	0.0721490
C	0.0490550	3.2727410	1.3032770
H	-0.3237180	3.0863230	2.3013320
C	1.4151990	3.4359540	0.9298900
H	2.2615770	3.4012160	1.6013630
C	1.4688400	3.7021170	-0.4728870
H	2.3561960	3.9070670	-1.0567390
C	3.8494480	0.1588580	0.2756590
C	4.3934290	1.3795210	1.0435630
H	4.1340310	1.3496010	2.1053160
H	4.0131580	2.3099770	0.6127550
H	5.4868530	1.3987780	0.9702410
C	4.4011220	-1.1311640	0.9110490
H	4.0941840	-1.2257370	1.9573030
H	5.4970220	-1.1240380	0.8794140
H	4.0466480	-2.0164550	0.3764210
C	4.3050000	0.2718450	-1.1875530
H	3.9325750	-0.5616710	-1.7875300
H	5.3993920	0.2752490	-1.2452070
H	3.9301130	1.1978410	-1.6354270
C	-2.4664510	-0.1940990	-1.3403640
H	-1.8096110	-0.5175050	-2.1594120
C	-3.5757560	-1.2538960	-1.1722030
H	-4.2599410	-0.9432880	-0.3718780
H	-3.1534310	-2.2162160	-0.8588980
C	-4.3870860	-1.4267340	-2.4693430
H	-3.7313050	-1.8252700	-3.2580570
H	-5.1792830	-2.1712090	-2.3165100
C	-4.9886570	-0.0934370	-2.9362510
H	-5.5220330	-0.2276310	-3.8859930
H	-5.7369970	0.2405060	-2.2018420
C	-3.9042750	0.9841360	-3.0802100
H	-4.3564700	1.9449770	-3.3590570
H	-3.2258670	0.7086320	-3.9010480
C	-3.0833080	1.1504570	-1.7882840
H	-3.7336020	1.5471440	-0.9967610
H	-2.2865580	1.8846340	-1.9467340
C	-2.1753810	0.0165250	1.7324480
H	-1.3681920	0.3129570	2.4176600
C	-3.2788800	1.0912990	1.8336980
H	-2.8974680	2.0662270	1.5110500
H	-4.1065960	0.8375430	1.1576050
C	-3.8280960	1.1992240	3.2685130
H	-3.0290050	1.5616480	3.9325740
H	-4.6282570	1.9502570	3.3048820
C	-4.3386900	-0.1536320	3.7841380
H	-5.2172930	-0.4559210	3.1944700
H	-4.6780480	-0.0606810	4.8238370
C	-3.2551390	-1.2352200	3.6679120
H	-3.6502880	-2.2074500	3.9897710
H	-2.4259560	-0.9958500	4.3498540
C	-2.7095690	-1.3454440	2.2327150
H	-3.5132970	-1.6968110	1.5735290
H	-1.9144280	-2.0952310	2.1949060
C	1.6654030	0.3985620	2.7729000
H	2.0682720	1.3976960	2.9735630
H	0.7139260	0.3108040	3.3047130
H	2.3490950	-0.3405660	3.2099310
Mo	0.8310040	-1.4199710	0.0100140
Mo	0.6685110	1.4747680	-0.1925760



G (a.u.) = -1850.77709

Table S10. Cartesian Coordinates for the Optimized Structure of 4 (μ-*C*:*N*-isomer)

P	-1.6270460	1.5239810	-0.7698040
N	1.8866250	3.1478500	-2.4577910
O	1.6754550	1.3139810	1.2369620
O	-1.3650650	3.2222920	-4.1405650
C	1.2037400	1.1543840	0.1715340
C	-0.8688520	3.2014640	-3.0780850
C	2.1681440	1.8988100	-2.2427120
C	-0.0891190	-1.1904920	-3.0785480
H	-0.7576330	-1.0362460	-3.9165580
C	1.3234980	-1.0178740	-3.0941000
H	1.9145440	-0.7572400	-3.9611460
C	1.8160090	-1.3100070	-1.7832470
H	2.8506870	-1.3339780	-1.4743500
C	0.6956870	-1.6523210	-0.9646900
H	0.7382950	-1.9496240	0.0745280
C	-0.4717140	-1.5906040	-1.7704750
H	-1.4765770	-1.8076650	-1.4406340
C	0.6873170	5.5757530	-0.5166410
H	1.6622940	5.9657630	-0.7697550
C	-0.5011050	5.7315020	-1.2827430
H	-0.6054550	6.2941890	-2.1998400
C	-1.5524750	5.0463780	-0.5963540
H	-2.5961480	5.0392950	-0.8756620
C	-0.9890960	4.4709600	0.5897880
H	-1.5276860	3.9440820	1.3618560
C	0.3944040	4.8074140	0.6347110
H	1.1012890	4.5015680	1.3954620
C	2.7430560	4.1148300	-3.2458110
C	1.8601830	5.2830440	-3.7295490
H	1.5111230	5.9083070	-2.9100980
H	0.9887440	4.9142780	-4.2776970
H	2.4443830	5.9199260	-4.4033010
C	3.8923210	4.6879280	-2.3901900
H	3.5087680	5.1089110	-1.4558450
H	4.4049460	5.4889320	-2.9369890
H	4.6403900	3.9361790	-2.1262680
C	3.2799130	3.4568080	-4.5415830
H	4.0313400	2.6862290	-4.3729750
H	3.7412980	4.2251500	-5.1722330
H	2.4526640	3.0127400	-5.1062620
C	-3.1605350	1.2751970	-1.8655190
H	-2.6982270	1.1739360	-2.8575560
C	-3.9776560	-0.0095750	-1.6122530
H	-4.4596830	0.0398700	-0.6273900
H	-3.3227610	-0.8868980	-1.5943100
C	-5.0663890	-0.2035870	-2.6841570
H	-4.5855070	-0.3639580	-3.6605170
H	-5.6432740	-1.1121170	-2.4664930
C	-5.9969890	1.0138900	-2.7727540
H	-6.7348310	0.8717370	-3.5728120
H	-6.5657890	1.1029300	-1.8348630
C	-5.1964500	2.3027420	-3.0052010
H	-5.8667400	3.1723460	-3.0130940
H	-4.7226000	2.2643830	-3.9966930
C	-4.1034210	2.4981220	-1.9391300
H	-4.5773080	2.6630130	-0.9620420
H	-3.5240580	3.3967950	-2.1699380
C	-2.0917450	1.1988040	1.0401150
H	-1.2503910	1.6679560	1.5693510
C	-3.3932060	1.8749410	1.5254630
H	-3.4110520	2.9366570	1.2538100
H	-4.2552530	1.4177870	1.0232190
C	-3.5722630	1.7179870	3.0467620
H	-2.7632790	2.2549450	3.5643780
H	-4.5120120	2.1904000	3.3613900
C	-3.5492390	0.2410050	3.4659100
H	-4.4300520	-0.2665900	3.0446790
H	-3.6307110	0.1533100	4.5568780
C	-2.2755780	-0.4566450	2.9671510
H	-2.2997480	-1.5236300	3.2250630
H	-1.4026060	-0.0303130	3.4827740
C	-2.0883720	-0.2915120	1.4478850
H	-2.8941920	-0.8245100	0.9253320
H	-1.1458260	-0.7531260	1.1373820
C	3.5628370	1.2993920	-2.3969440
H	4.3635340	2.0322220	-2.4979640
H	3.7754350	0.7078240	-1.5016820
H	3.6168290	0.6153240	-3.2513060
Mo	0.5164880	0.6541510	-1.5795770
Mo	-0.1012280	3.3680670	-1.2944670



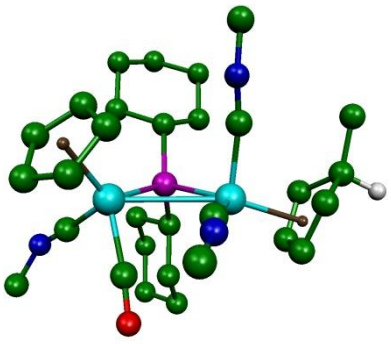
G (a.u.) = -1850.754293

Table S11. Relative Gibbs free energies (kcal/mol) at 298K of different isomers of the formimidoyl complex **4**.

	2	**2B**	**3A**	**3B**	**3**(trans-syn)	**3**(cis-anti)	**3**(cis-anti-L)	**3**(cis-syn)	**4**	**4**(C:N isomer)
ΔG_{gas}	14.5	15.9	9.4	9.7	14.9	15.8	18.1	19.1	0.0	14.3

Table S12. Cartesian Coordinates for the Optimized Structure of **5** (isomer **T**).

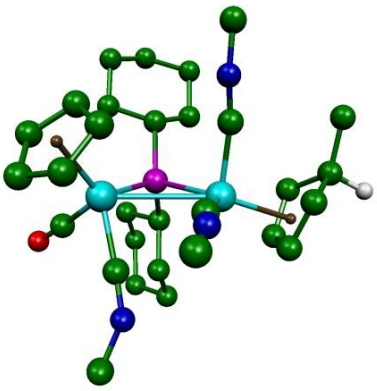
C	-0.01672	6.13572	15.05472
N	-0.33478	6.67437	16.07106
C	-0.34444	7.34943	17.26990
C	0.76427	8.11473	17.66476
C	0.74744	8.80245	18.87836
C	-0.37712	8.73211	19.71117
C	-1.48705	7.96864	19.31335
C	-1.47492	7.28712	18.10656
H	1.63099	8.16801	17.01388
H	1.61564	9.38709	19.15989
O	-0.49398	9.36207	20.91493
H	-2.34983	7.92773	19.97049
H	-2.33279	6.69904	17.79607
C	0.59679	10.14515	21.37270
H	1.50318	9.53868	21.50100
H	0.29162	10.54654	22.34075
H	0.81312	10.97576	20.68778
Mo	0.19860	5.44795	13.15937
Mo	2.54977	4.41214	14.87959
P	2.10993	4.00830	12.51877
C	-0.99774	3.94760	13.61162
C	2.86333	6.33660	14.93688
N	-1.60966	3.03566	14.10369
O	3.10810	7.48011	15.09124
C	4.45037	4.34236	14.32308
C	-0.84886	5.60359	10.81758
H	-0.60276	4.96051	9.97946
C	-0.06916	6.69251	11.21871
H	0.86582	7.00943	10.77225
C	-0.72057	7.32270	12.35306
H	-0.40783	8.23663	12.84457
C	-1.88006	6.54726	12.62905
H	-2.59918	6.81248	13.39732
C	-2.26414	5.80563	11.35115
H	-2.77461	6.52921	10.67746
C	1.89480	4.26296	17.20228
H	1.65678	5.15672	17.76293
C	0.96883	3.44668	16.49840
H	-0.09501	3.61466	16.41508
C	1.68373	2.35932	15.91300
H	1.25049	1.55906	15.32840
C	3.05325	2.50460	16.25695
H	3.85583	1.83432	15.97827
C	3.19056	3.68913	17.05098
H	4.10720	4.05468	17.49416
C	1.67468	2.23275	12.01413
H	0.81726	2.02568	12.66951
C	1.18348	2.07870	10.55920
H	1.98999	2.33562	9.85943
H	0.36562	2.78391	10.36938
C	0.71645	0.64080	10.26495
H	-0.18039	0.42239	10.86320
H	0.41863	0.55418	9.21143
C	1.80058	-0.39277	10.60236
H	1.42683	-1.40884	10.42068
H	2.66011	-0.25036	9.93009
C	2.26700	-0.24520	12.05800
H	3.06481	-0.96672	12.27851
H	1.43032	-0.48829	12.73033
C	2.75823	1.18344	12.35177
H	3.04537	1.27782	13.40467
H	3.66705	1.37279	11.76795
C	3.16739	4.71786	11.10414
H	2.47803	4.78052	10.24718
C	3.63760	6.15065	11.43134
H	2.79431	6.77764	11.74449
H	4.31717	6.11822	12.29012
C	4.36235	6.80108	10.24088
H	3.66085	6.91827	9.40040
H	4.69284	7.81121	10.51604
C	5.55888	5.95214	9.78889
H	6.04060	6.40335	8.91154
H	6.31190	5.93753	10.59009
C	5.12300	4.51412	9.47838
H	5.99332	3.90059	9.21025
H	4.46243	4.51916	8.59786
C	4.37907	3.86643	10.66212
H	4.05959	2.86225	10.36885
H	5.06670	3.74512	11.50780
C	-2.29191	1.83855	14.13704
C	-2.84095	1.38145	15.34269
C	-3.53764	0.17452	15.40018
C	-3.69821	-0.59570	14.24110
C	-3.15256	-0.14175	13.02942
C	-2.45754	1.05669	12.97479
H	-2.71694	1.98146	16.23864
H	-3.94834	-0.15130	16.34878
O	-4.35895	-1.78738	14.18342
H	-3.28625	-0.75060	12.14075
H	-2.03673	1.40224	12.03643
C	-4.92890	-2.29847	15.37746
H	-4.16408	-2.48147	16.14399
H	-5.39840	-3.24510	15.10398
H	-5.69108	-1.62019	15.78377
C	-3.19631	4.60024	11.42291
H	-2.77706	3.77788	12.00043
H	-3.41129	4.23210	10.41196
H	-4.15363	4.88196	11.87818
N	5.63305	4.24913	14.08690
C	6.83692	4.94507	14.09953
C	6.89356	6.30256	14.45202
C	8.11026	6.98469	14.45018
C	9.28924	6.31446	14.09682
C	9.23442	4.95706	13.74369
C	8.02312	4.28105	13.74312
H	5.97905	6.82134	14.72385
H	8.12436	8.03330	14.72472
O	10.52846	6.88615	14.06357
H	10.15738	4.45484	13.47170
H	7.97682	3.23160	13.46940
C	10.64503	8.25643	14.40832
H	10.06522	8.89534	13.72874
H	11.70500	8.50009	14.31466
H	10.32051	8.44281	15.44088



G (a.u.) = -2803.504197

Table S13. Cartesian Coordinates for the Optimized Structure of **5** (isomer **C**).

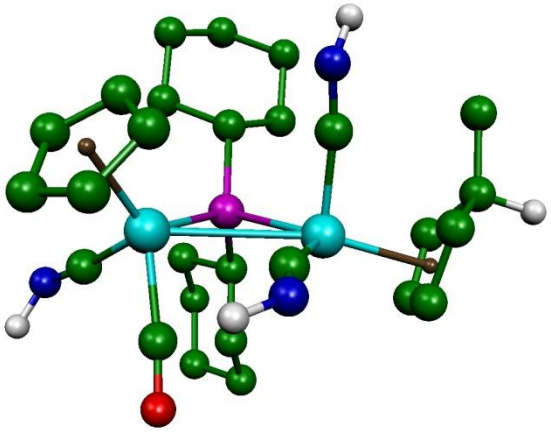
C	0.06576	6.14427	14.94681
N	-0.22980	6.67824	15.97105
C	-0.24283	7.34382	17.17433
C	0.88273	8.06545	17.60149
C	0.86332	8.74613	18.81895
C	-0.28249	8.71094	19.62472
C	-1.40939	7.98993	19.19570
C	-1.39373	7.31612	17.98474
H	1.76472	8.08948	16.97009
H	1.74546	9.29673	19.12463
O	-0.40509	9.33672	20.82934
H	-2.28814	7.97594	19.83246
H	-2.26476	6.76145	17.65029
C	0.70119	10.07940	21.31761
H	1.58265	9.44112	21.46325
H	0.38695	10.48571	22.28062
H	0.96183	10.90562	20.64303
Mo	0.20493	5.44412	13.04516
Mo	2.63905	4.43570	14.66021
P	2.06377	3.96761	12.33905
C	-0.98013	3.95546	13.56497
C	4.45591	4.36523	13.92735
N	-1.56308	3.04629	14.09398
O	5.57534	4.31144	13.58497
C	2.96634	6.37800	14.68088
C	-0.97463	5.55167	10.76978
H	-0.78919	4.87878	9.93953
C	-0.15095	6.63521	11.09234
H	0.76137	6.92125	10.58323
C	-0.72758	7.31259	12.24072
H	-0.36348	8.22828	12.69226
C	-1.88714	6.57644	12.60126
H	-2.55574	6.87843	13.40083
C	-2.35490	5.80577	11.36924
H	-2.88033	6.52276	10.70020
C	2.11610	4.33056	17.02270
H	1.90777	5.23380	17.57983
C	1.15265	3.49758	16.39120
H	0.08451	3.65845	16.37328
C	1.83631	2.40436	15.78200
H	1.37272	1.59269	15.23771
C	3.22431	2.56162	16.03766
H	4.01053	1.88415	15.73048
C	3.40291	3.76067	16.80318
H	4.34188	4.13554	17.18827
C	1.57827	2.18677	11.90139
H	0.75555	2.00718	12.60724
C	1.00801	2.00646	10.47886
H	1.77913	2.23644	9.73146
H	0.18986	2.71838	10.31691
C	0.50796	0.56875	10.24385
H	-0.35786	0.37630	10.89427
H	0.15310	0.46246	9.20999
C	1.59607	-0.47132	10.54662
H	1.20062	-1.48608	10.40914
H	2.41989	-0.35597	9.82625
C	2.14177	-0.29726	11.97140
H	2.94167	-1.02392	12.16566
H	1.33957	-0.51385	12.69296
C	2.66552	1.13088	12.20536
H	3.00955	1.24427	13.23923
H	3.54437	1.29433	11.57016
C	3.05395	4.62168	10.84961
H	2.31602	4.65878	10.03247
C	3.54743	6.06286	11.09791
H	2.72798	6.70346	11.44376
H	4.28288	6.05760	11.90949
C	4.19372	6.66832	9.84024
H	3.43867	6.75921	9.04405
H	4.54351	7.68584	10.05782
C	5.35622	5.79928	9.34019
H	5.77836	6.21686	8.41673
H	6.16144	5.81133	10.08901
C	4.90062	4.35192	9.11220
H	5.75154	3.72651	8.81152
H	4.18440	4.32617	8.27672
C	4.23483	3.74995	10.36485
H	3.89739	2.73649	10.12953
H	4.97722	3.65977	11.16668
C	-2.25042	1.85579	14.18854
C	-2.68763	1.39865	15.43909
C	-3.38772	0.19816	15.55752
C	-3.66546	-0.56475	14.41584
C	-3.23255	-0.11021	13.15958
C	-2.53343	1.08145	13.04398
H	-2.47354	1.99302	16.32169
H	-3.70989	-0.12832	16.53950
O	-4.34089	-1.74925	14.41634
H	-3.45645	-0.71315	12.28518
H	-2.20019	1.42764	12.07134
C	-4.80096	-2.26058	15.65693
H	-3.96910	-2.45518	16.34691
H	-5.30415	-3.20096	15.42512
H	-5.51410	-1.57655	16.13601
C	-3.31532	4.63136	11.52720
H	-2.89702	3.82112	12.12180
H	-3.58171	4.22964	10.54160
H	-4.24511	4.95977	12.00757
N	3.18743	7.57058	14.79242
C	4.20121	8.51175	14.89747
C	5.55255	8.15989	14.74484
C	6.55596	9.12391	14.84752
C	6.22298	10.45973	15.10657
C	4.87445	10.81666	15.25714
C	3.87747	9.85731	15.15146
H	5.81269	7.12613	14.53793
H	7.58917	8.81979	14.72287
O	7.12603	11.47978	15.22765
H	4.63261	11.85673	15.45300
H	2.83344	10.13498	15.26219
C	8.50132	11.17558	15.07524
H	8.84470	10.45845	15.83332
H	9.03455	12.11935	15.20584
H	8.71921	10.77231	14.07692



G (a.u.) = -2803.502642

Table S14. Cartesian Coordinates for the Optimized Structure of **5** (model isomer **T-H**).

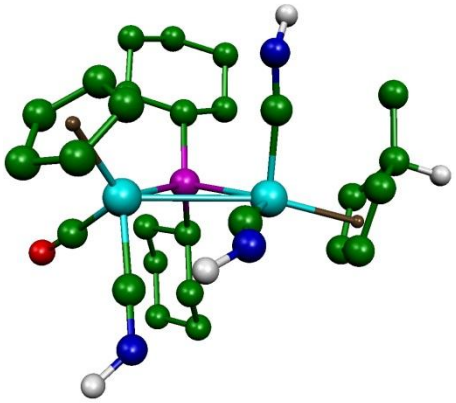
C	0.23431	6.17603	14.96945
N	-0.01445	6.82998	15.97056
Mo	0.20615	5.48838	13.11289
Mo	2.56926	4.42320	14.91162
P	2.12889	4.02620	12.54360
C	-0.92903	4.03751	13.68313
C	3.04917	6.32756	14.99218
N	-1.55887	3.15774	14.25850
O	3.38968	7.43800	15.14222
C	4.45482	4.24897	14.35296
C	-0.90652	5.79052	10.63078
H	-0.60907	5.28434	9.71855
C	-0.25827	6.87874	11.17615
H	0.63886	7.34354	10.77872
C	-0.92624	7.27324	12.40907
H	-0.74300	8.18155	12.97039
C	-1.96030	6.31784	12.62362
H	-2.69901	6.41497	13.41167
C	-2.27308	5.64031	11.28906
H	-2.97401	6.30111	10.73472
C	1.96079	4.23216	17.24185
H	1.79434	5.10684	17.85690
C	0.96818	3.50054	16.53617
H	-0.08645	3.73024	16.48234
C	1.60144	2.40016	15.88754
H	1.10138	1.65338	15.28707
C	2.98732	2.45085	16.19493
H	3.74087	1.74521	15.87090
C	3.21681	3.59284	17.03076
H	4.16347	3.88472	17.46534
C	1.63550	2.27011	12.03864
H	0.77886	2.08839	12.70263
C	1.12232	2.14823	10.58864
H	1.93810	2.35796	9.88327
H	0.34401	2.89882	10.40499
C	0.57291	0.73822	10.30515
H	-0.32434	0.57112	10.92011
H	0.25014	0.66691	9.25809
C	1.60979	-0.34994	10.62040
H	1.17969	-1.34567	10.45213
H	2.45717	-0.25391	9.92515
C	2.12398	-0.22600	12.06236
H	2.89514	-0.98227	12.25875
H	1.29772	-0.43480	12.75903
C	2.68461	1.17898	12.34732
H	3.00299	1.25530	13.39260
H	3.58452	1.33430	11.73981
C	3.17617	4.72145	11.12060
H	2.48558	4.75196	10.26341
C	3.60229	6.17226	11.42532
H	2.73027	6.78202	11.69812
H	4.25884	6.17936	12.30329
C	4.33412	6.81637	10.23579
H	3.64219	6.90707	9.38457
H	4.64253	7.83644	10.49893
C	5.55041	5.98152	9.81089
H	6.03594	6.43121	8.93515
H	6.29413	5.98983	10.62137
C	5.14408	4.53215	9.51228
H	6.02751	3.93229	9.25727
H	4.49085	4.51675	8.62652
C	4.40464	3.88486	10.69871
H	4.09920	2.87280	10.41543
H	5.08837	3.78238	11.54917
C	-2.90742	4.24963	11.26467
H	-2.22567	3.48586	11.64320
H	-3.17831	3.98000	10.23666
H	-3.82415	4.22811	11.86522
N	5.62290	4.05095	14.07782
H	-2.03128	2.37774	13.81608
H	0.57953	6.93507	16.78514
H	6.41281	4.64926	14.29237



G (a.u.) = -1767.087060

Table S15. Cartesian Coordinates for the Optimized Structure of **5** (model isomer **C-H).**

C	0.34373	6.25984	14.79433
N	0.14868	6.96550	15.77133
Mo	0.19918	5.49339	12.97089
Mo	2.63169	4.48436	14.69785
P	2.07475	4.00373	12.35509
C	-0.91720	4.07005	13.64036
C	4.43439	4.33248	13.93445
N	-1.52365	3.21354	14.27310
O	5.54112	4.22631	13.57335
C	3.15503	6.37868	14.85586
C	-1.04670	5.70498	10.55601
H	-0.80270	5.15806	9.65149
C	-0.35907	6.80789	11.01999
H	0.52052	7.24496	10.55743
C	-0.95956	7.26206	12.26687
H	-0.73205	8.18602	12.78474
C	-1.99057	6.33072	12.57383
H	-2.68193	6.46489	13.39847
C	-2.38143	5.60557	11.28544
H	-3.09843	6.25766	10.74138
C	2.10577	4.33474	17.04895
H	1.95617	5.22346	17.64773
C	1.08896	3.58084	16.40463
H	0.03168	3.80413	16.39061
C	1.70243	2.47346	15.75201
H	1.18307	1.71318	15.18553
C	3.10111	2.53769	15.99663
H	3.84280	1.82289	15.66479
C	3.35729	3.69759	16.79859
H	4.31974	4.00100	17.18901
C	1.55480	2.23146	11.94032
H	0.73704	2.07502	12.65755
C	0.96004	2.06341	10.52665
H	1.73434	2.24827	9.76955
H	0.17278	2.80946	10.36418
C	0.39491	0.64598	10.32175
H	-0.46599	0.50133	10.99186
H	0.01320	0.54096	9.29766
C	1.44763	-0.43350	10.61341
H	1.00843	-1.43327	10.50269
H	2.25439	-0.36224	9.86865
C	2.04251	-0.26359	12.01917
H	2.82333	-1.01457	12.19655
H	1.25702	-0.44732	12.76802
C	2.61905	1.14875	12.22537
H	2.99596	1.25819	13.24812
H	3.48285	1.28118	11.56252
C	3.05794	4.64043	10.85955
H	2.31887	4.64440	10.04322
C	3.50348	6.09996	11.08864
H	2.65036	6.72109	11.39295
H	4.21243	6.13750	11.92361
C	4.16231	6.69901	9.83448
H	3.41959	6.76355	9.02449
H	4.48826	7.72619	10.04312
C	5.34922	5.84550	9.36582
H	5.78081	6.26279	8.44686
H	6.14017	5.87784	10.12901
C	4.92249	4.38865	9.14151
H	5.78754	3.77692	8.85422
H	4.21567	4.34487	8.29886
C	4.25645	3.78446	10.39256
H	3.93257	2.76445	10.16335
H	4.99462	3.71010	11.19884
C	-3.03989	4.22720	11.34523
H	-2.34990	3.46173	11.70438
H	-3.37831	3.93181	10.34468
H	-3.91804	4.24127	12.00105
N	3.45706	7.54485	15.04165
H	0.84105	7.18768	16.47902
H	-2.01514	2.41924	13.87962
H	4.28877	7.92638	15.47465

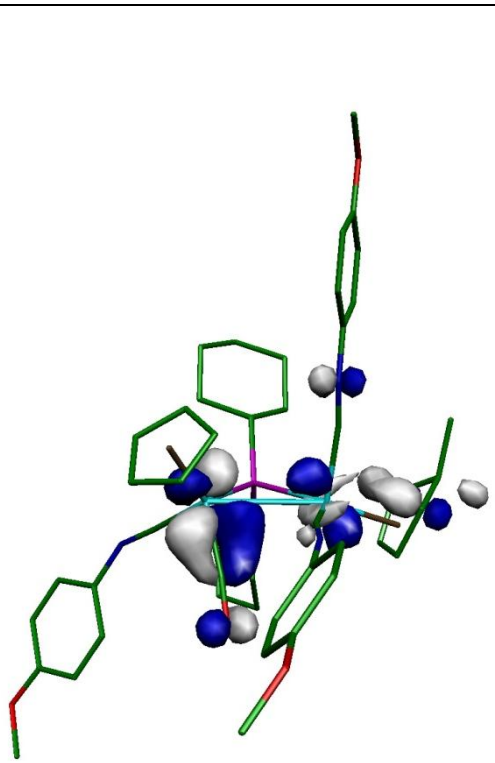
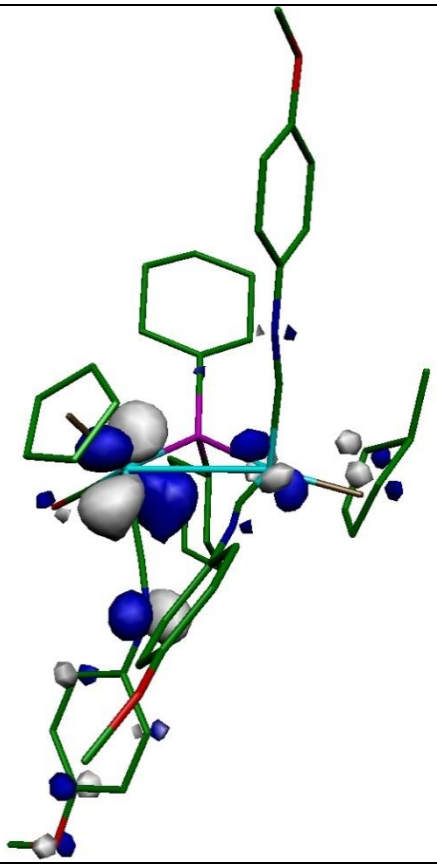
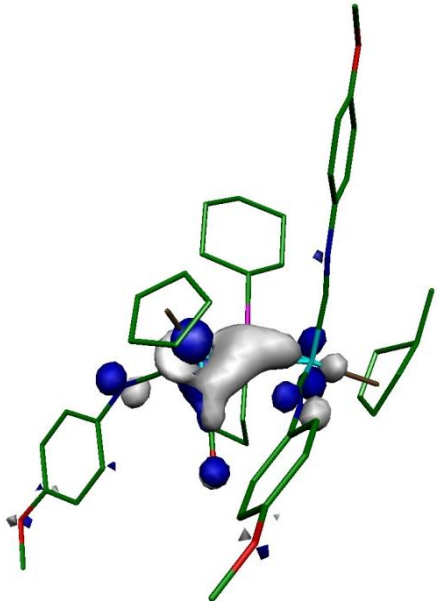
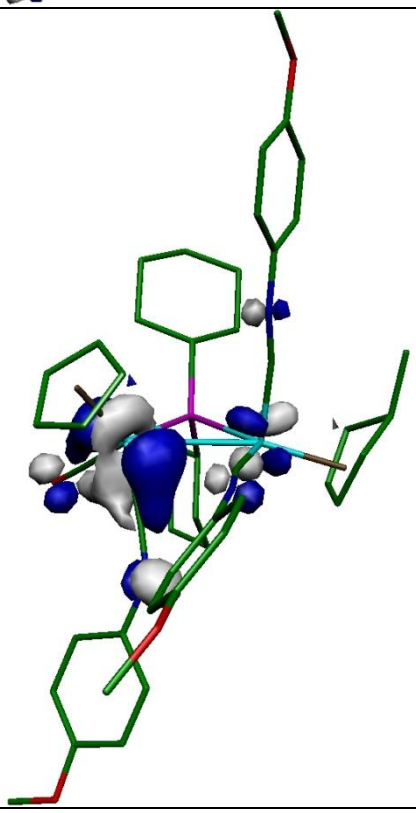


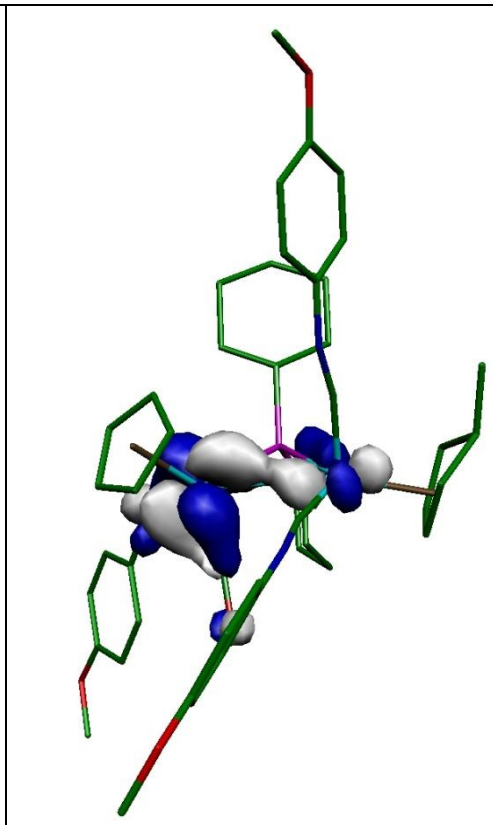
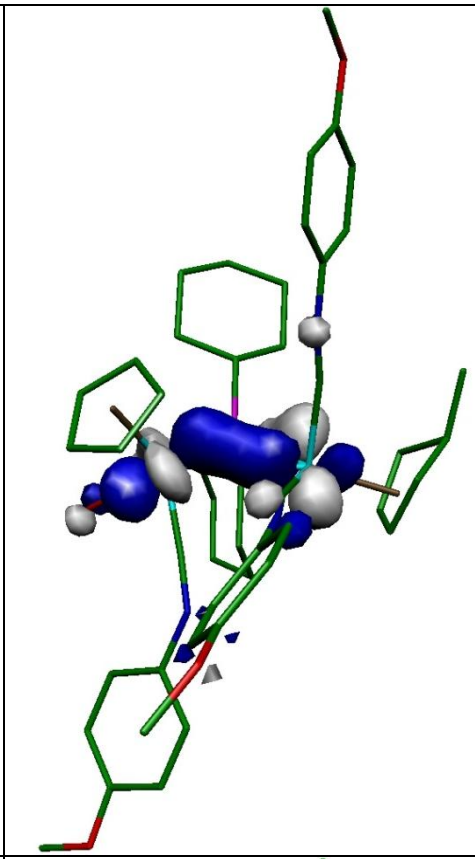
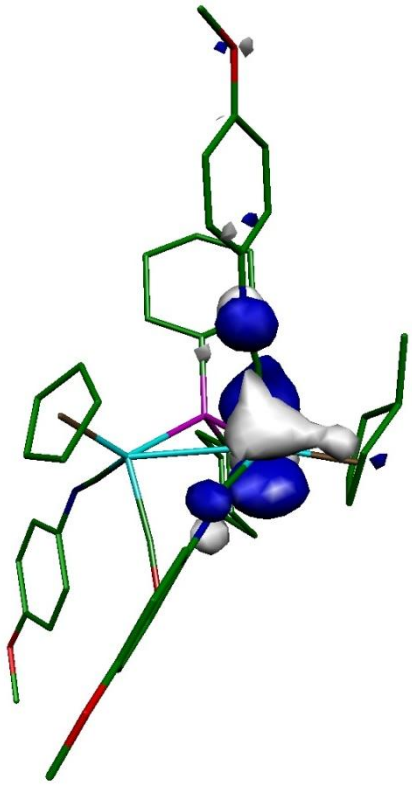
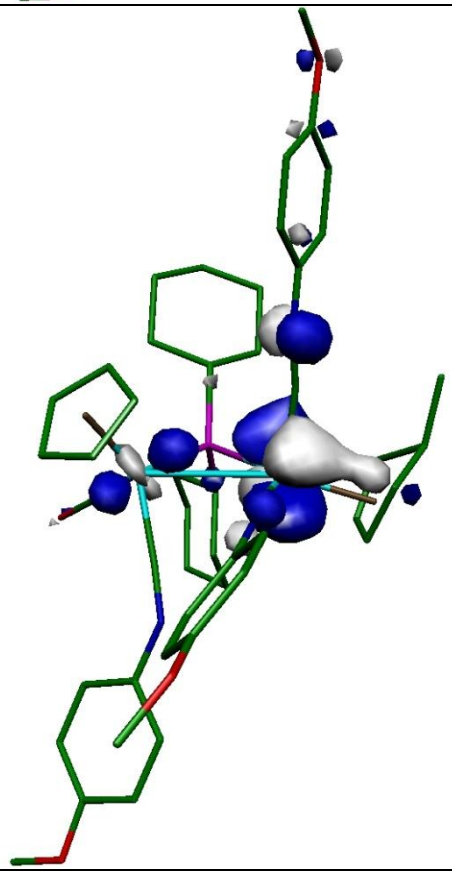
G (a.u.) = -1767.085948

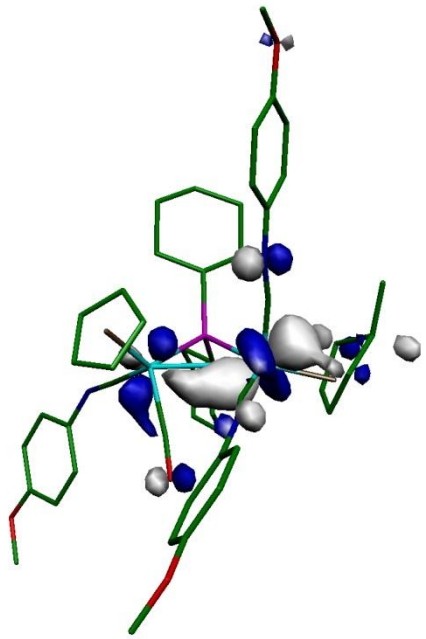
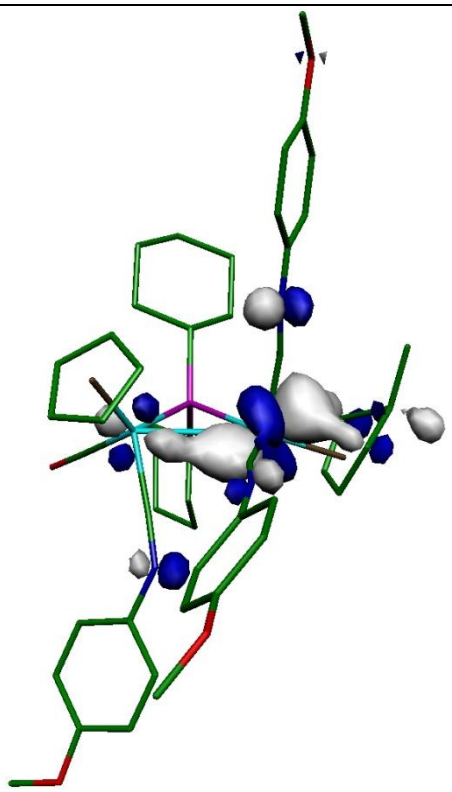
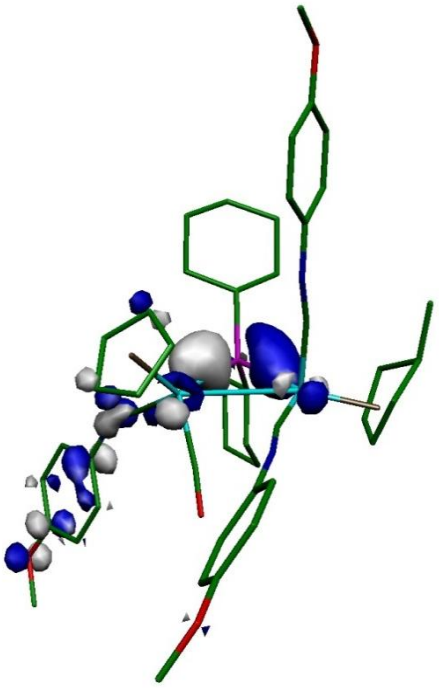
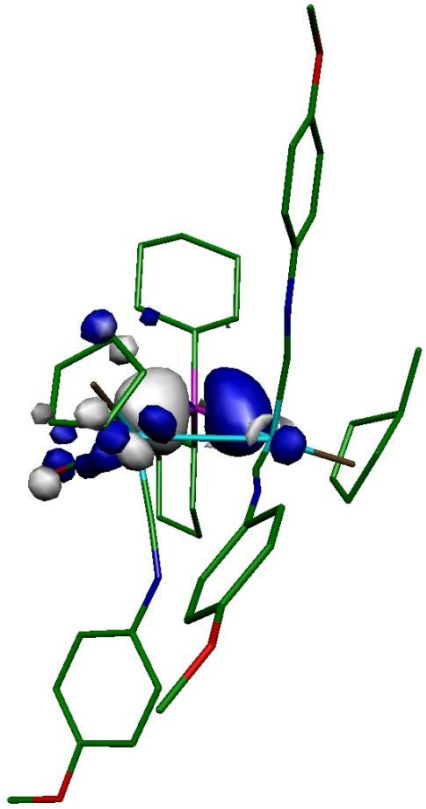
Table S16. Gibbs free energies (kcal/mol) at 298K of different models of the methylcyclopentadiene complex **5**, relative to the most stable one in each case.

	5-C	**5-T**	**5-C-H**	**5-T-H**
ΔG_{gas}	1.0	0.0	0.7	0.0

Table S17. Selected Molecular Orbitals for isomers **5-T** and **5-C**, with their energies (in eV) and main bonding character indicated in each case

MO	5-T	5-C	MO
HOMO 220 -4.27 $\pi_{M\text{-}CO} + \pi_{M\text{-}C5H5Me}$			HOMO 220 -4.13 $\pi_{M\text{-}CNAr}$
MO 219 -4.37 $\sigma_{M\text{-}M} + \pi_{M\text{-}CO} + \pi_{M\text{-}CNAr}$			MO 219 -4.52 $\pi_{M\text{-}CNAr} + \pi_{M\text{-}CO}$

MO 218 -4.58 $\sigma_{M-M} + \pi_{M-CO}$			MO 218 -4.74 $\sigma_{M-M} + \pi_{M-CO}$
MO 217 -4.73 π_{M-CNAr}			MO 217 -4.83 π_{M-CNAr}

MO 216 -5.11 $\pi_{M-M} + \pi_{M-C5H5Me}$			MO 216 -5.06 $\pi_{M-M} + \pi_{M-C5H5Me}$
MO 215 -5.55 σ_{M-P}			MO 215 -5.78 σ_{M-P}