

Supporting Information

Symmetrization in a Phosphinidene-Bridged Complex to give a Diphosphanediyl Derivative with a Metal-Centered Reactivity.

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1. General Procedures and Starting Materials

All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. All solvents were dried and purified according to literature procedures,¹ and distilled prior to use. Petroleum ether refers to that fraction distilling in the range 338-343 K. Compound $[\text{Mo}_2\text{Cp}(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^5\text{-PC}_5\text{H}_4)(\text{CO})_2(\eta^6\text{-HMes}^*)]$ (**1**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{Mes}^* = 2,4,6\text{-C}_6\text{H}_2\text{tBu}_3$) was prepared in situ as described previously.² All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K). Commercial aluminium oxide (Aldrich, activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. Nuclear Magnetic Resonance (NMR) spectra were routinely recorded at 290 K in CD_2Cl_2 solutions unless otherwise is stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^1H , ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz. The ^1H and ^{13}C NMR resonances of the new compounds were assigned using a combination of standard DEPT, COSY, HSQC and NOESY experiments. This allowed an unequivocal assignment of all proton and carbon resonances.

2. Preparative, Spectroscopic and Microanalytical Data for New Compounds

2.1. Preparation of $[\text{Mo}_2\{\mu\text{-}\kappa^1, \eta^5\text{:}\kappa^1, \eta^5\text{-(C}_5\text{H}_4)\text{PP(C}_5\text{H}_4)\}(\eta^6\text{-HMes}^*)_2]$ (2**).** A tetrahydrofuran solution (5 mL) of compound **1** (0.040 g, 0.062 mmol) was stirred at 318 K for 20 min under a CO atmosphere to give a brown solution. The solvent was then removed under vacuum, the residue was extracted with petroleum ether (this leaving a poorly soluble residue of $[\text{Mo}_2\text{Cp}_2(\text{CO})_6]$) and the extracts were chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/8) gave a green fraction yielding, after removal of solvents under vacuum, compound **2** as a purple microcrystalline solid (0.024 g, 88%). The crystals used in the X-ray study were grown by the slow diffusion of layers of diethyl ether and petroleum ether into a concentrated solution of the complex in dichloromethane at 253 K. Anal. Calcd for $\text{C}_{46}\text{H}_{68}\text{Mo}_2\text{P}_2$ (874.9 g mol⁻¹): C, 63.15; H, 7.83. Found: C, 62.86; H, 7.77. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz): δ 54.3 (s). ^1H NMR (300.13 MHz): δ 5.18 (m, 4H, C_5H_4), 4.92 (m, 2H, C_5H_4), 4.62 (s, 6H, C_6H_3), 4.24 (m, 2H, C_5H_4), 1.20 (s, 54H, tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6): δ 110.7 [AXX' false dd, apparent $J_{\text{CP}} = 30, 25, \text{C}^1(\text{C}_5\text{H}_4)$], 103.8 [s, $\text{C}(\text{C}_6\text{H}_3)$], 87.3 [s, $\text{C}^3(\text{C}_5\text{H}_4)$], 91.6 [AXX' false t, $J_{\text{CP}} + J_{\text{CP}'} = 21, \text{C}^2(\text{C}_5\text{H}_4)$], 88.0 [AXX' false t, $J_{\text{CP}} + J_{\text{CP}'} = 10, \text{C}^3(\text{C}_5\text{H}_4)$], 86.1

[AXX' false t, $J_{CP} + J_{CP} = 33$, $C^2(C_5H_4)$], 73.0 [s, CH(C_6H_3)], 34.5 [s, $C^1(tBu)$], 32.1 [s, $C^2(tBu)$].

2.2. Preparation of $[Mo_2\{\mu-\kappa^1, \eta^5:\kappa^1, \eta^5-(C_5H_4)PP(C_5H_4)\}(H)_2(\eta^6-HMes^*)_2](BF_4)_2$ (3). *Method A:* A diethyl ether solution of HBf_4 (12 μ L of a 54% solution, 0.088 mmol) was added to a dichloromethane solution (4 mL) of compound **2** (0.035 g, 0.040 mmol) previously cooled at 213 K, and the mixture was stirred for 1 min to give a brown solution. The solvent was then removed under vacuum, and the residue was washed with diethyl ether (2 x 3 mL) and petroleum ether (2 x 3 mL) to give compound **3** as a pale yellow microcrystalline solid (0.040 g, 96%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of toluene into a concentrated solution of the complex in dichloromethane at 273 K. Anal. Calcd for $C_{46}H_{70}B_2F_8Mo_2P_2$ (1050.5 g mol⁻¹): C, 52.59; H, 6.72. Found: C, 52.31; H, 6.80. $^{31}P\{^1H\}$ NMR (121.49 MHz): δ 112.5 (s). 1H NMR (300.09 MHz): δ 6.24, 6.17 (2m, 2 x 2H, C_5H_4), 5.90 (s, 8H, C_6H_3 and C_5H_4), 4.94 (m, 2H, C_5H_4), 1.29 (s, 54H, tBu), -7.10 (s, 2H, H-Mo).

Method B: A dichloromethane solution of $[FeCp_2](BF_4)$ (40 μ L of a 2M solution, 0.080 mmol) was added to a dichloromethane solution (4 mL) of compound **2** (0.035 g, 0.040 mmol) previously cooled at 213 K, and the mixture was stirred for 1 min to give a brown solution. The solvent was then removed under vacuum, and the residue was washed with toluene (2 x 3 mL) and petroleum ether (2 x 3 mL) to remove ferrocene from it. The residue was then extracted with dichloromethane and filtered with a canula. Removal of the solvent from the filtrate gave compound **3** as a pale yellow microcrystalline solid (0.033 g, 80%). 1H and ^{31}P NMR data for this material were identical to those of the material obtained through the method A (see below).

2.3. Preparation of $[Mo_2\{\mu-\kappa^1, \eta^5:\kappa^1, \eta^5-(C_5H_4)PP(C_5H_4)\}(H)(\eta^6-HMes^*)_2](BF_4)$ (4). A dichloromethane solution of $HBf_4 \cdot Et_2O$ (20 μ L of a 2 M solution, 0.040 mmol) was added to a dichloromethane solution (4 mL) of compound **2** (0.035 g, 0.040 mmol) previously cooled at 213 K, to give a dark violet solution. The solvent was then removed under vacuum, and the residue was washed with diethyl ether (2 x 3 mL) and petroleum ether (4 mL) to give compound **4** as a black solid (0.037 g, 95%). Anal. Calcd for $C_{46}H_{69}BF_4Mo_2P_2$ (962.7 g mol⁻¹): C, 57.39; H, 7.22. Found: C, 57.46; H, 7.28. $^{31}P\{^1H\}$ NMR (161.98 MHz, 233 K): δ 130.9 [d, $J_{PP} = 272$, P-Mo-H], 40.0 [d, $J_{PP} = 272$, P-Mo]. 1H NMR (400.13 MHz, 233 K): δ 6.29 [m, 1H, $HC^2(C_5H_4)$], 5.82 (m, 1H, C_5H_4), 5.63 (s, br, 4H, C_6H_3 and C_5H_4), 5.37 (m, 1H, C_5H_4), 5.00, 4.81 (2m, 2 x 1H, C_5H_4), 4.75 (s, 3H, C_6H_3), 4.66, 4.48 (2m, 2 x 1H, C_5H_4), 1.26, 1.19 (2s, 2 x 27H, tBu), -6.35 (s, 1H, H-Mo). A 2D-NOESY spectrum displayed only a single crosspeak involving the resonance at -6.35 ppm, this revealing a intense NOE effect from the resonance at $\delta_H = 6.29$ ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, 233 K) δ 123.3, 106.8 [2s,

C(C₆H₃)], 101.4 [d, J_{CP} = 19, CH(C₅H₄)], 96.2 [d, J_{CP} = 16, CH(C₅H₄)], 91.3 [d, J_{CP} = 28, CH(C₅H₄)], 88.3-87.5 [m, 4CH(C₅H₄)], 86.4 [s, CH(C₆H₃)], 85.5 [d, J_{CP} = 29, CH(C₅H₄)], 75.2 [s, CH(C₆H₃)], 35.7, 34.7 [2s, C¹(^tBu)], 31.6, 31.3 [2s, C²(^tBu)]. The resonances for the C¹(C₅H₄) carbon atoms could not be identified in the spectrum.

2.4. Preparation of [Mo{ κ^1, η^5 -PH(C₅H₄)}(η^6 -HMes*)] (5). A dichloromethane solution of [CoCp₂] (40 μ L of a 2M solution, 0.080 mmol) was added to a dichloromethane solution (4 mL) of compound **3** (0.042 g, 0.040 mmol) previously cooled at 213 K, and the mixture was stirred for 1 min to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with toluene/petroleum ether (1/2) and the extract was filtered with a canula. Removal of solvents from the filtrate gave compound **5** as a pale orange microcrystalline solid (0.031 g, 89%). No elemental analysis was obtained for this material due to its high sensitivity to air. ³¹P NMR (121.49 MHz): δ -49.6 (d, J_{HP} = 144). ¹H NMR (300.13 MHz): δ 5.15, 5.02, 4.81, 4.49 (4m, 4 x 1H, C₅H₄), 4.69 (d, J_{HP} = 2, 3H, C₆H₃), 2.07 (d, J_{HP} = 144, 1H, H-P), 1.16 (s, 27H, ^tBu).

3. X-ray Structure Determination of 2. The X-ray intensity data were collected on a Kappa-Apex-II Bruker diffractometer using graphite-monochromated Mo-K α radiation at 100 K. The software APEX³ was used for collecting frames with ω/ϕ scans measurement method. The Bruker SAINT⁴ software was used for the data reduction, and a multi-scan absorption correction was applied with SADABS.⁵ Using the program suite WinGX,⁶ the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least squares on F² using SHELXL97.⁷ During the solution process, the compound was found to be placed on the symmetry operation -x+1,-y+1,-z+1. During the refinement stages, the unit “C₅H₄-P” was found to be disordered and the best solution was obtained by modelling the disorder over two positions with C(1) and C(3) belonging to both parts, and with occupancy 0.8/0.2. All the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically, except for the carbon atoms C(2), C(4) and C(5), which were refined isotropically to prevent their temperature factors from becoming non-positive definite. All hydrogen atoms were geometrically placed and refined using a riding model.

4. X-ray Structure Determination of 3·2CH₂Cl₂. Data collection was performed at 150 K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation (λ = 1.5418 Å). Images were collected at a 63 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and a exposure time per image of 1.5 s. Data collection strategy was calculated with the program CrysAlis Pro CCD.⁸ Data reduction and cell refinement was performed with the program CrysAlis Pro

RED.⁸ An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED. Using the program suite WinGX,⁶ the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least squares on F^2 using SHELXL97.⁷ During the solution process, the compound was found to be placed on the symmetry operation $-x+1, -y, -z+1$ and to crystallize with two molecules of dichloromethane. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms (except the hydride H(1)) were geometrically placed and refined using a riding model. The H(1) atom could not be located in the final difference map; then, plausible positions were investigated by a potential energy minima search using the program HYDEX.⁹ Only one minimum was found at sensible distances from the Mo(1) atom, at approximately 1.80 Å, in agreement with the solution structure, therefore that position was assigned to the hydride ligand. The H(1) atom was then refined isotropically using a restraint in the Mo(1)–H(1) bond (to 1.80 Å), it reaching a satisfactory refinement.

5. CV measurements. Cyclic Voltammetry experiments were performed in an airtight custom-made electrolytic cell using a Pt working electrode, an Ag wire reference electrode and a Pt wire auxiliary electrode. $[\text{NBu}_4][\text{PF}_6]$ was used as the supporting electrolyte (0.1 M solutions). The analyte concentrations in a typical experiment were ca. 10^{-3} M in dichloromethane. The $E_{1/2}$ values were calculated from the average of the cathodic and anodic potentials. All the potentials were referenced versus the ferrocene/ferrocenium couple ($[\text{FeCp}_2]^{0/+}$), used as internal reference in all the experiments. The figure below shown a typical CV diagram for compound 2.

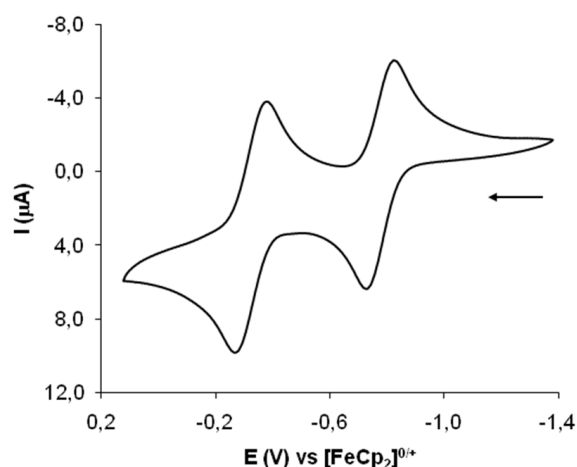


Figure S1. CV of compound **2** recorded at 200 mV s^{-1} in CH_2Cl_2 , from -1.38 to $+0.12$ V, starting at -1.88 V, relative to the $[\text{FeCp}_2]^{0/+}$ couple, with sweeping towards positive potentials.

6. DFT analysis of compound 2. All computations were carried out using the GAUSSIAN03 package,¹⁰ in which the hybrid method B3LYP was applied with the Becke three parameters exchange functional¹¹ and the Lee-Yang-Parr correlation functional.¹² Effective core potentials (ECP) and their associated double- ζ LANL2DZ basis set were used for the metal atoms.¹³ The light elements (P, O, C and H) were described with 6-31G* basis.¹⁴ Geometry optimization was performed under no symmetry restrictions, using initial coordinates derived from X-ray data of the complex, and a frequency analysis was performed to ensure that a minimum structure with no imaginary frequencies was achieved. For interpretation purposes, Mulliken charges were computed as usually,¹⁵ and natural population analysis (NPA) charges were derived from the natural bond order (NBO) analysis of the data.¹⁶ Molecular orbitals were visualized using the Molekel program.¹⁷

Optimized geometry.

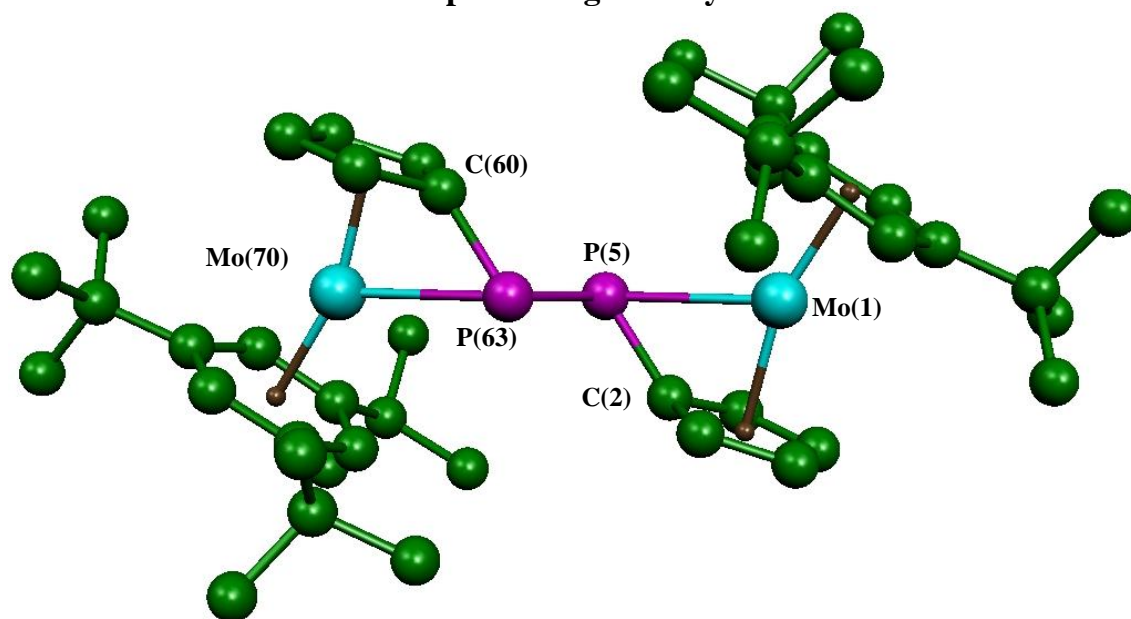
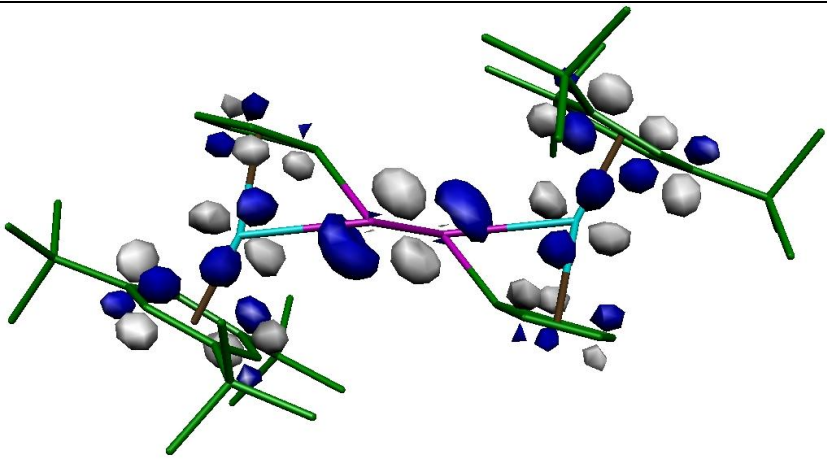
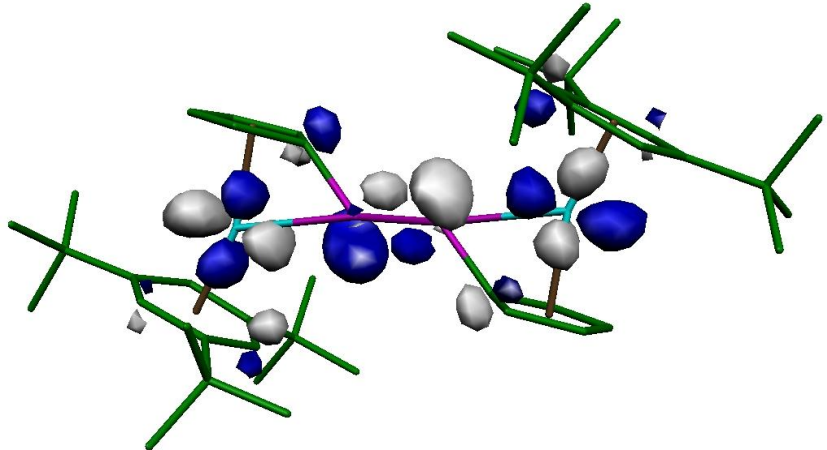
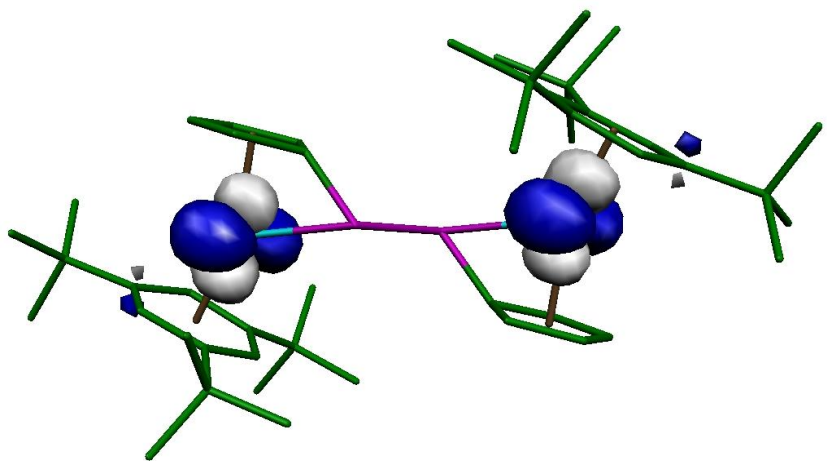


Figure S2

Table S1: X-ray Structural Data and DFT-Optimized Geometries for Compound **2** (distances in Å, angles in deg.).

Parameter	Optimized	X-Ray
Mo(1) – P(5)	2.672	2.607
Mo(70) – P(63)	2.672	2.607
P(5) – P(63)	2.241	2.203
P(5) – C(2)	1.795	1.809
P(63) – C(60)	1.794	1.809
Mo(1) – P(5) – P(63)	107.3	104.5
Mo(70) – P(63) – P(5)	107.3	104.5
Mo(1) – P(5) – C(2)	54.9	55.5
Mo(70) – P(63) – C(60)	54.9	55.5
C(2) – P(5) – P(63)	101.2	98.2
C(60) – P(63) – P(5)	101.2	98.2

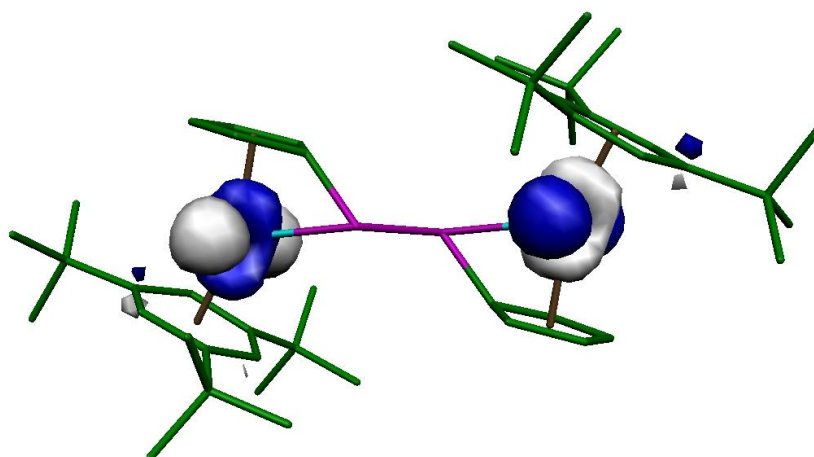
Table S2: Selected molecular orbitals of compound **2**.

MO	Energy (eV)	Assignment	Projection 1
MO 203	-0.57		
			Contributions (%): Mo(1) 8, Mo(70) 8, P(5) 10, P(63) 10, C(2) 1, C(60) 1, Other 62
LUMO 202	-1.09		
			Contributions (%): Mo(1) 17, Mo(70) 17, P(5) 13, P(63) 13, C(2) 3, C(60) 3, Other 34
HOMO 201	-4.00	L.P. Mo's	
			Contributions (%): Mo(1) 33, Mo(70) 33, P(5) 3, P(63) 3, C(2) 0, C(60) 0, Other 28

MO 200

-4.17

L.P. Mo's

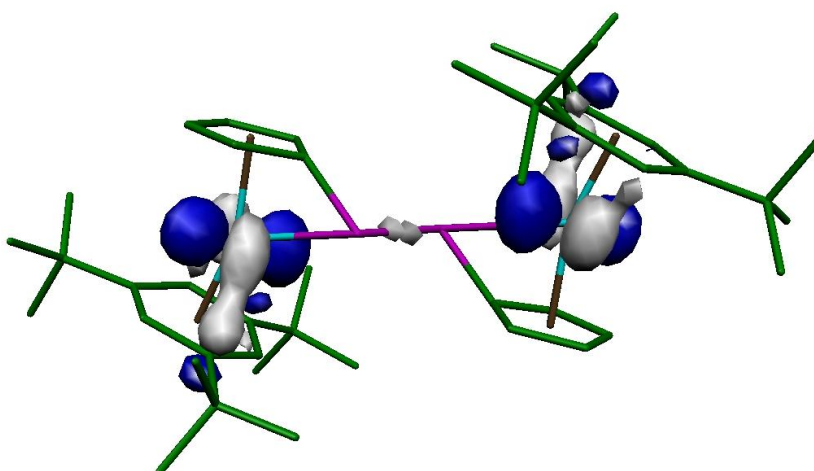


Contributions (%): Mo(1) 31, Mo(70) 31, P(5) 1, P(63) 1, C(2) 1, C(60) 1, Other 34

MO 199

-4.20

L.P. Mo's

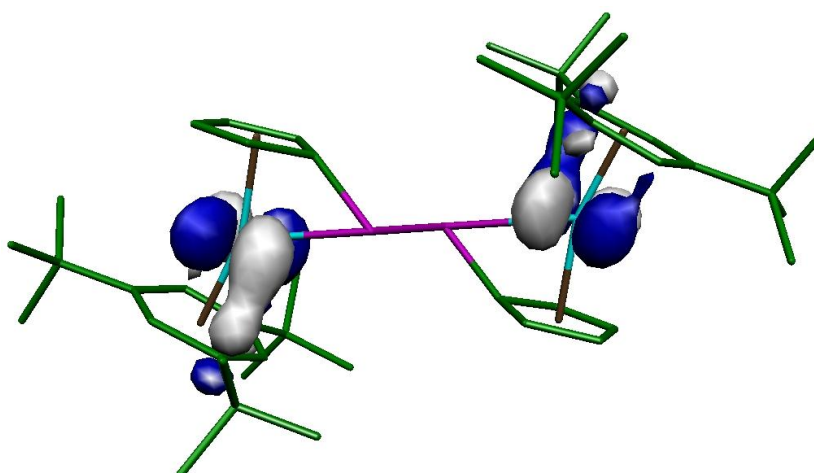


Contributions (%): Mo(1) 24, Mo(70) 24, P(5) 4, P(63) 4, C(2) 0, C(60) 0, Other 44

MO 198

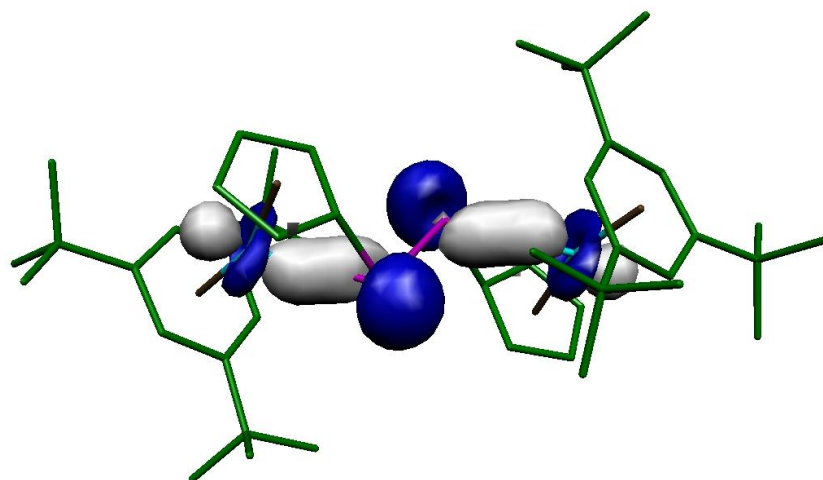
-4.39

L.P. Mo's



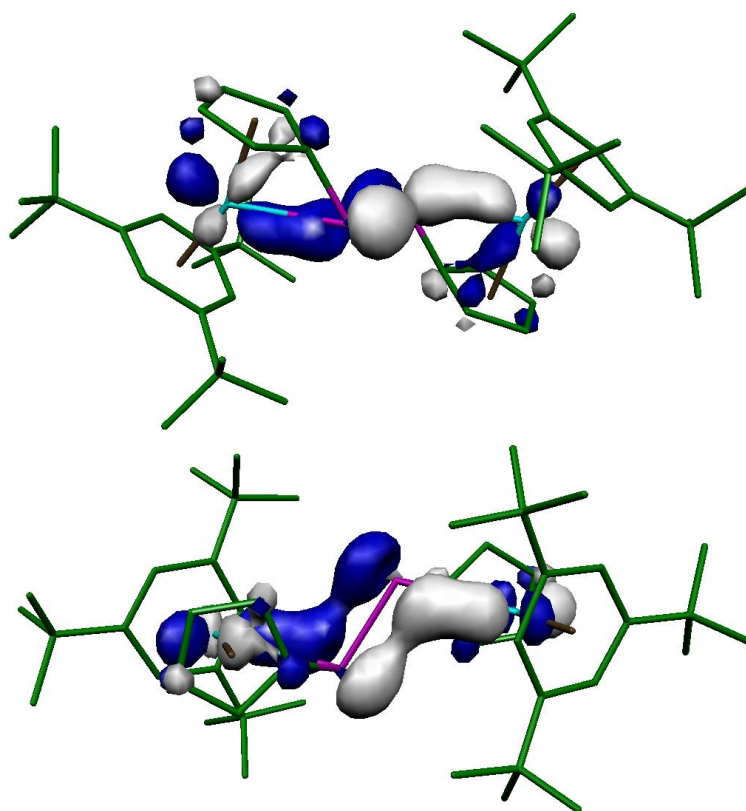
Contributions (%): Mo(1) 26, Mo(70) 26, P(5) 3, P(63) 3, C(2) 0, C(60) 0, Other 42

MO 197
-4.96
 $\sigma_{\text{Mo-P}} + \text{LP P}$



Contributions (%): Mo(1) 18, Mo(70) 18, P(5) 19, P(63) 19, C(2) 2, C(60) 2, Other 22

MO 196
-5.97
 $\sigma_{\text{Mo-P}} + \pi_{\text{P-P}}$

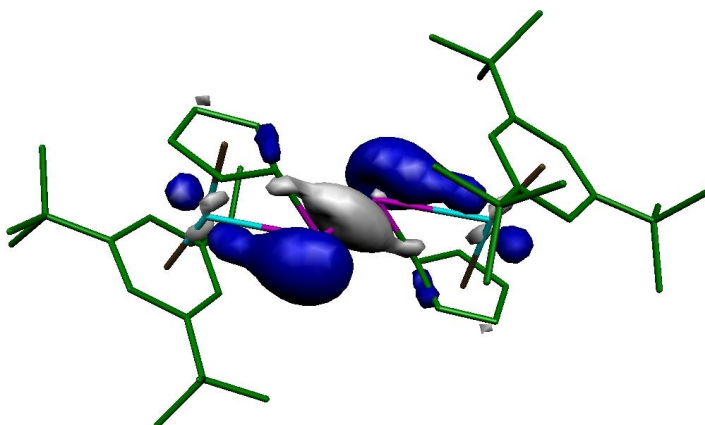


Contributions (%): Mo(1) 17, Mo(70) 17, P(5) 16, P(63) 16, C(2) 3, C(60) 3, Other 28

MO 195

-6.06

$\sigma_{\text{P-P}} + \sigma_{\text{P-C}} +$
LP P

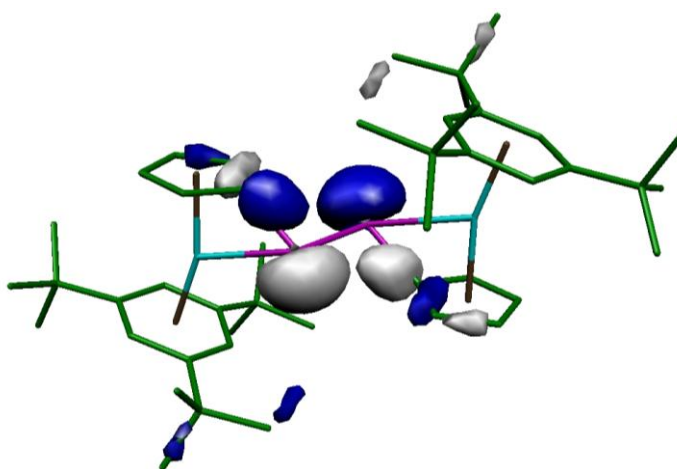


Contributions (%): Mo(1) 9, Mo(70) 9, P(5) 29, P(63) 29, C(2) 2, C(60) 2, Other 18

MO 186

-8.01

$\sigma_{\text{P-C}} + \text{LP P}$

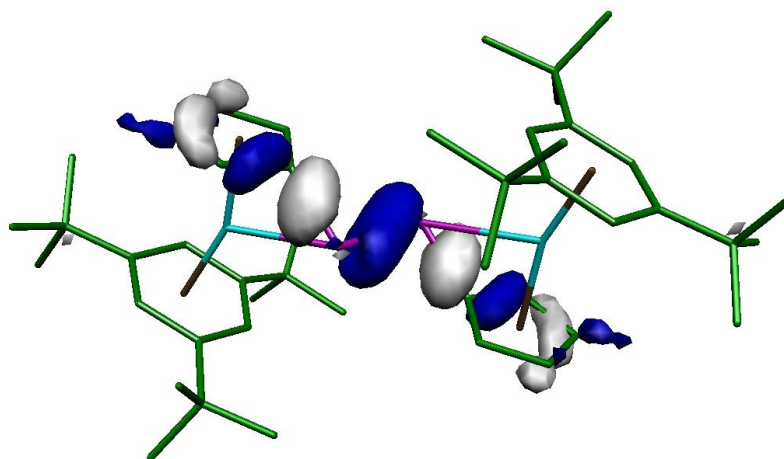


Contributions (%): Mo(1) 1, Mo(70) 1, P(5) 22, P(63) 22, C(2) 6, C(60) 6, Other 42

MO 181

-9.36

$\sigma_{\text{P-P}} + \sigma_{\text{P-C}}$

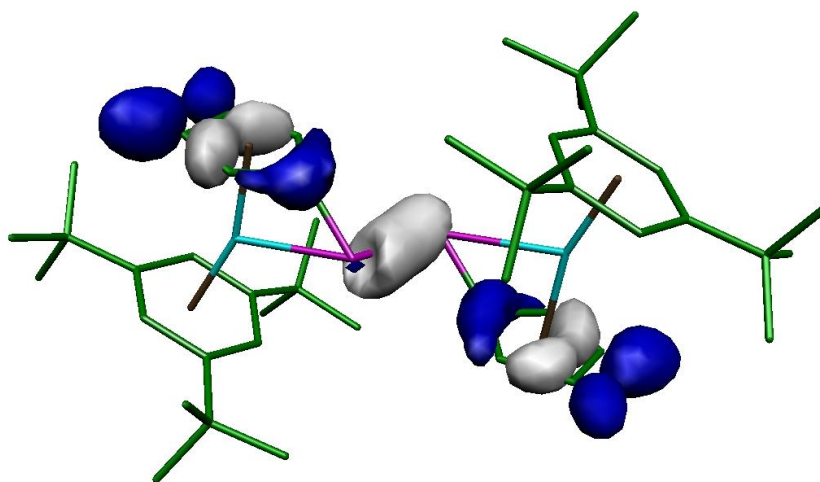


Contributions (%): Mo(1) 8, Mo(70) 8, P(5) 12, P(63) 12, C(2) 2, C(60) 2, Other 56

MO 113

-13.01

$\sigma_{P-P} + \sigma_{C-C}$

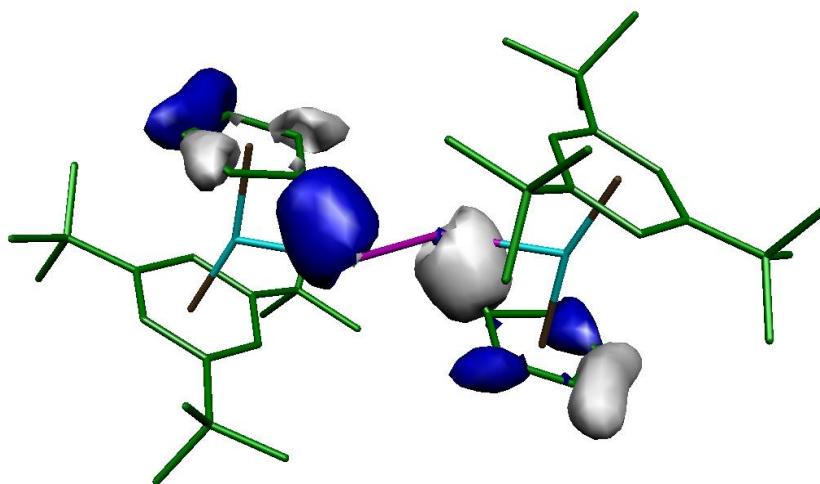


Contributions (%): Mo(1) 1, Mo(70) 1, P(5) 9, P(63) 9, C(2) 5, C(60) 5, Other 70

MO 102

-15.43

σ_{P-C}

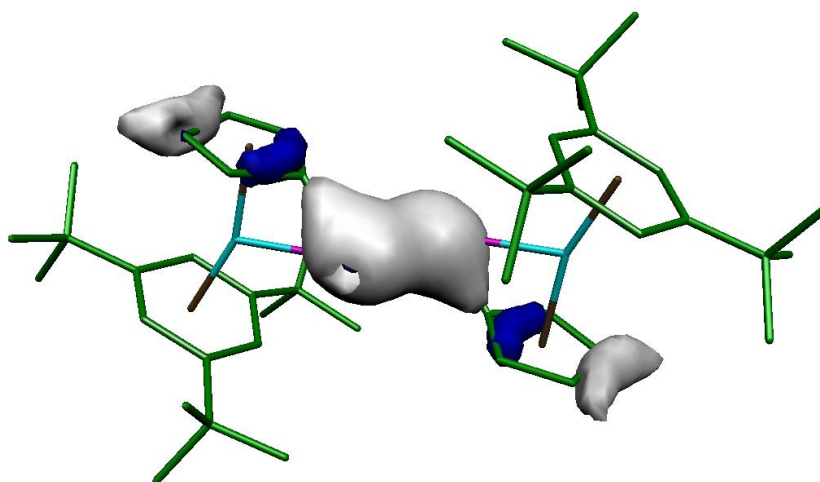


Contributions (%): Mo(1) 2, Mo(70) 2, P(5) 13, P(63) 13, C(2) 9, C(60) 9, Other 52

MO 95

-16.74

$\sigma_{P-P} + \sigma_{P-C}$



Contributions (%): Mo(1) 1, Mo(70) 1, P(5) 22, P(63) 22, C(2) 4, C(60) 4, Other 46

Table S3: Cartesian coordinates for the optimized geometry of compound **2**.

Mo	3.13163	0.04256	0.60807	C	-3.32629	-0.09927	-2.98920
C	1.31872	-0.04386	1.85646	H	-4.22171	0.15527	-3.54139
C	3.32688	0.09963	2.98920	P	-0.61706	0.84087	-0.40930
H	4.22243	-0.15471	3.54126	C	-2.31048	0.80423	-2.59425
P	0.61726	-0.84105	0.40983	H	-2.28314	1.86913	-2.78037
C	2.31113	-0.80407	2.59450	C	-2.95861	-1.41905	-2.56702
H	2.28398	-1.86895	2.78075	H	-3.54017	-2.31613	-2.73784
C	2.95889	1.41932	2.56701	C	-1.71598	-1.35405	-1.89815
H	3.54035	2.31651	2.73765	H	-1.17864	-2.18178	-1.45939
C	1.71615	1.35408	1.89840	Mo	-3.13150	-0.04243	-0.60799
H	1.17859	2.18170	1.45971	C	-4.75852	-1.21632	0.44659
C	4.75887	1.21614	-0.44659	H	-5.08113	-2.22308	0.21762
H	5.08178	2.22276	-0.21744	C	-3.73841	-1.03742	1.44565
C	3.73854	1.03772	-1.44550	C	-3.34573	0.29872	1.70386
C	3.34543	-0.29825	-1.70388	H	-2.52148	0.46125	2.38362
H	2.52102	-0.46043	-2.38352	C	-3.90177	1.44009	1.03410
C	3.90132	-1.43991	-1.03446	C	-4.96211	1.19635	0.10963
C	4.96182	-1.19666	-0.11008	H	-5.43150	2.04111	-0.37380
H	5.43104	-2.04165	0.37312	C	-5.45236	-0.11213	-0.14316
C	5.45239	0.11165	0.14299	C	-3.28504	-2.23394	2.29985
C	3.28522	2.23452	-2.29931	C	-4.49073	-2.67174	3.17072
C	4.49065	2.67203	-3.17069	H	-5.33595	-3.00035	2.55543
H	5.33628	3.00025	-2.55575	H	-4.20641	-3.50575	3.82411
H	4.20633	3.50623	-3.82383	H	-4.83749	-1.84734	3.80478
H	4.83682	1.84759	-3.80503	C	-2.83885	-3.42083	1.41919
C	2.83986	3.42145	-1.41828	H	-1.95472	-3.15246	0.83343
H	1.95600	3.15327	-0.83202	H	-2.58917	-4.28227	2.05097
H	2.59004	4.28300	-2.04984	H	-3.62382	-3.74120	0.72531
H	3.62532	3.74157	-0.72485	C	-2.12162	-1.87013	3.24126
C	2.12121	1.87123	-3.24019	H	-2.40815	-1.10131	3.96814
H	2.40708	1.10234	-3.96726	H	-1.82040	-2.75825	3.80906
H	1.82006	2.75950	-3.80778	H	-1.24760	-1.51676	2.68564
H	1.24732	1.51816	-2.68417	C	-3.57929	2.89027	1.44904
C	3.57838	-2.88993	-1.44960	C	-4.79517	3.43684	2.24072
C	4.79402	-3.43671	-2.24149	H	-5.69899	3.46680	1.62155
H	5.69788	-3.46715	-1.62239	H	-5.00831	2.81063	3.11512
H	5.00734	-2.81035	-3.11574	H	-4.59667	4.45634	2.59431
H	4.59515	-4.45605	-2.59533	C	-2.34175	2.97473	2.36372
C	2.34077	-2.97387	-2.36422	H	-2.13273	4.02487	2.59880
H	2.13140	-4.02391	-2.59944	H	-2.49757	2.45439	3.31562
H	2.49669	-2.45343	-3.31604	H	-1.45422	2.55603	1.87986
H	1.45338	-2.55499	-1.88026	C	-3.33025	3.79178	0.22074
C	3.32918	-3.79160	-0.22145	H	-4.18160	3.79787	-0.46867
H	4.18042	-3.79771	0.46810	H	-3.16455	4.82702	0.54422
H	3.16357	-4.82681	-0.54507	H	-2.44906	3.45461	-0.33307
H	2.44791	-3.45452	0.33228	C	-6.72609	-0.34204	-0.98415
C	6.72633	0.34094	0.98384	C	-7.06955	0.86185	-1.88579
C	7.06883	-0.86274	1.88613	H	-7.32085	1.75534	-1.30457
H	7.31960	-1.75670	1.30542	H	-6.24190	1.11386	-2.55766
H	6.24090	-1.11385	2.55800	H	-7.94446	0.62313	-2.50108
H	7.94382	-0.62432	2.50141	C	-7.88464	-0.53735	0.02887
C	7.88504	0.53478	-0.02928	H	-8.83481	-0.68486	-0.49948
H	8.83530	0.68198	0.49899	H	-7.71085	-1.41147	0.66624
H	7.71185	1.40859	-0.66722	H	-7.98925	0.33762	0.68032
H	7.98906	-0.34070	-0.68014	C	-6.64607	-1.59776	-1.87864
C	6.64729	1.59723	1.87761	H	-5.85663	-1.50538	-2.63011
H	5.85725	1.50625	2.62863	H	-6.46337	-2.51156	-1.30479
H	6.46610	2.51093	1.30312	H	-7.59825	-1.73391	-2.40480
H	7.59930	1.73254	2.40428				
C	-1.31834	0.04382	-1.85605				

Table S4: Mulliken charges of compound 2.

1	Mo	-0.094376	61	C	-0.145516
2	C	-0.251441	62	H	0.152542
3	C	-0.145527	63	P	0.139026
4	H	0.152535	64	C	-0.167213
5	P	0.139012	65	H	0.168058
6	C	-0.167214	66	C	-0.133049
7	H	0.168057	67	H	0.158995
8	C	-0.133042	68	C	-0.159763
9	H	0.159001	69	H	0.179270
10	C	-0.159778	70	Mo	-0.094372
11	H	0.179276	71	C	-0.313076
12	C	-0.313020	72	H	0.132777
13	H	0.132780	73	C	0.183574
14	C	0.183619	74	C	-0.272943
15	C	-0.273000	75	H	0.160331
16	H	0.160339	76	C	0.109609
17	C	0.109641	77	C	-0.242933
18	C	-0.242851	78	H	0.141774
19	H	0.141768	79	C	0.196225
20	C	0.196112	80	C	0.043404
21	C	0.043403	81	C	-0.441124
22	C	-0.441121	82	H	0.139346
23	H	0.139347	83	H	0.138302
24	H	0.138304	84	H	0.147793
25	H	0.147792	85	C	-0.461071
26	C	-0.461058	86	H	0.188515
27	H	0.188489	87	H	0.133153
28	H	0.133161	88	H	0.141247
29	H	0.141244	89	C	-0.485780
30	C	-0.485786	90	H	0.139681
31	H	0.139681	91	H	0.136496
32	H	0.136487	92	H	0.195524
33	H	0.195545	93	C	0.048584
34	C	0.048593	94	C	-0.439667
35	C	-0.439670	95	H	0.138255
36	H	0.138255	96	H	0.146994
37	H	0.146995	97	H	0.137076
38	H	0.137078	98	C	-0.479650
39	C	-0.479650	99	H	0.137343
40	H	0.137346	100	H	0.142188
41	H	0.142188	101	H	0.183929
42	H	0.183924	102	C	-0.461099
43	C	-0.461110	103	H	0.141967
44	H	0.141978	104	H	0.131852
45	H	0.131848	105	H	0.189060
46	H	0.189069	106	C	0.044360
47	C	0.044354	107	C	-0.473662
48	C	-0.473650	108	H	0.149184
49	H	0.149179	109	H	0.168058
50	H	0.168074	110	H	0.143217
51	H	0.143214	111	C	-0.441624
52	C	-0.441611	112	H	0.140240
53	H	0.140240	113	H	0.150865
54	H	0.150871	114	H	0.153163
55	H	0.153151	115	C	-0.462820
56	C	-0.462851	116	H	0.161927
57	H	0.161949	117	H	0.150779
58	H	0.150763	118	H	0.142106
59	H	0.142110	Sum of Mulliken charges= 0.00		
60	C	-0.251446			

Table S5: NPA charges of compound 2.

Mo	1	0.01748	H	67	0.26321
C	2	-0.39136	C	68	-0.28100
C	3	-0.25682	H	69	0.27405
H	4	0.25970	Mo	70	0.01751
P	5	0.29624	C	71	-0.25890
C	6	-0.27904	H	72	0.25570
H	7	0.27180	C	73	-0.04517
C	8	-0.24900	C	74	-0.21801
H	9	0.26321	H	75	0.26637
C	10	-0.28099	C	76	-0.06602
H	11	0.27405	C	77	-0.23009
C	12	-0.25891	H	78	0.25954
H	13	0.25571	C	79	-0.02875
C	14	-0.04514	C	80	-0.05258
C	15	-0.21804	C	81	-0.65752
H	16	0.26637	H	82	0.22625
C	17	-0.06596	H	83	0.22982
C	18	-0.23007	H	84	0.23221
H	19	0.25953	C	85	-0.65861
C	20	-0.02877	H	86	0.24623
C	21	-0.05258	H	87	0.22724
C	22	-0.65752	H	88	0.22095
H	23	0.22625	C	89	-0.67182
H	24	0.22982	H	90	0.22684
H	25	0.23221	H	91	0.23313
C	26	-0.65861	H	92	0.24568
H	27	0.24622	C	93	-0.05077
H	28	0.22725	C	94	-0.65744
H	29	0.22095	H	95	0.22592
C	30	-0.67182	H	96	0.23165
H	31	0.22684	H	97	0.22892
H	32	0.23312	C	98	-0.66995
H	33	0.24568	H	99	0.23342
C	34	-0.05077	H	100	0.22746
C	35	-0.65744	H	101	0.24193
H	36	0.22592	C	102	-0.65885
H	37	0.23165	H	103	0.22170
H	38	0.22893	H	104	0.22634
C	39	-0.66995	H	105	0.24576
H	40	0.23342	C	106	-0.05497
H	41	0.22746	C	107	-0.66930
H	42	0.24192	H	108	0.22987
C	43	-0.65885	H	109	0.23395
H	44	0.22170	H	110	0.23568
H	45	0.22634	C	111	-0.65767
H	46	0.24576	H	112	0.23005
C	47	-0.05497	H	113	0.23330
C	48	-0.66928	H	114	0.23464
H	49	0.22986	C	115	-0.65897
H	50	0.23394	H	116	0.22929
H	51	0.23567	H	117	0.22762
C	52	-0.65767	H	118	0.23265
H	53	0.23005	=====		
H	54	0.23331	* Total *		
H	55	0.23464	0.00000		
C	56	-0.65899			
H	57	0.22930			
H	58	0.22762			
H	59	0.23266			
C	60	-0.39138			
C	61	-0.25682			
H	62	0.25970			
P	63	0.29626			
C	64	-0.27904			
H	65	0.27180			
C	66	-0.24899			

7. References

- (1) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals, 5th Edition*; Butterworth-Heinemann: Oxford, U.K., 2003.
- (2) Amor, I.; García, M. E.; Ruiz, M. A.; Sáez, D.; Hamidov, H.; Jeffery, J. C. *Organometallics* **2006**, 25, 4857.
- (3) *APEX 2, version 2.0-1*; Bruker AXS Inc: Madison, WI, 2005.
- (4) *SMART & SAINT Software Reference Manuals, Version 5.051 (Windows NT Version)*; Bruker Analytical X-ray Instruments: Madison, WI, 1998.
- (5) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1996.
- (6) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, 32, 837.
- (7) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, 64, 112.
- (8) *CrysAlis Pro*; Oxford Diffraction Ltd.: Oxford, U. K., 2006.
- (9) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.
- (10) 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.
- (11) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
- (12) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
- (13) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 299.
- (14) (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.
- (15) Mulliken, R. S. *J. Chem. Phys.* **1955**, 23, 1833.
- (16) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, 83, 735. (b) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899.
- (17) Portmann, S.; Lüthi, H. P. MOLEKEL: An Interactive Molecular Graphics Tool. *CHIMIA* **2000**, 54, 766.