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Synthesis and Characterization of a New Series of η^6-Arene Compounds of Molybdenum and Tungsten: $M(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(X)(L)_2$ (M = Mo, W; X = H, Cl) Compounds Containing Chelated 2,6-Diphenylphenoxide Ligands

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Reaction of the group 6 metal tetrahydrides $MH_4(PMePh_2)_4$ (M = Mo, W) with 2,6-diphenylphenol (HOAr-2,6-Ph_2; excess) in a melt at temperatures above 150 °C leads to the formation of a deep red mixture from which the 18-electron compounds $M(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(H)(PMePh_2)_2$ (M = Mo (**1**), W (**2**)) can be isolated. Spectroscopic data on deep red **1** and **2** indicate the presence of a 2,6-diphenylphenoxide ligand chelated to the metal via an η^6-interaction through one of the side-chain aryl rings. A solid-state structural study of both **1** and **2** showed them to be isomorphous and confirmed the presence of the η^6-arene ring. Chelation of this ring through the aryloxide oxygen atom causes no noticeable asymmetry in the π-interaction with the metal centers. The overall geometry about the metal is best described as a four-legged piano stool with the phosphine ligands mutually trans. The resulting virtual plane of symmetry in the molecules is found to be maintained in solution, with ^1H, ^{13}C, and ^{31}P NMR spectra indicating equivalent phosphine ligands being present along with equivalent ortho and meta hydrogens on the η^6-bound aryl ring. These monohydrides are found to be extremely stable to thermolysis, with no indication for the activation of the ortho-CH bonds of the substituent aryl rings of the OAr-2,6-Ph_2 ligand. Formation of related compounds containing η^6-bound 2,6-diphenylphenoxide by reduction of high-valent derivatives of this ligand proved successful. Hence reduction of $W(OAr\text{-}2,6\text{-}Ph_2)Cl_5$ (**3**) with sodium amalgam (4Na/W) in the presence of phosphine ligands produced the 18-electron monochlorides $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)L_2$ (L = PMe_2Ph, **4**; $L_2 = Ph_2PCH_2CH_2PPh_2$, **5**). Compounds **4** and **5** have spectroscopic properties similar to the monohydrides. Structural studies of **4** and **5** also show the coordination environment about the tungsten atom to be similar to that seen in **2**. In the case of **5** the trans arrangement of the phosphorus atoms of the dppe ligand is achieved without unusual distortions. Attempts to prepare chelated 2,6-diphenylphenoxide compounds of molybdenum by heating HOAr-2,6-Ph_2 with $Mo(CO)_6$ in octane led only to the η^6-arene compound $Mo(HOC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(CO)_3$ (**6**) in high yield. Both spectroscopic as well as structural studies showed the phenolic group to be protonated. Attempts to obtain chelation by inducing oxidative addition of the OH bond to the Mo metal center failed. Crystal data for $MoC_{44}H_{40}P_2O$ (**1**) at −145 °C: $a = 17.310$ (7) Å, $b = 10.149$ (3) Å, $c = 21.090$ (5) Å, $\beta = 108.89$ (2)°, $Z = 4$, $d_{calcd} = 1.407$ g cm^{-3} in space group $P2_1/c$. For $WC_{44}H_{40}P_2O$ (**2**) at −155 °C: $a = 17.358$ (4) Å, $b = 10.20$ (1) Å, $c = 21.127$ (5) Å, $\beta = 108.85$ (1)°, $Z = 4$, $d_{calcd} = 1.558$ g cm^{-3}. For $WC_{34}H_{35}ClP_2O$ (**4**) at 22 °C: $a = 14.942$ (2) Å, $b = 12.6796$ (8) Å, $c = 16.233$ (1) Å, $\beta = 98.104$ (8)°, $Z = 4$, $d_{calcd} = 1.616$ g cm^{-3} in space group $P2_1/c$. For $WC_{44}H_{37}ClP_2O$ (**5**) at 20 °C: $a = 9.172$ (1) Å, $b = 19.765$ (6) Å, $c = 10.293$ (3) Å, $\beta = 110.22$ (2)°, $Z = 2$, $d_{calcd} = 1.637$ g cm^{-3} in space group $P2_1$. For $MoO_4C_{21}H_{14}$ (**6**) at 20 °C: $a = 20.304$ (1) Å, $b = 12.188$ (2) Å, $c = 14.464$ (2) Å, $Z = 8$, $d_{calcd} = 1.582$ g cm^{-3} in space group *Pbcn*.

Introduction

Recently there has been a burgeoning of research activity into the early-transition-metal chemistry associated with alkoxide and aryloxide ligation.[2-7] In particular, the use of sterically demanding alkoxide or aryloxide ligands surrounding early d-block metal centers in high or medium oxidation states has led to a plethora of new and exciting chemistry. A sometimes troublesome problem which is common to most bulky ligands is the fact that cyclometallation chemistry associated with the ligands themselves can sometimes dominate.[8-10] In the case of aryloxide chemistry, the two bulky ligands 2,6-di-*tert*-butyl-

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(1) Camille and Henry Dreyfus Teacher-Scholar, 1985–1990. Fellow of the Alfred P. Sloan Foundation, 1986–1990.

(2) (a) Durfee, L. D.; Kobriger, L. M.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 1463. (b) Fanwick, P. E.; Ogilvy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73. (c) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (d) Latesky, S. L.; McMullen, A. K.; Keddington, J.; Rothwell, I. P.; Huffman, J. C. *Inorg Chem.* **1985**, *24*, 995. (e) Durfee, L. D.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 4569. (f) Coffindaffer, T. W.; Niccolai, G.; Powell, D.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3572. (g) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E. Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390. (h) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.

(3) (a) Neithamer, D. R.; Parkanyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421. (b) Lapointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6832.

(4) (a) Chisholm, M. H. *Angew. Chem.* **1986**, *98*, 21. (b) Chisholm, M. H. *Polyhedron* **1986**, *5*, 25. (c) Chisholm, M. H. *J. Solid State Chem.* **1985**, *57*, 120.

(5) Bruck, M. A.; Gpenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

(6) (a) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (b) Latham, I. A.; Sita, L. R.; Schrock, R. R. *Organometallics* **1986**, *5*, 1508. (c) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2161. (d) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554.

(7) (a) Duff, A. W.; Kamarudin, R. A.; Lappert, M. F.; Norton, R. J. *J. Chem. Soc., Dalton Trans.* **1986**, 489 and references therein. (b) Dilworth, J. R.; Hanich, J.; Krestel, M.; Beuk, J.; Strahle, J., *J. Organomet. Chem.* **1986**, *315*, C9.

(8) (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (b) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245; *Chemtech* **1982**, *12*, 506. (d) Constable, E. C. *Polyhedron* **1984**, *3*, 1037.

(9) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

(10) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219.

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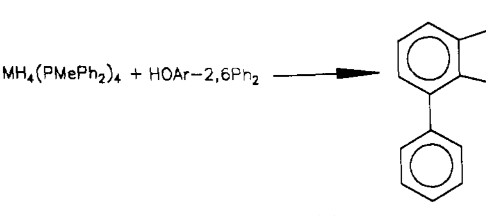
Scheme I



M = Mo (1), W (2)

HOAr-2,6Ph$_2$ = 2,6-diphenylphenol

phenoxide and 2,6-diphenylphenoxide (OAr-2,6-Ph$_2$) have been shown to undergo facile intramolecular activation of their aliphatic and aromatic CH bonds, respectively, to generate six-membered metallacycle rings.[11,12] This activation has been demonstrated to occur both via an oxidative addition pathway (for d^n, $n \geq 2$ metal centers)[12] as well as by more electrophilic (heterolytic) pathways (for d^0 metal configurations).[11] However, another type of "interference" of the aryl side groups in OAr-2,6-Ph$_2$ ligands has been observed.[13,14] This bonding mode involves chelation to low-valent metal centers via both the oxygen donor atom as well as via an η^6-interaction with one of these aryl rings. Far from being troublesome, this chelation allows the 2,6-diphenylphenoxide ligand to stabilize the metal in lower oxidation states. In some cases the low-valent aryloxides thus stabilized can prove to be potent intermediates, with the displacement of the aryl ring leading to highly reducing metal substrates.[15] In this paper we wish to report on the synthesis of a series of 18-electron derivatives of the heavier group 6 metals containing 2,6-diphenylphenoxide chelated in this fashion. Besides their spectroscopic properties, structural studies are also reported that characterize the structural parameters for these new types of η^6-arene compounds.

Results and Discussion

Previous studies have shown that treatment of the molybdenum(IV) amido compound Mo(NMe$_2$)$_4$ with 2,6-diphenylphenol (HOAr-2,6-Ph$_2$) leads to the cyclometalated compound Mo(OC$_6$H$_3$PhC$_6$H$_4$)(OAr-2,6-Ph$_2$)$_2$(HNMe$_2$).[16] The new metallacycle ring is formed by intramolecular activation of an aromatic CH bond by an Mo–NMe$_2$ function. Following this result we turned our attention to the well-known 18-electron hydride substrates MH$_4$(PMePh$_2$)$_4$ (M = Mo, W).[17] The molybdenum compound has previously been shown to undergo facile substitution with small phenols to produce Mo(IV) aryloxides and dihydrogen.[18] The bright yellow tetrahydrides prove to be extremely resistant to attack by 2,6-diphenylphenol.

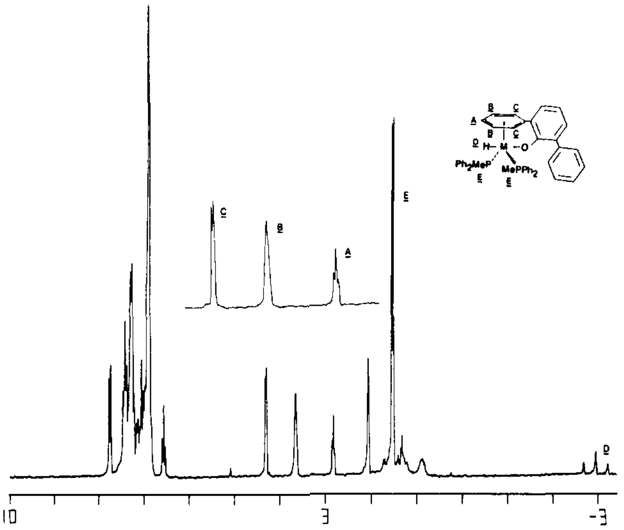


Figure 1. ^{1}H NMR spectrum of Mo(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(H)(PMePh$_2$)$_2$ (1).

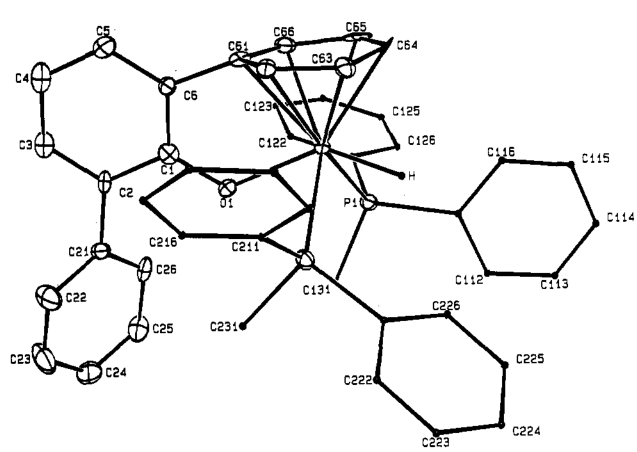


Figure 2. ORTEP view of Mo(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(H)(PMePh$_2$)$_2$ (1) emphasizing the central coordination sphere. The tungsten compound 2 is isomorphous and isostructural and has the same labeling scheme. However, the hydride ligand in 2 was not located.

However, when the reaction is carried out in a neat melt of MH$_4$(PMePh$_2$)$_4$ and HOAr-2,6-Ph$_2$ (typically 2–5 equiv) at temperatures greater than 150 °C, there is the slow formation of a new deep red product. After extended thermolysis, workup of the crude reaction mixture allows the isolation of the monohydride compounds M(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(H)(PMePh$_2$)$_2$ (M = Mo (1), W (2)) as deep red blocks (Scheme I). Analysis of the reaction mixtures before complete reaction had occurred indicated the presence of MH$_4$(PMePh$_2$)$_4$ and 1 or 2 along with free HOAr-2,6-Ph$_2$ and PMePh$_2$.

The spectroscopic properties of 1 and 2 are very similar. In the ^{1}H NMR spectrum an upfield triplet located at δ −2.92 (1) or δ −1.50 ppm (2) is characteristic of a metal hydride ligand(s) coupled to two equivalent phosphorus nuclei. Besides the normal P*Me*Ph$_2$ doublet and typical grouping of aromatic resonances, the most striking feature of the ^{1}H NMR spectra of 1 and 2 are a series of three multiplets in the δ 2.5–6.0 ppm region (Figure 1). Both the position of these signals as well as their patterns, d (2 H), t (2 H), t (1 H), indicates their assignment as a phenyl ring π-bound to the metal center. Integration is consistent with one hydride, two PMePh$_2$ ligands, and one η^6-C$_6$H$_5$ group being present. Both the ^{13}C and ^{31}P NMR spectra of 1 and 2 are also consistent with the proposed formulation.

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[11] Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153.

[12] (a) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P. Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (c) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. D.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc.* **1987**, *109*, 6471. (d) Chesnut, R. W.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1988**, *7*, 753.

[13] Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1987**, *109*, 5840.

[14] (a) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121. (b) Bishop, P. T., Blower, P. J.; Dilworth, J. R.; Zubieta, J. A. *Polyhedron* **1986**, *5*, 363.

[15] Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.*, submitted for publication.

[16] Kerschner, J. L.; Fanwick, P. E.; Yu, J.; Rothwell, I. P.; Huffman, J. C. *Organometallics*, first of four papers in this issue.

[17] Crabtree, R. H.; Hltaky, G. G. *Inorg. Chem.* **1982**, *21*, 1273 and references therein.

[18] Beshouri, S. M.; Coffindaffer, T. W.; Pirzard, S.; Rothwell, I. P. *Inorg. Chim. Acta* **1985**, *103*, 111.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $Mo(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(H)(PMePh_2)$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo	0.20153 (3)	0.07839 (6)	0.14419 (3)	0.724 (8)
P(1)	0.2623 (1)	−0.0909 (2)	0.22852 (7)	0.91 (3)
P(2)	0.2139 (1)	−0.0413 (2)	0.04686 (8)	1.03 (3)
O(1)	0.3289 (3)	0.1107 (5)	0.1557 (2)	1.07 (9)
C(1)	0.3518 (4)	0.2311 (7)	0.1455 (3)	1.1 (1)
C(2)	0.4294 (4)	0.2571 (7)	0.1393 (3)	1.1 (1)
C(3)	0.4481 (4)	0.3843 (7)	0.1271 (3)	1.3 (1)
C(4)	0.3941 (5)	0.4888 (8)	0.1189 (3)	1.7 (1)
C(5)	0.3173 (4)	0.4638 (8)	0.1235 (4)	1.6 (1)
C(6)	0.2968 (4)	0.3373 (7)	0.1368 (3)	1.0 (1)
C(21)	0.4890 (4)	0.1514 (7)	0.1431 (3)	1.1 (1)
C(22)	0.5318 (5)	0.1463 (9)	0.0979 (4)	2.2 (2)
C(23)	0.5911 (5)	0.0516 (9)	0.1034 (4)	2.6 (2)
C(24)	0.6082 (5)	−0.0407 (8)	0.1536 (4)	2.1 (2)
C(25)	0.5660 (5)	−0.0391 (8)	0.1991 (4)	1.7 (2)
C(26)	0.5076 (4)	0.0562 (7)	0.1944 (3)	1.3 (1)
C(61)	0.2156 (4)	0.2998 (7)	0.1424 (3)	0.8 (1)
C(62)	0.1518 (4)	0.2701 (7)	0.0842 (3)	1.0 (1)
C(63)	0.0867 (4)	0.1907 (7)	0.0899 (3)	1.2 (1)
C(64)	0.0825 (4)	0.1634 (7)	0.1550 (3)	1.2 (1)
C(65)	0.1467 (5)	0.1926 (7)	0.2137 (3)	1.5 (1)
C(66)	0.2146 (4)	0.2594 (7)	0.2074 (3)	1.1 (1)
C(111)	0.1947 (4)	−0.2134 (8)	0.2439 (3)	1.2 (1)
C(112)	0.2132 (5)	−0.3504 (8)	0.2502 (4)	2.4 (2)
C(113)	0.1594 (6)	−0.4355 (9)	0.2649 (4)	3.2 (2)
C(114)	0.0899 (5)	−0.3940 (9)	0.2739 (4)	2.5 (2)
C(115)	0.0696 (5)	−0.2631 (9)	0.2674 (3)	1.8 (1)
C(116)	0.1222 (5)	−0.1747 (8)	0.2531 (3)	1.5 (1)
C(121)	0.3121 (4)	−0.0268 (7)	0.3139 (3)	1.1 (1)
C(122)	0.3656 (4)	0.0773 (8)	0.3223 (3)	1.5 (1)
C(123)	0.4076 (4)	0.1284 (8)	0.3860 (4)	1.7 (1)
C(124)	0.3960 (5)	0.0698 (9)	0.4420 (3)	2.0 (2)
C(125)	0.3418 (5)	−0.0339 (9)	0.4339 (3)	2.0 (2)
C(126)	0.3015 (4)	−0.0821 (9)	0.3707 (3)	1.8 (1)
C(131)	0.3462 (4)	−0.1865 (8)	0.2183 (3)	1.4 (1)
C(211)	0.1743 (4)	0.0634 (7)	−0.0269 (3)	1.2 (1)
C(212)	0.0905 (4)	0.0727 (8)	−0.0578 (3)	1.5 (1)
C(213)	0.0574 (5)	0.1691 (8)	−0.1052 (3)	1.6 (1)
C(214)	0.1085 (5)	0.2549 (8)	−0.1234 (3)	1.8 (2)
C(215)	0.1911 (5)	0.2475 (8)	−0.0952 (3)	1.9 (2)
C(216)	0.2248 (4)	0.1488 (8)	−0.0466 (3)	1.5 (1)
C(221)	0.1603 (4)	−0.1982 (7)	0.0179 (3)	1.1 (1)
C(222)	0.1524 (5)	−0.2463 (8)	−0.0454 (3)	1.7 (1)
C(223)	0.1192 (5)	−0.3695 (8)	−0.0643 (4)	2.0 (2)
C(224)	0.0945 (4)	−0.4455 (7)	−0.0200 (4)	1.6 (1)
C(225)	0.1025 (5)	−0.3981 (8)	0.0428 (3)	1.5 (1)
C(226)	0.1349 (4)	−0.2738 (8)	0.0617 (3)	1.4 (1)
C(231)	0.3157 (4)	−0.0819 (9)	0.0455 (3)	1.7 (1)
H	0.134 (5)	−0.041 (8)	0.126 (4)	2 (2)*

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(H)(PMePh_2)_2$ (2)[a]

atom	*x*	*y*	*z*	*B*, Å^2
W	0.20090 (3)	0.0774 (1)	0.14445 (4)	1.40 (2)
P(1)	0.2635 (2)	−0.0902 (5)	0.2289 (3)	1.6 (1)
P(2)	0.2135 (2)	−0.0416 (4)	0.0474 (3)	1.7 (1)
O(1)	0.3276 (5)	0.109 (1)	0.1547 (6)	1.7 (3)
C(1)	0.3517 (7)	0.231 (2)	0.145 (1)	1.7 (5)
C(2)	0.4288 (7)	0.256 (2)	0.140 (1)	1.7 (5)
C(3)	0.4485 (9)	0.386 (2)	0.129 (1)	2.2 (5)
C(4)	0.3937 (9)	0.488 (2)	0.121 (1)	2.8 (6)
C(5)	0.3176 (8)	0.465 (2)	0.125 (1)	2.1 (5)
C(6)	0.2969 (7)	0.337 (2)	0.138 (1)	1.6 (5)
C(21)	0.4883 (8)	0.149 (2)	0.1442 (9)	1.5 (4)
C(22)	0.530 (1)	0.144 (2)	0.097 (1)	2.9 (5)
C(23)	0.588 (1)	0.049 (2)	0.101 (1)	3.7 (6)
C(24)	0.608 (1)	−0.040 (2)	0.151 (1)	3.6 (6)
C(25)	0.5659 (9)	−0.040 (2)	0.199 (1)	2.4 (5)
C(26)	0.5072 (8)	0.055 (2)	0.195 (1)	2.1 (5)
C(61)	0.2159 (9)	0.299 (2)	0.143 (1)	1.9 (5)
C(62)	0.1533 (8)	0.268 (2)	0.084 (1)	2.1 (5)
C(63)	0.0872 (8)	0.190 (2)	0.088 (1)	1.6 (5)
C(64)	0.0792 (9)	0.162 (2)	0.153 (1)	1.7 (4)
C(65)	0.1458 (9)	0.188 (2)	0.214 (1)	1.8 (5)
C(66)	0.2156 (9)	0.255 (2)	0.210 (1)	2.4 (5)
C(111)	0.1961 (8)	−0.215 (2)	0.245 (1)	1.5 (3)*
C(112)	0.2137 (9)	−0.349 (2)	0.249 (1)	2.4 (4)*
C(113)	0.162 (1)	−0.439 (2)	0.264 (1)	3.8 (4)*
C(114)	0.0908 (9)	−0.398 (2)	0.272 (1)	2.8 (4)*
C(115)	0.0697 (9)	−0.265 (2)	0.266 (1)	2.6 (4)*
C(116)	0.1221 (9)	−0.175 (2)	0.251 (1)	2.5 (4)*
C(121)	0.3129 (8)	−0.026 (2)	0.316 (1)	1.5 (3)*
C(122)	0.3660 (8)	0.076 (2)	0.324 (1)	1.8 (3)*
C(123)	0.409 (1)	0.126 (2)	0.388 (1)	2.8 (4)*
C(124)	0.3960 (9)	0.069 (2)	0.442 (1)	2.4 (3)*
C(125)	0.3419 (9)	−0.034 (2)	0.434 (1)	2.7 (4)*
C(126)	0.3003 (9)	−0.086 (2)	0.370 (1)	2.7 (4)*
C(131)	0.3482 (9)	−0.187 (2)	0.218 (1)	2.2 (3)*
C(211)	0.1756 (9)	0.063 (2)	−0.026 (1)	2.6 (4)*
C(212)	0.0901 (8)	0.073 (2)	−0.0572 (9)	1.6 (3)*
C(213)	0.0558 (9)	0.170 (2)	−0.106 (1)	2.5 (4)*
C(214)	0.1067 (9)	0.255 (2)	−0.124 (1)	2.8 (4)*
C(215)	0.1907 (8)	0.245 (2)	−0.096 (1)	2.0 (3)*
C(216)	0.2253 (9)	0.147 (2)	−0.046 (1)	2.5 (4)*
C(221)	0.1597 (9)	−0.195 (2)	0.019 (1)	2.1 (3)*
C(222)	0.1517 (8)	−0.247 (2)	−0.044 (1)	1.9 (3)*
C(223)	0.117 (1)	−0.368 (2)	−0.064 (1)	2.7 (4)*
C(224)	0.0941 (9)	−0.444 (2)	−0.021 (1)	2.2 (3)*
C(225)	0.1029 (9)	−0.399 (2)	0.043 (1)	2.3 (3)*
C(226)	0.1361 (8)	−0.275 (2)	0.064 (1)	2.0 (3)*
C(231)	0.3158 (8)	−0.086 (2)	0.0462 (9)	1.6 (3)*

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Bond Distances (Å) and Angle (deg) for $M(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(H)(PMePh_2)_2$ (M = Mo (1), W (2))

	M = Mo (1)	M = W (2)
M–O(1)	2.164 (5)	2.163 (9)
M–P(1)	2.451 (2)	2.456 (5)
M–P(2)	2.453 (2)	2.454 (6)
M–C(61)	2.262 (7)	2.28 (2)
M–C(62)	2.329 (7)	2.32 (2)
M–C(63)	2.255 (6)	2.26 (1)
M–C(64)	2.313 (7)	2.34 (2)
M–C(65)	2.301 (8)	2.30 (2)
M–C(66)	2.238 (7)	2.25 (2)
M–H	1.64 (8)	
M–O(1)–C(1)	118.0 (4)	118.5 (8)
Pnl)–M–P(2)	97.3 (6)	97.1 (2)
P(1)–M–O(1)	80.9 (1)	80.5 (3)
P(2)–M–O(1)	78.9 (1)	78.2 (3)

The solid-state structures of **1** and **2** were determined by X-ray diffraction techniques. An ORTEP view of the molybdenum molecule is shown in Figure 2, while Tables I and II contain fractional coordinates and isotropic thermal parameters. Some selected bond distances and angles are collected in Table III. The two compounds were found to be isomorphous. However, in the case of the tungsten compound **2** the problems encountered in the data collection precluded the determination of the position of the hydride ligand. The two molecules can best be described as four-legged "piano-stool" structures in which the η^6-arene "seat" is chelated to the oxyten atom which forms one of the legs. The hydride ligand is found to be located across from the aryloxide oxygen atom, so that a virtual (although not crystallographic) plane of symmetry in the molecule makes the two phosphorus atoms equivalent. Furthermore, the orientation of the substituents on the two $PMePh_2$ ligands is almost identical, so that asymmetry due to rotameric forms of these groups is precluded.[19]

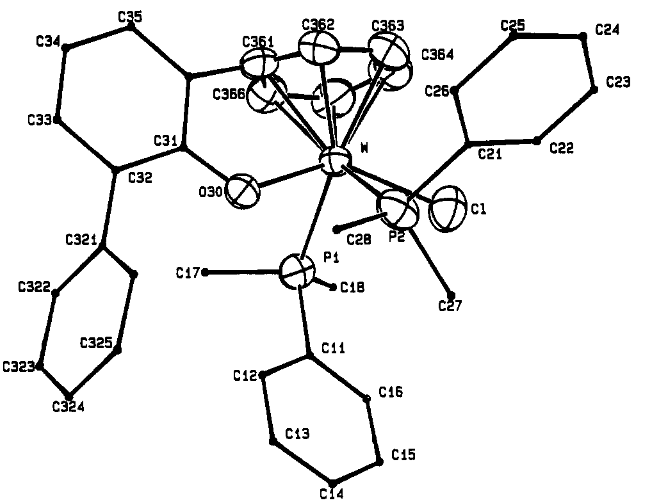
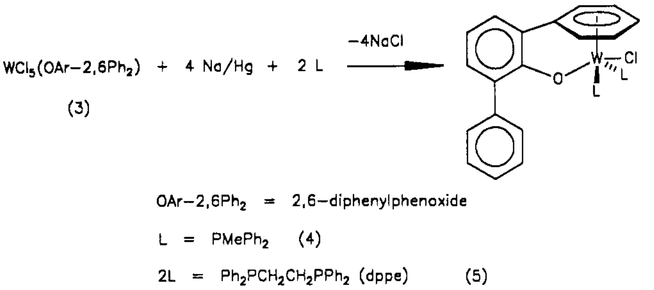


Figure 3. ORTEP view of $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(PMe_2Ph)_2$ (4) emphasizing the central coordination sphere.

Scheme II



A search for alternative synthetic methods for the formation of 2,6-diphenylphenoxide derivatives of these metals in which the ligand is chelated to the metal via an η^6-interaction led us to investigate the classical reduction chemistry of the tungsten(VI) compound $W(OAr\text{-}2,6\text{-}Ph_2)Cl_5$ (3). We have shown that reduction of the related bis(aryloxide) *cis*-$W(OAr\text{-}2,6\text{-}Ph_2)_2Cl_4$ with sodium amalgam (4Na/W) can lead to either bis-cyclometalated compounds $W(OC_6H_3PhC_6H_4)_2(PR_3)_2$ or the 16-electron bis(aryloxides) $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(OAr\text{-}2,6\text{-}Ph_2)(PR_3)$, the latter in low yield.[13] In contrast we find that the reduction of toluene solutions of the pentachloride 3 with sodium amalgam (4Na/W) in the presence of either PMe_2Ph or dppe ($Ph_2PCH_2CH_2PPh_2$) leads to the moderate yield formation of the 18-electron compounds $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(PMe_2Ph)_2$ (4) and $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(dppe)$ (5), respectively (Scheme II). Spectroscopic data on 4 and 5 is consistent with their adopting structures in solution closely related to the monohydride 2 with the W–H group simply being substituted by W–Cl. In the case of 4 there is only one type of PMe_2Ph group, containing diastereotopic, nonequivalent methyl groups that appear as two doublets. The characteristic pattern for a symmetrical η^6-bound arene ring is also present in the δ 2.5–6.0 ppm region. In the case of 5, the ^{31}P NMR spectrum shows equivalent phosphorus nuclei for the dppe chelate. Hence, this implies that the ethylene backbone of the dppe chelate must pass below (instead of around) the base of the piano stool, trans to the η^6-arene ring.

These conclusions about the structures of 4 and 5 were confirmed by X-ray diffraction analyses of both compounds (Figures 3 and 4). The fractional coordinates and isotropic thermal parameters are contained in Tables IV and V while Tables VI and VII contain some selected at bond distances and angles for 4 and 5, respectively. The structural similarity between the monohydrides 1 and 2 and the monochlorides 4 and 5 is clearly seen.[20] The structural parameters for the bis(dimethylphenyl-

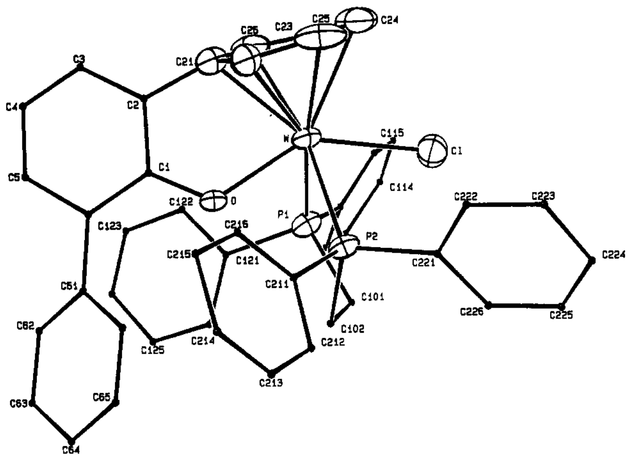


Figure 4. ORTEP view of $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(dppe)_2$ (5).

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(PMe_2Ph)_2$ (4)[a]

atom	x	y	z	B, Å^2
W	0.28782 (2)	0.03352 (2)	0.17780 (1)	2.865 (4)
Cl	0.4185 (1)	−0.0557 (2)	0.1260 (1)	5.38 (4)
P(1)	0.4098 (1)	0.1655 (1)	0.2133 (1)	3.43 (3)
P(2)	0.2566 (1)	0.0616 (1)	0.0244 (1)	4.11 (4)
O(30)	0.2202 (2)	0.1815 (3)	0.1745 (2)	3.31 (9)
C(11)	0.4376 (4)	0.2516 (5)	0.1310 (4)	3.7 (1)
C(12)	0.3805 (5)	0.3356 (5)	0.1054 (4)	4.5 (2)
C(13)	0.3951 (6)	0.3983 (6)	0.0379 (4)	5.8 (2)
C(14)	0.4656 (6)	0.3759 (6)	−0.0041 (4)	6.4 (2)
C(15)	0.5219 (5)	0.2925 (6)	0.0192 (4)	6.1 (2)
C(16)	0.5092 (5)	0.2314 (6)	0.0869 (4)	5.0 (2)
C(17)	0.3845 (5)	0.2599 (6)	0.2919 (4)	4.8 (2)
C(18)	0.5189 (5)	0.1133 (6)	0.2601 (5)	5.6 (2)
C(21)	0.2039 (4)	−0.0539 (5)	−0.0293 (4)	4.2 (1)
C(22)	0.2558 (5)	−0.1383 (6)	−0.0466 (4)	5.5 (2)
C(23)	0.2184 (6)	−0.2275 (7)	−0.0860 (5)	7.0 (2)
C(24)	0.1301 (7)	−0.2343 (7)	−0.1056 (5)	8.3 (2)
C(25)	0.0755 (6)	−0.1540 (8)	−0.0895 (7)	9.5 (3)
C(26)	0.1115 (5)	−0.0624 (7)	−0.0505 (6)	7.2 (2)
C(27)	0.3461 (6)	0.0886 (7)	−0.0377 (4)	7.8 (2)
C(28)	0.1796 (7)	0.1679 (6)	−0.0100 (5)	8.1 (2)
C(31)	0.1533 (4)	0.2013 (5)	0.2200 (4)	3.4 (1)
C(32)	0.1148 (4)	0.3022 (5)	0.2239 (4)	3.8 (1)
C(33)	0.0461 (4)	0.3138 (6)	0.2731 (4)	4.9 (2)
C(34)	0.0156 (5)	0.2316 (7)	0.3167 (5)	6.0 (2)
C(35)	0.0540 (4)	0.1335 (6)	0.3150 (4)	4.9 (2)
C(36)	0.1244 (4)	0.1189 (5)	0.2673 (4)	3.7 (1)
C(321)	0.1435 (4)	0.3949 (5)	0.1791 (4)	4.0 (1)
C(322)	0.1861 (6)	0.4790 (6)	0.2232 (5)	5.8 (2)
C(323)	0.2111 (7)	0.5681 (7)	0.1819 (6)	7.8 (3)
C(324)	0.1927 (7)	0.5767 (6)	0.0975 (6)	7.7 (3)
C(325)	0.1497 (8)	0.4949 (7)	0.0535 (6)	8.4 (3)
C(326)	0.1251 (6)	0.4057 (6)	0.0936 (5)	6.4 (2)
C(361)	0.1751 (4)	0.0192 (5)	0.2607 (4)	3.9 (1)
C(362)	0.1547 (4)	−0.0401 (5)	0.1880 (4)	4.4 (1)
C(363)	0.2148 (5)	−0.1232 (5)	0.1707 (5)	5.3 (2)
C(364)	0.2914 (5)	−0.1401 (5)	0.2274 (5)	6.2 (2)
C(365)	0.3218 (5)	−0.0675 (5)	0.2914 (4)	5.0 (2)
C(366)	0.2605 (5)	0.0123 (5)	0.3109 (4)	4.2 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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(19) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 3833.

(20) (a) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1139. (b) Green, M. L. H. *J. Organomet. Chem.* **1980**, *250*, 119.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(Ph_2PCH_2CH_2PPh_2)$ (5)[a]

atom	*x*	*y*	*z*	*B*, Å^2
W	0.12788 (5)	0	0.15812 (5)	2.228 (5)
Cl	0.2786 (4)	0.1068 (2)	0.2321 (4)	3.31 (8)
P(1)	0.2360 (4)	0.0203 (2)	−0.0294 (3)	2.58 (9)
P(2)	0.3999 (4)	−0.0411 (2)	0.2793 (4)	2.37 (8)
O	0.1456 (9)	−0.0975 (5)	0.0757 (9)	2.4 (2)
C(1)	0.019 (2)	−0.1348 (7)	0.011 (1)	2.6 (3)
C(2)	−0.125 (2)	−0.1114 (9)	0.014 (2)	3.7 (4)
C(3)	−0.264 (2)	−0.144 (1)	−0.064 (2)	5.7 (5)
C(4)	−0.261 (2)	−0.199 (1)	−0.136 (2)	5.2 (5)
C(5)	−0.125 (2)	−0.2240 (9)	−0.140 (2)	3.9 (4)
C(6)	0.026 (2)	−0.1939 (8)	−0.061 (1)	3.1 (3)
C(21)	−0.113 (2)	−0.0509 (8)	0.099 (2)	3.0 (3)
C(22)	−0.031 (2)	−0.0568 (8)	0.243 (1)	2.6 (3)*
C(23)	0.015 (1)	0.002 (2)	0.329 (1)	4.0 (3)
C(24)	−0.013 (2)	0.066 (1)	0.270 (2)	4.6 (4)
C(25)	−0.078 (1)	0.0724 (9)	0.120 (2)	4.3 (4)
C(26)	−0.135 (1)	0.0140 (8)	0.037 (1)	3.4 (3)
C(61)	0.164 (2)	−0.2264 (8)	−0.070 (1)	3.1 (3)
C(62)	0.166 (2)	−0.2591 (9)	−0.190 (2)	4.5 (4)
C(63)	0.297 (2)	−0.292 (1)	−0.195 (2)	6.2 (5)
C(64)	0.432 (2)	−0.292 (1)	−0.080 (3)	7.4 (6)
C(65)	0.428 (2)	−0.261 (1)	0.039 (2)	7.2 (6)
C(66)	0.299 (2)	−0.228 (1)	0.042 (2)	4.9 (5)
C(101)	0.451 (1)	0.013 (1)	0.048 (1)	4.0 (4)
C(102)	0.496 (1)	−0.0461 (8)	0.147 (1)	2.8 (3)
C(111)	0.198 (2)	0.0970 (9)	−0.134 (1)	3.3 (4)
C(112)	0.235 (2)	0.099 (1)	−0.254 (2)	4.1 (4)
C(113)	0.200 (2)	0.154 (1)	−0.340 (2)	5.5 (5)
C(114)	0.128 (2)	0.210 (1)	−0.307 (2)	5.1 (5)
C(115)	0.087 (2)	0.208 (1)	−0.191 (2)	4.6 (4)
C(116)	0.124 (2)	0.1524 (9)	−0.107 (2)	3.5 (4)
C(121)	0.184 (2)	−0.0417 (8)	−0.168 (1)	3.0 (3)
C(122)	0.028 (2)	−0.050 (1)	−0.247 (2)	4.1 (4)
C(123)	−0.014 (3)	−0.092 (1)	−0.360 (2)	6.0 (6)
C(124)	0.092 (3)	−0.125 (1)	−0.397 (2)	6.6 (6)
C(125)	0.251 (3)	−0.118 (1)	−0.322 (2)	6.4 (6)
C(126)	0.298 (2)	−0.078 (1)	−0.209 (2)	4.0 (4)
C(211)	0.436 (2)	−0.1247 (8)	0.356 (1)	2.9 (3)
C(212)	0.586 (2)	−0.1502 (9)	0.412 (2)	4.3 (4)
C(213)	0.612 (2)	−0.212 (1)	0.475 (2)	5.0 (5)
C(214)	0.505 (3)	−0.251 (1)	0.496 (3)	4.6 (3)
C(215)	0.342 (2)	−0.2267 (9)	0.430 (2)	4.4 (4)
C(216)	0.317 (2)	−0.1653 (9)	0.369 (2)	3.6 (4)
C(221)	0.528 (1)	0.007 (1)	0.421 (1)	3.1 (3)
C(222)	0.495 (1)	0.016 (1)	0.537 (1)	3.9 (4)
C(223)	0.585 (2)	0.055 (1)	0.649 (2)	4.9 (4)
C(224)	0.720 (2)	0.085 (1)	0.641 (2)	4.6 (4)
C(225)	0.752 (2)	0.078 (1)	0.528 (2)	4.6 (4)
C(226)	0.664 (2)	0.405 (9)	0.417 (2)	4.0 (4)

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(PMe_2Ph)_2$ (4)

W–Cl	2.503 (2)	W–P(1)	2.481 (2)
W–P(2)	2.494 (2)	W–O(30)	2.128 (4)
W–C(361)	2.306 (7)	W–C(362)	2.224 (7)
W–C(361)	2.262 (8)	W–C(364)	2.342 (8)
W–C(365)	2.244 (7)	W–C(366)	2.270 (7)

Cl–W–P(1)	78.50 (7)	O(30)–W–P(1)	75.0 (1)
Cl–W–P(2)	76.97 (7)	O(30)–W–P(2)	80.1 (1)
Cl–W–O(30)	141.3 (1)	P(1)–W–P(2)	99.39 (6)
W–O(30)–C(31)	122.5 (4)		

Table VII. Selected Bond Distances (Å) and Angles (deg) for $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(Ph_2PCH_2CH_2PPh_2)$ (5)

W–Cl	2.495 (3)	W–P(1)	2.490 (3)
W–P(2)	2.510 (3)	W–O	2.135 (8)
W–C(21)	2.31 (2)	W–C(22)	2.24 (2)
W–C(23)	2.33 (1)	W–C(24)	2.39 (2)
W–C(25)	2.29 (2)	W–C(26)	2.32 (1)

Cl–W–P(1)	76.8 (1)	O–W–P(1)	74.4 (2)
Cl–W–P(2)	76.7 (1)	O–W–P(2)	72.9 (2)
Cl–W–O	140.8 (2)	P(1)–W–P(2)	80.9 (1)
W–O–C(1)	121.3 (7)		

Table VIII. Fractional Coordinates and Isotropic Thermal Parameters for $Mo(HOC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(CO)_3$ (6)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo	0.06020 (2)	0.21312 (4)	0.03934 (3)	2.847 (9)
O(1)	0.1256 (3)	0.0457 (4)	0.1736 (3)	5.8 (1)
O(2)	0.1115 (3)	0.3944 (5)	0.1720 (4)	8.9 (2)
O(3)	−0.0639 (2)	0.1894 (5)	0.1619 (3)	6.6 (1)
O(10)	−0.0688 (2)	0.4147 (3)	0.0221 (3)	3.71 (9)
C(1)	0.1015 (3)	0.1089 (5)	0.1239 (4)	3.6 (1)
C(2)	0.0922 (4)	0.3266 (6)	0.1236 (4)	4.8 (2)
C(3)	−0.0168 (3)	0.1998 (5)	0.1171 (4)	3.7 (1)
C(11)	−0.1045 (3)	0.3564 (4)	−0.0417 (4)	2.7 (1)
C(12)	−0.0752 (2)	0.2789 (4)	−0.1009 (4)	2.6 (1)
C(13)	−0.1144 (3)	0.2258 (5)	−0.1661 (4)	3.1 (1)
C(14)	−0.1805 (3)	0.2481 (5)	−0.1735 (4)	3.3 (1)
C(15)	−0.2092 (3)	0.3239 (5)	−0.1141 (4)	3.2 (1)
C(16)	−0.1727 (3)	0.3777 (4)	−0.0466 (4)	2.8 (1)
C(121)	−0.0041 (3)	0.2484 (4)	−0.0950 (4)	2.7 (1)
C(122)	0.0472 (3)	0.3255 (5)	−0.0931 (4)	3.3 (1)
C(123)	0.1133 (3)	0.2917 (5)	−0.0896 (4)	3.7 (1)
C(124)	0.1298 (3)	0.1822 (5)	−0.0888 (4)	3.7 (1)
C(125)	0.0796 (3)	0.1010 (5)	−0.0904 (4)	3.7 (1)
C(126)	0.0131 (3)	0.1333 (5)	−0.0942 (4)	3.2 (1)
C(161)	−0.2064 (3)	0.4517 (4)	0.0201 (4)	2.7 (1)
C(162)	−0.2504 (3)	0.5314 (4)	−0.0108 (4)	3.2 (1)
C(163)	−0.2846 (3)	0.5961 (4)	0.0505 (4)	3.6 (1)
C(164)	−0.2755 (3)	0.5826 (5)	0.1439 (4)	3.6 (1)
C(165)	−0.2323 (3)	0.5053 (5)	0.1772 (4)	3.6 (1)
C(166)	−0.1972 (3)	0.4397 (4)	0.1156 (4)	3.1 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

phosphine) compound **4** shows that the angles between the chlorine atom and the two phosphine atoms are almost identical, 77–78°, while the two phosphine atoms form an angle of 99° between each other. The replacement of the two monodentate phosphines by a dppe ligand offers the possibility for forcing the molecule to adopt a new structural type with one phosphorus atom trans to the aryloxide oxygen. However, the molecule retains the same overall geometry. This may be due to the 81° bite of the dppe being better accommodated in this fashion, although a more plausible explanation is that this geometry allows the bulky phenyl substituents on the dppe to point away from the other ligands within the coordination sphere. Besides the slight closing up of the P–W–P angle on going from **4** to **5**, all other angles about the metal remain essentially identical.

In an attempt to obtain carbonyl compounds related to **1** and **2** using low-valent metal substrates,[14] the parent phenol HOAr-2,6-Ph$_2$, was reacted with $Mo(CO)_6$. Refluxing a mixture of these two in octane (24 h) led to the formation of the simple, unchelated η^6-arene tricarbonyl compound $Mo(HOC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(CO)_3$ (**6**) in high yields.[21] The π-bonding of the $Mo(CO)_3$ fragment to the side aryl ring, and not the central phenolic ring, was indicated by the ^1H NMR of **6** which again shows a d (H), t (H), t (H) pattern in the δ 3–6 ppm region. Also evident in this region of the spectrum is a sharp singlet due to the OH function. This data combined with the infrared spectrum of **6** are consistent with no significant interaction

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(21) For a general review of group 6 metal η^6-arene complexes see: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds., Pergamon Press: New York, 1981.

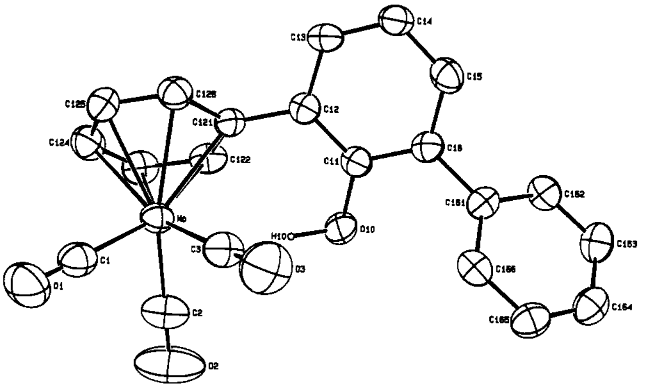

Figure 5. ORTEP view of Mo(HOC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(CO)$_3$ (6).

Table IX. Selected Bond Distances (Å) and Angles (deg) for Mo(HOC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(CO)$_3$ (6)

Mo–C(1)	1.953 (7)	Mo–C(2)	1.955 (7)
Mo–C(3)	1.933 (6)	Mo–C(121)	2.380 (5)
Mo–C(122)	2.369 (6)	Mo–C(123)	2.258 (6)
Mo–C(124)	2.360 (6)	Mo–C(125)	2.354 (6)
Mo–C(126)	2.364 (5)		
C(1)–Mo–C(2)	85.8 (3)	Mo–C(1)–O(1)	179.0 (5)
C(1)–Mo–C(3)	85.9 (2)	Mo–C(2)–O(2)	178.9 (6)
C(2)–Mo–C(3)	88.0 (3)	Mo–C(3)–O(3)	177.8 (6)

Table X. Comparison of M–η^6-Arene Distances

compound	M–C, Å
Mo(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)H(PMePh$_2$)$_2$ (1)	2.238–2.329
W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)H(PMePh$_2$)$_2$ (2)	2.25–2.34
W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)Cl(PMe$_2$Ph)$_2$ (4)	2.224–2.342
W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)Cl(dppe) (5)	2.24–2.39
Mo(HOC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(CO)$_3$ (6)	2.258–2.369

between the metal and the oxygen atom of the phenolic function.

A single-crystal X-ray diffraction analysis of 6 confirmed this formulation (Figure 5). The fractional coordinates and isotropic thermal parameters for 6 are contained in Table VIII while Table IX contains some selected bond distances and angles. The reaction of HOAr-2,6-Ph$_2$ with Mo(CO)$_3$, therefore, leads to another example of the extremely large class of (η^6-arene)M(CO)$_3$ (M = Cr, Mo, W) compounds.[21] Attempts to induce intramolecular oxidative addition of the OH bond in 6 by thermolysis or photolysis failed. The η^6-arene ring in 6 is readily displaced by aromatic solvents or phosphine ligands to generate free 2,6-diphenylphenol. The thermolysis at temperatures up to 300 °C of a mixture of Mo(CO)$_6$HOAr-2,6-Ph$_2$/PMePh$_2$ failed to produce any detectable amounts of 1 in the reaction mixture. It would, therefore, appear that the new chelate type in 1, 2, 4, 5, and 6 is more readily achieved by first forming the M–O bond prior to the π-arene interaction.

The 18-electron compounds obtained in this study allows one to accurately determine the structural characteristics of the chelation of 2,6-diphenylphenoxide ligands to metal centers via an η^6-interaction with one of the substituent arene rings. In Table X are collected some of the important structural parameters for compounds 1, 2, 4, 5, and 6. It can be seen that the physical geometry of the 2,6-diphenylphenoxide ligand allows the metal center to interact equally with all six of the arene carbon atoms with little distortion. The metal–carbon distances vary little either internally for each compound or between the various compounds themselves. The Mo–arene distance is, however, slightly longer in the tricarbonyl 6 than in the other derivatives. An important feature of the chelation via the *o*-phenyl ring is the impact on the M–O–Ar angle. In high- and mid-valent early d-block metal derivatives of chelated 2,6-diphenylphenoxide this angle typically is found to lie in the 130–180° range.[2,11,12] The almost linear values for this angle are most often associated with the ligand being bound to metal centers with a d^0-electron configuration. This large angle, coupled with short M–O distances, is typically attributed to the presence of significant amounts of oxygen p to metal d π-bonding.[22] The cyclometalation of 2,6-diphenylphenoxide, i.e. chelation through formation of a new metal–carbon σ-bond, is found to reduce this angle into a much narrower range of 130–145°.[11,12] This value allows the six-membered metallacycle to maintain an approximately 90° bite at the metal with little or no puckering of the ring. This value is also not inconsistent with π-donation to the metal from the oxygen atom to still be important. In the compounds obtained in this study the chelation via the η^6-arene interaction reduces the M–O–Ar angle even further to a range of 118–123°. This is the value one might expect for a phenoxide ligand bound in a completely π-innocent function; e.g. a methyl group cf. a value of 121° for the Ar–O–CH$_3$ angle in 4-methoxy-2,6-di-*tert*-butylphenoxide ligands.[23] This very small value for the M–O–Ar angle is, however, taking place in compounds in which the metal center is not likely to invite π-donation from the aryloxide oxygen atom. In fact the 18-electron nature of these compounds means that oxygen p to metal d π-donation is destabilizing. Consistent with this picture is the very long value found in these compounds for the M–O distances (Table X). For comparison, the (Mo–O and W–O) distances found for derivatives of these metals in higher oxidation states are typically 0.2–0.3 Å shorter than those reported in this work.[24] It can, therefore, be concluded that 2,6-diphenylphenoxide groups are indeed very versatile ligands, being able not only to interact with transition metal centers in a variety of ways but also to be able to actively stabilize the metal center in whatever the oxidation state it happens to be in.

Experimental Section

General experimental procedures have been described previously.[24] The tetrahydride substrates WH$_4$(PPh$_2$Me)$_4$ and MoH$_4$(PMePh$_2$)$_4$ were prepared by literature methods.[17] ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained on a Varian Associates XL-200 spectrometer and a General Electric QE-300 spectrometer and are referenced to Me$_4$Si by using the protio impurities of commercial benzene-d_6 or toluene-d_8 as internal standards (^{1}H and ^{13}C NMR) and to 85% H$_3$PO$_4$ (^{31}P NMR). The infrared spectra were obtained on a Perkin-Elmer Fourier transform infrared spectrometer. The microanalysis were carried out "in-house" at Purdue.

Mo(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)H(PMePh$_2$)$_2$ (1). A mixture of MoH$_4$(PMePh$_2$)$_4$ (0.50 g, 0.55 mmol) and HOAr-2,6-Ph$_2$ (0.41 g, 1.66 mmol) were heated to a temperature of >150 °C for several days in a neat melt under a N$_2$ atmosphere. Red crystalline blocks of product were isolated by dissolving the crude mixture in toluene and cooling. Typical yield: 10%. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ −2.92 (t, Mo–*H*), 1.55 (d, P*Me*) 2.87 (t), 3.68 (m), 4.38 (d, the *p*-, *m*-, and *o*-H's, of η^6-C$_6$H$_5$ ring). ^{13}C NMR (C$_6$D$_6$, 30 °C): 15.2 (d, P*Me*), 77.9, 79.9, 85.6, 112.7 (the para, meta, ortho, and ipso carbon atoms of the η^6-C$_6$H$_5$ ring). ^{13}P NMR (C$_6$D$_6$, 30 °C): δ 37.93. Infrared (Nujol mull): $\bar{\nu}$(Mo–H) = 1804 cm^{-1}.

W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)H(PMePh$_2$)$_2$ (2). An identical procedure of that above only using WH$_4$(PMePh$_2$)$_4$ (0.50 g, 0.51 mmol) and HOAr-2,6-Ph$_2$ (0.37 g, 1.50 mmol) yielded red crystalline

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(22) (a) Coffindaffer, J. W.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. *J. Chem. Soc., Chem. Commun.* **1985**, 1519. (b) Coffindaffer, T. W.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.*, submitted for publication.

(23) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

(24) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics*, in press.

Table XI. Crystallographic Data

	1	2	4	5	6
formula	$MoP_2OC_{44}H_{40}$	$WC_{44}H_{40}P_2O$	$WClP_2OC_{34}H_{35}$	$WClP_2C_{44}H_{37}$	$MoO_4C_{21}H_{14}$
fw	742.70	830.60	740.91	863.04	426.28
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1$	*Pbcn*
a, Å	17.310 (7)	17.358 (4)	14.942 (2)	9.172 (1)	20.304 (1)
b, Å	10.149 (3)	10.201 (1)	12.6796 (8)	19.765 (6)	12.188 (2)
c, Å	21.090 (5)	21.127 (5)	16.233 (1)	10.293 (3)	14.464 (2)
α, deg	90.0	90.00	90.00	90.00	90
β, deg	108.89 (2)	108.85 (1)	98.104 (8)	110.22 (2)	90
γ, deg	90.00	90.00	90.00	2	8
Z	4	4	4	2	8
V, Å^3	3506 (4)	3540.07	3044.6 (8)	1751 (1)	3579 (1)
d_{calcd}, g cm^{-3}	1.407	1.558	1.616	1.637	1.582
cryst size, mm	0.50 × 0.38 × 0.15	0.15 × 0.15 × 0.30	0.39 × 0.22 × 0.17	0.47 × 0.30 × 0.28	0.43 × 0.25 × 0.20
cryst color	red	red	red	red	yellow
radiatn	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
linear abs. coeff, cm^{-1}	4.87	34.541	40.92	35.70	7.36
temp, °C	−145	−155	22	20	20
detector aperature	(1.5 + tan θ) mm × 4.00 mm	3.0 × 4.0 mm	(1.5 + tan β) mm × 4.00 mm	(1.5 + tan θ) mm × 4.00 mm	(1.5 + tan θ) mm × 4.0 mm
takeoff angle, deg	4.70	2.0	2.80	2.80	2.80
scan speed, deg/min	variable	4.0	variable	variable	variable
scan width, deg	0.80 + 0.35 tan θ	2.0 + dispersion	0.42 + 0.35 tan θ	0.94 + 0.35 tan θ	0.8 + 0.35 tan θ
bkgd counts, s	50% of scan time	6.0	50% of scan time	50% of scan time	50% of scan time
2θ range, deg	4.0–50.0	6–45	4.00–45.00	4.00–45.00	4–45
unique data	6567	4642	4126	2349	2658
unique data with $F_o > 3.00\sigma(F)$	3709	3511	2949	2127	1568
R(*F*)	0.054	.0603	0.024	0.037	0.032
$R_w(F)$	0.071	.0568	0.029	0.045	0.041
goodness of fit	1.020	1.258	0.828	1.511	1.167
largest Δ/σ	0.08	.05	0.01	0.13	0.12

blocks from concentrated toluene solutions in typical yields of 10%. ^{1}H NMR (C_6D_6, 30 °C): δ −1.50 (t, W–*H*), 1.69 (d, P*Me*), 2.69 (t), 3.56 (m), 4.04 (d, the *p*-, *m*-, and *o*-H's of η^6-C_6H_5 ring). ^{13}C NMR (C_6D_6, 30 °C): δ 12.6 (d, P*Me*), 70.8, 71.9, 78.1, 113.4 (the para, meta, ortho, and ipso carbon atoms of the η^6-C_6H_5 ring). ^{31}P NMR (C_6D_6, 30 °C): 13.85. Infrared (Nujol mull): $\bar{\nu}$(W–H) = 1870 cm^{-1}.

WCl$_5$(OAr-2,6-Ph$_2$) (3). To a solution of WCl_6 (29.5 g, 74.5 mmol) in toluene (300 mL) was added HOAr-2,6-Ph$_2$ (20.15 g, 81.9 mmol). The mixture was stirred and refluxed for 6 h, and a deep purple crystalline compound was obtained on slow cooling of the hot toluene solution. Yield: 88%. Anal. Calcd for $WC_{18}H_{13}OCl_5$: C, 35.65; H, 2.16; Cl, 29.23. Found: C, 35.14; H, 2.15; Cl, 28.57.

W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)Cl(PMe$_2$Ph)$_2$ (4). To a sodium amalgam containing Na (0.31 g 13.4 mmol) below toluene (100 mL) was added WCl$_5$(OAr-2,6Ph$_2$) (2.00 g, 3.30 mmol) and PMe$_2$Ph (0.96 g, 6.9 mmol). The mixture was stirred at room temperature for 24 h in a drybox. The resulting red solution was allowed to settle for 1 h before the solution was decanted off the mercury and filtered. Red crystalline blocks were obtained from a concentrated toluene/hexane (1:1) solution. Typical yield: 50%. Anal. Calcd for $WC_{34}H_{35}ClP_2O$: C, 55.1; H, 4.73; Cl, 4.78; P, 8.38. Found: C, 55.48: H, 4.96; Cl, 4.33; P, 8.84. ^{1}H NMR (C_7D_8, 30 °C): 81.23 (d) 1.53 (d, diastereotopic P*Me*$_2$), 2.78 (t), 3.13 (m), 4.20 (d, the *p*-, *m*-, and *o*-*H*'s on the η^6-C_6H_5 ring). ^{13}C NMR (C_6D_6, 30 °C): δ 14.83 (d), 15.49 (d, diastereotopic P*Me*$_2$), 80.29, 83.05, 98.66, 113.62 (the para, meta, ortho, and ipso carbon atoms on the η^6-C_6H_5 ring). ^{31}P NMR (C_6D_6, 30 °C): δ −0.21 ppm.

W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)Cl(dppe) (5). An identical procedure to that above only using dppe (1.45 g, 3.64 mmol) yielded the red crystalline product from a concentrated toluene solution in typical yields of 55%. Anal. Calcd for $WC_{44}H_{37}ClOP_2$: C, 61.24; H, 4.32; Cl, 4.11; P, 7.18. Found: C, 60.74; H, 4.36; Cl, 4.91; P, 7.50. ^{1}H NMR (C_7D_8, 30 °C): δ 2.59 (d of mult, PC*H*$_2$C*H*$_2$P), 2.73 (t), 4.24 (m), 5.11 (d, the *p*-, *m*-, and *o*-*H*'s on the η_6-C_6H_5 ring). ^{31}P (C_6D_6, 30 °C: δ 45.33 ppm.

Mo(HOC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(CO)$_3$ (6). To a solution of HOAr-2,6-Ph$_2$ (4.6 g, 19 mmol) in octane (40 mL) was added Mo(CO)$_6$ (5.00 g, 19 mmol) and hexane (10 mL). The solution was degassed and allowed to reflux under nitrogen for 28 h, resulting in a yellow precipitate of crude product on cooling. Recrystallization by slow diffusion of hexane through a saturated chloroform solution yielded the pure yellow crystalline product. Yield: 78.0%. Anal. Calcd for $MoC_{21}H_{14}O_4$: C, 59.17; H, 3.31. Found: C, 58.16; H, 3.44. ^{1}H NMR ($CDCl_3$, 30 °C): δ 5.91 (s, *H*OAr), 5.65 (t), 5.72 (t), 6.04 (d, the *p*-, *m*-, and *o*-H's of the η^6-C_6H_5 ring). ^{13}C (C_6D_6, 30 °C); δ 91.88, 92.06, 96.03, 99.12 (para, meta, ortho, and ipso carbon atoms of the η^6-C_6H_5 ring), 221.74 (Mo–*C*O). Mass spectrum base peak, *m*/*e* 429. IR (Nujol mull): $\bar{\nu}$(CO) = 1926, 1988 cm^{-1}.

Crystallographic Studies

Four of the X-ray diffraction studies were completed in-house at Purdue, while the fifth, that of 2 was obtained through the Indiana University Molecular Structure Center. General operating procedures have been reviewed.[25] Some selected crystallographic data is collected in Table XI.

Mo(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)H(PMePh$_2$)$_2$ (1), W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)Cl(PMe$_2$Ph)$_2$ (4), W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)Cl(dppe) (5), and Mo(HOC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(CO)$_3$ (6). A suitable sample of these four compounds was examined under deoxygenated Nujol and mounted in an appropriate sized glass capillary surrounded by epoxy resin. The hydrogen atom positions were calculated after several cycles of anisotropic refinement idealized geometries and a carbon–hydrogen bond distance of 0.95 Å. For methyl groups, one hydrogen position was located in the difference Fourier map, this position idealized and the other two hydrogen positions calculated. No correction for extinction was applied, and there was no decay in the standards for all samples. With the exception of the hydrogen bonded to the metal in compound 1, no hydrogens were refined. Another enantiomorph of compound 5 was resolved with *R* = 0.0419, R_w = 0.0517, and GOF = 1.750.

W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)H(PMePh$_2$)$_2$ (2). A suitable crystal was located and transferred to the goniostat by using standard inert-atmosphere handling techniques employed by IUMSC and cooled to −155 °C for characterization and data collection. A

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[25] (a) Ogilvy, A. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 72. (b) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/a$. Subsequent solution and refinement of the structure confirmed this choice.

There was a surprising amount of difficulty encountered during data collection. Lowering the temperature an additional 15 °C did not indicate a phase transition, and no reasonable explanation is given. Since many of the crystals were badly split, the final data set was the average of three different crystals merged together. In spite of the difficulty and the lack of an absorption correction, the R for averaging was 0.064.

Data were collected in the usual manner by using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. Many of the hydrogen atom positions were visible in a difference Fourier phased on the non-hydrogen atoms. Positions were calculated for all hydrogens assuming idealized geometry (with d(C–H) = 0.95), and they were included as fixed atom contributors in the final cycles. Attempts to locate the hydride in the final difference Fourier were unsuccessful, although a position (see Table VII) in approximate bonding position trans to O(2) yields reasonable contacts to the other atoms in the molecule.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8612063 to I.P.R.) for financial support of this work as well as for support of the Crystallographic Center at Purdue.

Supplementary Material Available: Tables of anisotropic thermal parameters and full listings of bond distances and angles for **1**, **2**, **4**, **5**, and **6** (49 pages); listings of observed and calculated structure factors for **1**, **2**, **4**, **5**, and **6** (73 pages). Ordering information is given on any current masthead page.

Intramolecular Activation of Arene CH Bonds by Tungsten(II) Metal Centers and the Possible Role of Metal π-Arene Intermediates

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The reduction of toluene solutions of the tungsten(VI) bis(aryloxide) W(OAr-2,6-Ph$_2$)$_2$Cl$_4$ (**1**) (OAr-2,6-Ph$_2$ = 2,6-diphenylphenoxide) with sodium amalgam (4Na/W) in the presence of phosphine ligands results in the formation of the bis-cyclometalated compounds W(OC$_6$H$_3$PhC$_6$H$_4$)$_2$L$_2$ (**2**; **a**, L = PMe$_2$Ph; **b**, L = PMePh$_2$; **c**, L = PMe$_3$; **d**, L$_2$ = dppe). A structural study of **2b** confirms the cyclometalation of the two 2,6-diphenylphenoxide ligands involving the activation and cleavage of one of the ortho-CH bonds of a substituent aryl ring. The solid-state structure of **2b** involves a pseudooctahedral WO$_2$C$_2$P$_2$ core with cis phosphine ligands and trans oxygen atoms. The two six-membered metallacycles maintain a comfortable bite at the metal center close to 90° with little puckering of the chelate ring due to the large 145° angle associated with the W–O–Ar linkage. Spectroscopic data on compounds **2** are consistent with them all adopting a structure in solution identical with that found in the solid state for **2b**. Particularly informative is the presence in the ^{13}C NMR spectrum of a resonance for the new W–C bond as a doublet of doublets due to coupling to one cis and one trans phosphorus nuclei. Also isolated as a minor component from the reaction mixture involving PMePh$_2$ was a 16-electron tungsten(II) compound W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(PMePh$_2$) (**3**). Deep green crystals of **3** were obtained from a toluene solution, and a structural study shows the presence of one of the 2,6-diphenylphenoxide ligands chelated to the metal in a π-fashion with one of the side aryl rings. The overall structure of **3** is best described as a three-legged "piano stool" with two oxygen atoms and one phosphorus atom forming the feet. The ^{1}H NMR spectra of **3** show it to be fluxional involving rapid room-temperature exchange of π-bound and free aryl groups of the OAr-2,6-Ph$_2$ ligands. Reduction of **1** in the presence of dppm (Ph$_2$PCH$_2$PPh$_2$) allows the isolation of a deep green compound (**4**). Despite the chelating potential of the dppm, both spectroscopic and structural data on **4** show it to be the 16-electron compound W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(η^1-dppm). Although the η^6-arene compound **3** does not readily convert thermally to the bis-cyclometalated compound **2b**, its treatment with excess PMePh$_2$ or smaller phosphines does lead to the formation of **2** along with H$_2$ gas. These observations are interpreted from a mechanistic view point. Crystal data for WC$_{62}$H$_{50}$P$_2$O$_2$ (**2b**) at −140 °C: a = 19.828 (8) Å, b = 26.214 (13) Å, c = 10.380 (4) Å, β = 111.53 (2)°, Z = 4, d_{calcd} = 1.490 g/cm^{-3} in space group $P2_1/a$. For WC$_{49}$H$_{39}$PO$_2$ (**3**) at −155 °C: a = 15.162 (6) Å, b = 14.096 (5) Å, c = 10.246 (4) Å, α = 61.25 (2)°, β = 101.92 (2)°, γ = 100.75 (2)°, Z = 2, d_{calcd} = 1.544 g cm^{-3} in space group $P\bar{1}$. For WC$_{61}$H$_{48}$P$_2$O$_2$ (**4**) at 20 °C: a = 15.008 (2) Å, b = 39.449 (3) Å, c = 9.854 (2) Å, β = 105.86 (1)°, Z = 4, d_{calcd} = 1.253 g cm^{-3} in space group $P2_1/c$.

Introduction

The homogeneous activation of arene CH bonds by transition-metal compounds has been known and studied for many years.[2–5] A crucial and recurring mechanistic question has been the possible importance of metal π-arene complexes as intermediates prior to the actual cleavage of

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(1) Camille and Henry Dreyfus Teacher-Scholar, 1985–1990. Fellow of the Alfred P. sloan Foundation, 1986–1990.

(2) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel Publishers: Hingham, MA, 1984.

(3) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245; *Chemtech* **1982**, *12*, 506.3.

0276-7333/89/2308-1431$01.50/0