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.

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

Judith L. Kerschner, Philip E. Fanwick, and Ian P. Rothwell*,[1]

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

John C. Huffman

Molecular Structure Center, Bloomington, Indiana 47405

The reduction of toluene solutions of the tungsten(VI) bis(aryloxide) $W(OAr-2,6-Ph_2)_2Cl_4$ (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 $W(OC_6H_3PhC_6H_4)_2L_2$ (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 $WO_2C_2P_2$ 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 $W(OC_6H_3Ph-\eta^6-C_6H_5)$-(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 $W(OC_6H_3Ph-\eta^6-C_6H_5)(OAr-2,6-Ph_2)(\eta^1-dppm)$. 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 $WC_{62}H_{50}P_2O_2$ (2b) at –140 °C: $a = 19.828$ (8) Å, $b = 26.214$ (13) Å, $c = 10.380$ (4) Å, $\beta = 111.53$ (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, $\alpha = 61.25$ (2)°, $\beta = 101.92$ (2)°, $\gamma = 100.75$ (2)°, $Z = 2$, $d_{calcd} = 1.544$ g cm^{-3} in space group $P\bar{1}$. For $WC_{61}H_{48}P_2O_2$ (4) at 20 °C: $a = 15.008$ (2) Å, $b = 39.449$ (3) Å, $c = 9.854$ (2) Å, $\beta = 105.86$ (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

(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.

the aromatic CH bond.[6,7] In the case of the oxidative addition of arene CH bonds to low-valent, electron-rich metal centers, evidence for the reactions proceeding via η^2-arene intermediate has been documented.[7] However, in some systems the related formation of σ-vinyl ligands by the activation of olefinic CH bonds has been shown to proceed without prior π-coordination of the olefin to the metal center.[8] In the case of more electrophilic systems such as the high-valent d block lanthanide and actinide metals where heterolytic pathways are thought to be present for the activation of arene CH bonds, the necessity for an η^2-arene intermediate appears doubtful at best.[9,10] Instead a direct interaction of the sp²-CH bond with an M–X bond via a four-center transition state appears a more likely pathway than η^2-arene coordination prior to electrophilic substitution sequence. In other electrophilic metal systems, cationic η^2-arene complexes have conclusively been shown to precede formation of σ-aryl compounds.[11] In these latter cases some similarity to electrophilic aromatic substitution by p-block metals such as Hg^{2+} is probably present.[12]

During our study of the early d-block metal chemistry associated with sterically demanding aryloxide ligation we have shown that the two groups 2,6-di-*tert*-butylphenoxide (OAr-2,6-Bu$^t_2$) and 2,6-diphenylphenoxide (OAr-2,6-Ph₂) can sometimes undergo facile cyclometalation at d⁰ metal centers.[13] The resulting six-membered metallacycles are formed by intramolecular activation of aliphatic or aromatic CH bonds respectively. In the case of 2,6-diphenylphenoxide we have also shown that chelation to a metal center is possible by an η^6-interaction with one of the o-phenyl rings.[14] A series of stable 18-electron derivatives of the group 6 metals of stoichiometry M-(OC₆H₃Ph-η^6-C₆H₅)(X)(L)₂ (M = Mo, W; X = H, Cl; L = phosphine) have been isolated and characterized.[14] In this paper we wish to report on the cyclometalation of 2,6-diphenylphenoxide ligands by oxidative addition to W(II) metal centers. The use of ligand tuning has also allowed the isolation of a series of 16-electron η^6-arene compounds
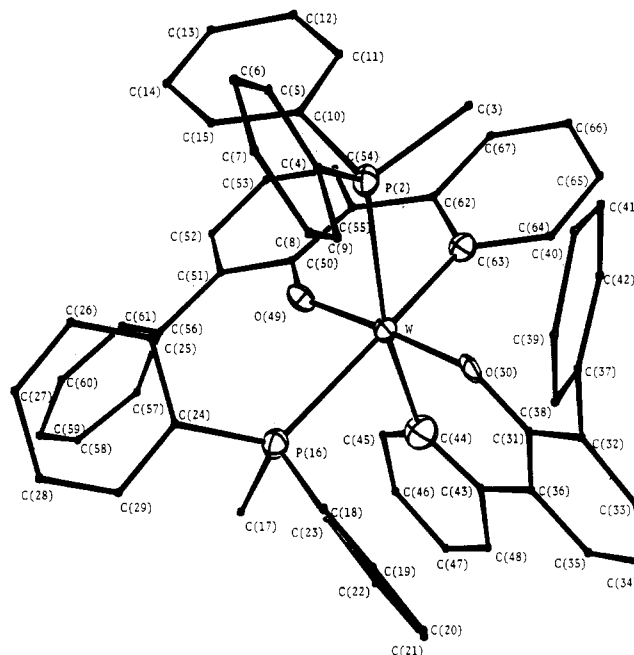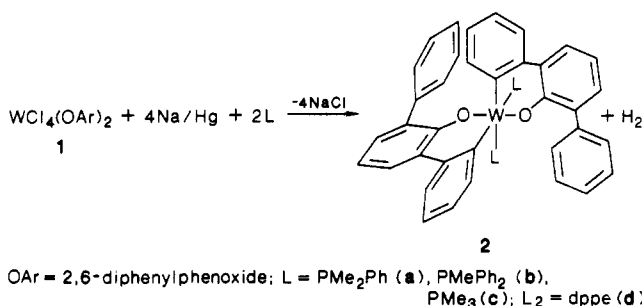

Figure 1. ORTEP view of W(OC₆H₃PhC₆H₄)₂(PMePh₂)₂ (**2b**) emphasizing the central coordination sphere.

Scheme I

WCl₄(OAr)₂ + 4Na/Hg + 2L $\xrightarrow{-4NaCl}$ [structure] + H₂

1

2

OAr = 2,6-diphenylphenoxide; L = PMe₂Ph (**a**), PMePh₂ (**b**), PMe₃ (**c**); L₂ = dppe (**d**)

that are shown to be precursors to the cyclometalated compounds. Besides the synthetic, spectroscopic, and structural characteristics of the new compounds, the possible mechanistic relevance of the intramolecular metallation of η^6-arene rings in these systems is discussed.

Results and Discussion

The sodium amalgam reduction of the bis(aryloxide) substrate *cis*-W(OAr-2,6-Ph₂)₂Cl₄ (**1**) in toluene solution in the presence of added phosphine ligands has been shown to lead to the formation of the octahedral adducts W-(OAr-2,6-Ph₂)₂Cl₃(L)(1Na/W) and W(OAr-2,6-Ph₂)₂Cl₂(L)₂ (2Na/W) which have been structurally characterized for L = PMe₂Ph.[15] The reduction of toluene solutions of W(OAr-2,6-Ph₂)₂Cl₄ (**1**) with sodium amalgam under more forcing conditions (4Na/W) in the presence of 2 equiv of monodentate phosphines is found to lead to dark brown solutions from which orange-red crystals of the bis-cyclometalated compounds W(OC₆H₃PhC₆H₄)₂(L)₂ (**2**: **a**, L = PMe₂Ph; **b**, L = PMePh₂; **c**, L = PMe₃) in good yield (Scheme I). Use of the bidentate phosphine Ph₂PCH₂CH₂PPh₂ (dppe) led to the analogous compound **2d** (L₂ = dppe). Unlike the W(IV) compounds W(O-Ar)₂Cl₂(L)₂,[15] the bis-cyclometalated compounds **2** exhibit sharp, noncontact-shifted NMR spectra. In the ¹³C NMR spectrum the formation of the new W–C(σ-aryl) bonds is

(4) (a) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (b) Bruce, M. I. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 73. (c) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (d) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (e) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436 and references therein.

(5) (a) Berry M.; Elmitt, K.; Green M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950. (b) Green M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27.

(6) *Principles and Applications of Organotransitionmetal Chemistry*, 2nd ed.; Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G., Eds.; University Science Books: Mill Valley CA, 1987.

(7) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

(8) (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

(9) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) McDade, C.; Green J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629.

(10) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51 and references therein.

(11) (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305. (b) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73. (c) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* **1986**, *5*, 168.

(12) Jensen, F. R.; Rickborn, B. *Electrophilic Substitution of Organomercuials*; McGraw-Hill: New York, 1968.

(13) (a) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153. (b) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (c) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. (d) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. D.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471. (e) Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2019. (f) Chesnut, R. W.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1988**, *7*, 753.

(14) (a) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1987**, *109*, 5840. (b) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1988**, *7*, 1871.

(15) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P., Huffman, J. C. *Inorg. Chem.* **1989**, *28*, 780.

Table I. Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters (×10) for W(OC₆H₃PhC₆H₄)₂(PMePh₂)₂ (2b)

atom	x	y	z	B_{iso}, Å²
W(1)	7481 (1)	3427.6 (3)	7357 (1)	12
P(2)	6344 (3)	3246 (2)	5115 (5)	15
P(16)	6952 (3)	3660 (2)	9290 (5)	15
O(30)	7375 (6)	4115 (5)	6806 (11)	16
O(49)	7551 (7)	2732 (4)	7817 (11)	15
C(3)	6501 (10)	3430 (9)	3546 (17)	23 (3)
C(4)	5405 (9)	3478 (8)	4724 (17)	18 (3)
C(5)	4862 (10)	3379 (8)	3438 (18)	25 (4)
C(6)	4166 (10)	3561 (7)	3127 (19)	23 (4)
C(7)	4026 (11)	3866 (8)	4111 (21)	29 (4)
C(8)	4557 (10)	3967 (7)	5346 (18)	19 (4)
C(9)	5251 (9)	3782 (7)	5685 (17)	14 (3)
C(10)	6212 (9)	2563 (6)	4906 (16)	11 (3)
C(11)	6624 (11)	2260 (8)	4370 (19)	23 (4)
C(12)	6565 (11)	1734 (8)	4340 (21)	29 (4)
C(13)	6076 (11)	1503 (9)	4768 (20)	31 (4)
C(14)	5631 (12)	1776 (9)	5259 (22)	34 (5)
C(15)	5703 (10)	2315 (7)	5342 (19)	21 (4)
C(17)	7532 (10)	3467 (8)	11045 (17)	21 (3)
C(18)	6960 (10)	4363 (7)	9436 (18)	16 (3)
C(19)	6401 (10)	4659 (7)	8553 (18)	19 (4)
C(20)	6464 (10)	5190 (8)	8529 (19)	20 (4)
C(21)	7094 (11)	5415 (8)	9470 (20)	23 (4)
C(22)	7636 (11)	5138 (8)	10397 (19)	24 (4)
C(23)	7566 (11)	4608 (8)	10383 (20)	25 (4)
C(24)	6068 (9)	3474 (8)	9294 (17)	19 (3)
C(25)	5808 (12)	2988 (8)	8793 (21)	30 (4)
C(26)	5176 (12)	2787 (9)	8852 (21)	33 (5)
C(27)	4779 (12)	3092 (8)	9420 (21)	29 (5)
C(28)	5029 (12)	3578 (8)	9912 (21)	31 (4)
C(29)	5668 (10)	3761 (7)	9881 (19)	18 (4)
C(31)	7761 (10)	4552 (7)	7004 (18)	15 (4)
C(32)	7487 (10)	4957 (7)	6043 (19)	21 (4)
C(33)	7853 (11)	5411 (8)	6266 (20)	25 (4)
C(34)	8460 (9)	5491 (7)	7479 (18)	14 (3)
C(35)	8724 (11)	5094 (8)	8366 (20)	28 (4)
C(36)	8405 (10)	4622 (8)	8185 (19)	22 (4)
C(37)	6841 (10)	4884 (7)	4733 (18)	18 (4)
C(38)	6174 (10)	4749 (7)	4761 (18)	19 (4)
C(39)	5569 (11)	4707 (8)	3557 (20)	26 (4)
C(40)	5620 (10)	4808 (7)	2319 (18)	20 (4)
C(41)	6282 (9)	4946 (7)	2247 (17)	14 (3)
C(42)	6886 (10)	4959 (7)	3445 (19)	19 (4)
C(43)	8726 (11)	4194 (8)	9152 (19)	25 (4)
C(44)	8480 (10)	3670 (7)	8902 (18)	16 (3)
C(45)	8926 (11)	3297 (8)	9875 (19)	22 (4)
C(46)	9483 (10)	3423 (9)	10994 (18)	26 (4)
C(47)	9677 (11)	3923 (8)	11302 (19)	24 (4)
C(48)	9331 (12)	4286 (8)	10406 (21)	28 (4)
C(50)	7804 (9)	2272 (7)	7562 (17)	14 (3)
C(51)	7632 (10)	1823 (7)	8162 (17)	16 (4)
C(52)	7860 (10)	1372 (7)	7822 (19)	20 (4)
C(53)	8247 (11)	1345 (8)	6986 (20)	23 (4)
C(54)	8396 (10)	1782 (7)	6388 (18)	15 (4)
C(55)	8173 (10)	2267 (7)	6634 (18)	18 (4)
C(56)	7218 (10)	1838 (7)	9115 (18)	18 (4)
C(57)	7494 (12)	2102 (9)	10331 (22)	34 (5)
C(58)	7101 (11)	2086 (8)	11245 (21)	28 (4)
C(59)	6479 (12)	1849 (8)	10900 (21)	28 (4)
C(60)	6205 (12)	1559 (10)	9678 (21)	37 (4)
C(61)	6583 (10)	1568 (9)	8779 (17)	23 (4)
C(62)	8330 (9)	2709 (7)	5930 (17)	14 (3)
C(63)	8091 (11)	3199 (8)	6081 (21)	25 (4)
C(64)	8309 (11)	3615 (8)	5405 (19)	21 (4)
C(65)	8660 (9)	3537 (7)	4515 (17)	16 (4)
C(66)	8829 (11)	3037 (8)	4280 (19)	24 (4)
C(67)	8688 (11)	2646 (8)	4980 (21)	27 (4)
C(68)	5024 (19)	271 (13)	6063 (34)	75 (13)
C(69)	4368 (19)	117 (12)	5290 (33)	69 (13)
C(70)	5744 (19)	182 (13)	5878 (35)	95 (15)
C(71)	5147 (21)	557 (16)	7180 (43)	69 (15)

Table II. Selected Bond Distances (Å) and Angles (deg) for W(OC₆H₃PhC₆H₄)₂(PMePh₂)₂ (2b)

W-P(2)	2.622 (5)	W-P(16)	2.653 (5)
W-O(30)	1.88 (1)	W-O(49)	1.87 (1)
W-C(44)	2.14 (2)	W-C(63)	2.18 (2)

P(2)-W-P(16)	105.3 (2)	P(16)-W-O(30)	88.8 (4)
P(2)-W-O(30)	86.6 (3)	P(16)-W-O(49)	92.4 (4)
P(2)-W-O(49)	90.5 (4)	P(16)-W-C(44)	88.0 (5)
P(2)-W-C(44)	97.9 (5)	P(16)-W-C(63)	169.7 (5)
P(2)-W-C(63)	84.2 (5)	O(30)-W-O(49)	177.0 (5)
O(49)-W-C(44)	97.9 (6)	O(49)-W-O(44)	85.0 (6)
O(49)-W-C(63)	83.3 (7)	O(49)-W-C(63)	95.9 (7)
C(44)-W-C(63)	88.3 (7)	W-O(30)-C(31)	140.7 (1)
W-O(49)-C(50)	143.5 (1)		

nation environment about the metal as shown (Scheme I). Hence one large, trans, coupling as well as a smaller, cis, coupling to the ³¹P nuclei of the mutually cis phosphine ligands is taking place. This results in a formulation with the aryloxide oxygen atoms being mutually trans about the tungsten metal center. In the case of the dimethylphenylphosphine compound **2a** the presence of the P*Me*₂Ph groups as two doublets in the ¹H NMR spectrum is also consistent with their being mutually cis and containing diastereotropic methyl groups. In the aromatic region of the ¹H NMR spectrum the complexity of the pattern as well as the downfield shifts of some of the aryloxide proton signals is also indicative of cyclometalation (vide infra).[13]

The structure of compounds **2** inferred from spectroscopic data was confirmed by a single-crystal X-ray diffraction study of the PMePh₂ derivative **2b**. An ORTEP view of the molecule is given in Figure 1 while Tables I and II contain fractional coordinates and some selected bond distances and angles, respectively. The central WO₂P₂C₂ core of **(2b)** can be seen to be best described as octahedral, with trans oxygen atoms. The two six-membered metallacycle rings formed by the cyclometalation of the OAr-2,6-Ph₂ ligands chelate the metal such that the new W-C bonds are mutually cis and each trans to a phosphorus atom. The most significant distortion from octahedral coordination involves the moving apart of the bulky PMePh₂ groups resulting in a P-W-P angle of 105.3 (2)°. The bite of the chelate rings are slightly less than 90°, 83.3 (7)°, and 85.0 (6)°, although very little puckering of the six-membered rings takes place. This is due to the large W-O-C angles of 140.7 (1)° and 143.5 (1)° which have the effect of "flattening" out the chelate ring. Large M-O-Ar angles are a characteristic of early d-block metal aryloxide compounds, where oxygen p to metal d π-bonding is important.[16] A consequence of the formation of the cyclometalated rings in **2** is that the metallated aryl ring is now forced into an approximately coplanar orientation with the central phenoxy ring (angles of 5.1° and 5.9°). This coplanarity contrasts with the 54.5° and 61.4° angles found between the non-metalated and phenoxy rings. We believe this structural feature also has a spectroscopic consequence. In the ¹H NMR spectra of **2** there are a series of multiplets which are well separated from the rest of the aromatic signals. Two downfield doublets and one upfield triplet of equal intensities can be readily resolved (Figure 2). Selective decoupling shows the furthest downfield doublet to be coupled to the upfield

confirmed by the presence of a new resonance in the δ 200 ppm region. The appearance of this signal as a double doublet in all compounds **2** leads us to propose a coordi-

(16) (a) Latesky, S. L.; McMullen, A. K.; Keddington, J.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995. (b) Durfee, L. D.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 4569. (c) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906. (d) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, Chapter 15.3.
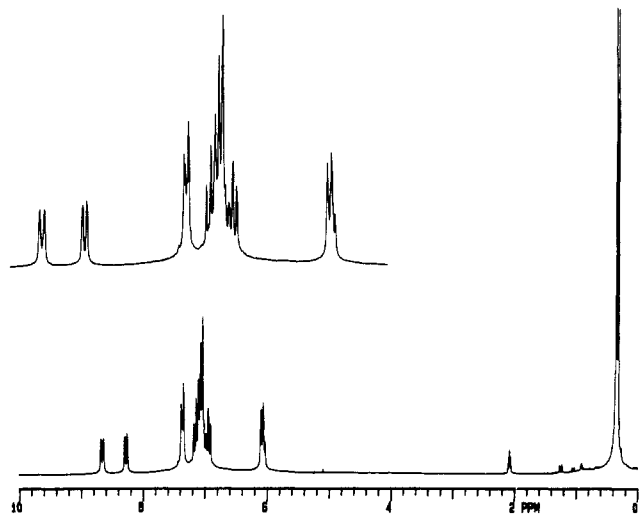
Figure 2. ¹H NMR spectrum (200 MHz) of W-(OC₆H₃PhC₆H₄)₂(PMe₃)₂ (2c).
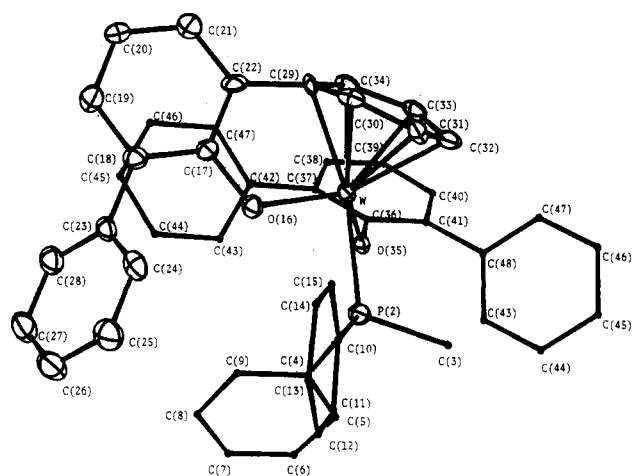
Figure 3. ORTEP view of W(OC₆H₃Ph-η⁶-C₆H₅)(OAr-2,6-Ph₂)-(PMePh₂) (3).

triplet. We believe that the upfield triplet is the hydrogen in the 4-position of the phenoxide ring. Hence the furthest downfield doublet represents one of the meta (3 or 5) hydrogen atoms in this central ring. Its unusually low chemical shift would be consistent with it being the meta hydrogen next to the metalated phenyl substituent. This is because the coplanarity of these two rings will lead to an enhanced shielding of this proton by the diamagnetic ring current of the two rings. The other downfield doublet can then be assigned to the hydrogen atom meta to the W–C(ipso) bond, also shifted downfield by the combined anisotropies of the two coplanar aryl rings. In compounds containing only one cyclometalated 2,6-diphenylphenoxide ligand there are typically three downfield doublets of equal intensity.[13] The third doublet, which is missing in the ¹H NMR spectra of 2, represents the hydrogen ortho to the W–C(ipso) carbon bond. Early-transition-metal aryl compounds typically have the ortho-hydrogen atoms resonating to low field.[17] However, in the bis-cyclometalated compounds 2 the molecular geometry is such that there are two new tungsten aryl groups mutually cis and held in an approximately coplanar arrangement relative each other by chelation. Hence, the diamagnetic anisotropies in this case will have the effect of causing an upfield shift of the ortho hydrogen atoms back into the normal aromatic region.
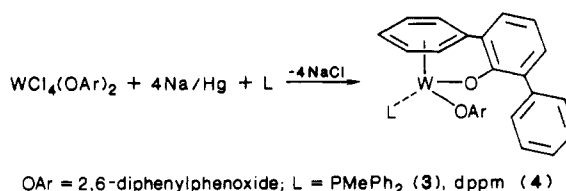
(17) Steffey, B. D.; Rothwell, I. P., results to be published.

Scheme II

WCl₄(OAr)₂ + 4Na/Hg + L $\xrightarrow{-4NaCl}$

OAr = 2,6-diphenylphenoxide; L = PMePh₂ (3), dppm (4)

Table III. Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters (×10) for W(OC₆H₃Ph-η⁶-C₆H₅)(OAr-2,6-Ph₂)(PMePh₂) (3)

| atom	x	y	z	B_{iso}, Å²
W(1)	3319.4 (3)	1968.5 (3)	1945.6 (4)	11
P(2)	1854 (2)	2354 (2)	2213 (3)	13
C(3)	1571 (7)	1538 (8)	4115 (12)	24
C(4)	888 (6)	2071 (8)	995 (11)	18
C(5)	251 (7)	1173 (9)	1518 (11)	23
C(6)	−423 (7)	987 (10)	493 (15)	34
C(7)	−472 (7)	1672 (10)	−1003 (12)	29
C(8)	150 (7)	2588 (9)	8457 (12)	26
C(9)	841 (6)	2768 (8)	−548 (11)	19
C(10)	1706 (6)	3730 (8)	1868 (10)	14
C(11)	859 (6)	4001 (8)	1755 (12)	23
C(12)	744 (6)	5015 (8)	1531 (8)	22
C(13)	1484 (7)	5776 (8)	1449 (12)	25
C(14)	2327 (7)	5489 (9)	1591 (13)	28
C(15)	2444 (6)	4471 (8)	1801 (11)	18
O(16)	3082 (4)	3338 (5)	−21 (6)	13
C(17)	3735 (6)	3766 (7)	−950 (10)	14
C(18)	3561 (6)	4566 (7)	−2445 (10)	14
C(19)	4237 (6)	4894 (8)	−3353 (10)	19
C(20)	5076 (6)	4478 (8)	−2820 (10)	17
C(21)	5252 (6)	3709 (8)	−1319 (10)	18
C(22)	4591 (6)	3360 (7)	−375 (10)	15
C(23)	2670 (6)	5028 (7)	−3028 (10)	15
C(24)	2350 (6)	5461 (7)	−2257 (10)	18
C(25)	1527 (7)	5884 (8)	−2776 (12)	25
C(26)	1000 (7)	5903 (9)	−4081 (12)	25
C(27)	1322 (7)	5494 (9)	−4864 (11)	28
C(28)	2149 (6)	5055 (8)	−4338 (11)	20
C(29)	4668 (5)	2662 (7)	1238 (9)	10
C(30)	4600 (5)	3140 (7)	2188 (10)	11
C(31)	4268 (6)	2515 (8)	3566 (10)	16
C(32)	4150 (6)	1356 (8)	4202 (11)	18
C(33)	4435 (6)	862 (7)	3455 (10)	16
C(34)	4675 (6)	1471 (7)	1960 (10)	16
O(35)	2538 (4)	602 (5)	2168 (6)	13
C(36)	2793 (6)	−293 (7)	2235 (11)	14
C(37)	2800 (6)	8737 (8)	3612 (10)	17
C(38)	3132 (7)	−2163 (8)	3748 (11)	21
C(39)	3446 (7)	−2136 (9)	2535 (12)	27
C(40)	3412 (7)	−1204 (8)	1185 (11)	22
C(41)	3094 (6)	−252 (8)	983 (11)	18
C(42)	2499 (6)	−1326 (8)	4941 (10)	17
C(43)	1596 (7)	8777 (8)	4930 (11)	23
C(44)	1320 (7)	−1357 (9)	6230 (12)	27
C(45)	1919 (8)	−1574 (9)	7545 (13)	33
C(46)	2806 (7)	−1736 (10)	7586 (12)	30
C(47)	3089 (7)	−1581 (9)	6269 (12)	26
C(48)	3100 (6)	720 (8)	−490 (10)	16
C(49)	2355 (6)	1351 (8)	−1156 (10)	18
C(50)	2365 (7)	2229 (9)	−2591 (10)	21
C(51)	3094 (7)	2515 (8)	−3374 (11)	22
C(52)	3823 (7)	1918 (9)	−2733 (10)	22
C(53)	3826 (7)	1013 (8)	−1275 (11)	22

This is compounded by the fact that each ortho hydrogen is also being shielded by the non-metalated aryl rings of the aryloxide chelate (Figure 1).

Besides the bright orange bis-cyclometalated compound **2b**, the reduction of **1** in the presence of PMePh₂ also produced a dark green crystalline material in very low yields. Structural analysis of this new compound showed it to be a 16-electron, bis(aryloxide) of stoichiometry W(OC₆H₃Ph-η⁶-C₆H₅)(OAr-2,6-Ph₂)(PMePh₂) (3) (Scheme

Table IV. Selected Bond Distances (Å) and Angles (deg) for W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(PMePh$_2$) (3)

W–P(2)	2.480 (3)	W–O(16)	2.033 (6)
W–O(35)	2.001 (6)	W–C(29)	2.202 (8)
W–C(39)	2.357 (8)	W–C(31)	2.292 (9)
W–C(32)	2.227 (9)	W–C(33)	2.296 (8)
W–C(34)	2.286 (9)		
P(2)–W(1)–O(16)	79.1 (2)	O(16)–W–O(35)	117.1 (2)
P(2)–W(1)–O(35)	79.0 (2)	W–O(16)–C(17)	117.5 (5)
W–O(35)–C(36)	127.4 (5)		
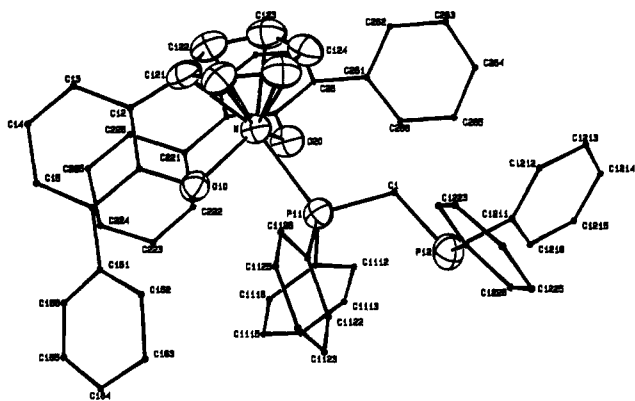
Figure 4. ORTEP view of W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)-(dppm) (4).

II). An ORTEP view of 3 is given in Figure 3 while fractional coordinates and some selected bond distances and angles are collected in Tables III and IV, respectively. The molecular structure of 3 is best described as a three-legged piano-stool configuration about the tungsten atom with a capping η^6-arene ring. One of the aryloxide ligands is bound to the metal in a normal coordination mode. However, the second group is chelated to the tungsten atom via π-bonding with one of its phenyl substituents. Compound 3 is closely related to the 18-electron derivatives M(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(X)(L)$_2$ (M = Mo, W; X = H, Cl; L = phosphine) where similar chelation of the aryloxide is seen.[14] The presence of two bulky OAr-2,6-Ph$_2$ groups in the coordination sphere presumably hinders the bonding of a second phosphine ligand. The reduction of WCl$_4$-(OAr-2,6-Ph$_2$)$_2$ (1) with Na/Hg in the presence of the small bite diphosphine dppm (Ph$_2$PCH$_2$PPh$_2$) leads to the formation of the deep green 16-electron W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(dppm) (4) in yields which are certainly greater than those obtained for 3. Again a single-crystal X-ray diffraction analysis of 4 (Tables V and VI) was carried out and shows the dppm ligand to be bound to the tungsten in a monodentate fashion (Figure 4). Apart from this feature the molecular structures of 3 and 4 can be seen to be almost identical (Tables IV and VI). Despite the chemical nonequivalence of the aryloxide ligands within 3 and 4, the P–W–O angles are essentially identical. The η^6-arene ring is bound to the metal with little distortion, all W–C distances being essentially the same, despite the chelation to the metal via the phenoxy framework. As with the 18-electron derivatives mentioned earlier, the molecular geometry of the OAr-2,6-Ph$_2$ ligand itself can accommodate this type of chelation with no significant distortions.[14] The bond distances between the metal and the aryloxide oxygen atoms in 3 and 4 are larger than those found for bis-cyclometalated 2b but are slightly shorter than in the 18-electron compounds W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(X)(L)$_2$ where oxygen p to metal d π-bonding would be destabilizing.[14]

The NMR spectra of 3 and 4 show both molecules to be fluxional in solution. In the ^{31}P NMR spectrum, both 3

Table V. Fractional Coordinates and Isotropic Thermal Parameters for W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$) (dppm) (4)

| atom	x	y	z	B, Å^2
W	0.12100 (3)	0.11826 (1)	0.19223 (4)	3.570 (8)
P(11)	0.1382 (2)	0.10383 (7)	–0.0466 (3)	3.59 (6)
P(12)	0.2708 (2)	0.06953 (8)	–0.2035 (3)	4.82 (7)
O(10)	–0.0141 (4)	0.1201 (2)	0.0764 (6)	3.8 (1)
O(20)	0.2014 (5)	0.1566 (2)	0.1691 (7)	4.5 (2)
C(1)	0.2503 (7)	0.0845 (3)	–0.034 (1)	4.6 (3)
C(11)	–0.0803 (7)	0.1249 (2)	0.143 (1)	4.3 (3)
C(12)	–0.0515 (7)	0.1217 (3)	0.292 (1)	4.4 (2)
C(13)	–0.1124 (8)	0.1296 (3)	0.371 (1)	5.7 (3)
C(14)	–0.2000 (9)	0.1407 (4)	0.302 (1)	7.2 (4)
C(15)	–0.2293 (8)	0.1415 (4)	0.157 (1)	6.5 (3)
C(16)	–0.1715 (7)	0.1337 (3)	0.072 (1)	4.8 (3)
C(21)	0.2314 (8)	0.1826 (3)	0.260 (1)	4.9 (3)
C(22)	0.1723 (8)	0.2068 (3)	0.288 (1)	5.2 (3)
C(23)	0.208 (1)	0.2316 (3)	0.391 (1)	6.5 (3)
C(24)	0.300 (1)	0.2316 (3)	0.462 (1)	7.7 (4)
C(25)	0.360 (1)	0.2084 (3)	0.434 (1)	7.4 (4)
C(26)	0.3258 (9)	0.1842 (3)	0.332 (1)	6.1 (3)
C(121)	0.0423 (7)	0.1079 (3)	0.345 (1)	4.3 (3)
C(122)	0.1215 (8)	0.1282 (3)	0.421 (1)	4.7 (3)
C(123)	0.2094 (8)	0.1158 (3)	0.423 (1)	5.2 (3)
C(124)	0.2248 (8)	0.0867 (3)	0.347 (1)	4.7 (3)
C(125)	0.1466 (8)	0.0547 (3)	0.287 (1)	4.7 (3)
C(126)	0.0587 (7)	0.0742 (3)	0.299 (1)	4.2 (2)
C(161)	–0.2043 (7)	0.1348 (3)	–0.079 (1)	5.7 (3)
C(162)	–0.1791 (8)	0.1111 (4)	–0.161 (1)	6.7 (4)
C(163)	–0.219 (1)	0.1116 (5)	–0.312 (2)	10.6 (5)
C(164)	–0.284 (1)	0.140C (6)	–0.358 (2)	14.6 (6)
C(165)	–0.303 (1)	0.1616 (6)	–0.266 (3)	14.9 (8)
C(166)	–0.265 (1)	0.1594 (4)	–0.137 (2)	9.0 (5)
C(221)	0.0744 (9)	0.2083 (3)	0.209 (1)	5.6 (3)
C(222)	0.0420 (9)	0.2057 (3)	0.062 (1)	5.7 (3)
C(223)	0.0468 (9)	0.2113 (3)	–0.011 (1)	6.6 (4)
C(224)	–0.112 (1)	0.2189 (3)	0.060 (2)	8.7 (5)
C(225)	–0.086 (1)	0.2207 (4)	0.214 (2)	7.9 (4)
C(226)	0.005 (1)	0.2156 (3)	0.284 (1)	7.0 (4)
C(261)	0.3903 (9)	0.1594 (4)	0.307 (1)	7.3 (4)
C(262)	0.447 (1)	0.1394 (5)	0.417 (2)	9.4 (5)
C(263)	0.512 (1)	0.1146 (5)	0.390 (3)	12.9 (7)
C(264)	0.521 (1)	0.1131 (5)	0.260 (2)	13.5 (6)
C(265)	0.469 (1)	0.1316 (6)	0.149 (2)	11.8 (6)
C(266)	0.404 (1)	0.1542 (4)	0.174 (2)	8.7 (5)
C(1111)	0.1303 (7)	0.1399 (3)	–0.163 (1)	3.8 (2)
C(1112)	0.2079 (8)	0.1564 (3)	–0.182 (1)	5.4 (3)
C(1113)	0.195 (1)	0.1864 (3)	–0.261 (1)	7.3 (4)
C(1114)	0.111 (1)	0.2002 (3)	–0.321 (1)	7.1 (4)
C(1115)	0.035 (1)	0.1840 (3)	–0.304 (1)	7.1 (4)
C(1116)	0.0442 (9)	0.1538 (3)	–0.223 (1)	5.4 (3)
C(1121)	0.0573 (6)	0.0736 (3)	–0.155 (1)	3.7 (2)
C(1122)	0.0431 (7)	0.0720 (3)	–0.300 (1)	4.4 (3)
C(1123)	–0.0117 (8)	0.0470 (3)	–0.378 (1)	5.1 (3)
C(1124)	–0.0547 (8)	0.0232 (3)	–0.314 (1)	5.5 (3)
C(1125)	–0.0420 (8)	0.0247 (3)	–0.172 (1)	5.5 (3)
C(1126)	0.0134 (7)	0.0500 (3)	–0.092 (1)	4.6 (3)
C(1211)	0.3977 (7)	0.0595 (3)	–0.152 (1)	5.4 (3)
C(1212)	0.4515 (8)	0.0480 (3)	–0.049 (2)	6.7 (4)
C(1213)	0.5501 (9)	0.0500 (4)	–0.011 (2)	8.5 (5)
C(1214)	0.5904 (9)	0.0759 (4)	–0.079 (2)	9.5 (5)
C(1215)	0.537 (1)	0.0964 (5)	–0.180 (2)	9.4 (5)
C(1216)	0.4389 (9)	0.0932 (4)	–0.219 (1)	7.6 (4)
C(1221)	0.2465 (7)	0.0246 (3)	–0.202 (1)	5.1 (3)
C(1222)	0.2137 (9)	0.0076 (3)	–0.10C (2)	6.6 (3)
C(1223)	0.194 (1)	–0.0267 (4)	–0.122 (2)	8.5 (5)
C(1224)	0.2092 (9)	–0.0042 (4)	–0.232 (2)	8.5 (5)
C(1225)	0.242 (1)	–0.0288 (4)	–0.333 (2)	9.2 (5)
C(1226)	0.260 (1)	0.0074 (4)	–0.320 (2)	7.8 (4)

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

and 4 show a sharp resonance for the metal bound phosphorus atom along with the expected ^{183}W satellites. Also in 4 can be seen the resonance for the nonbound phos-

**Table VI. Selected Bond Distances (Å) and Angles (deg)
for W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(dppm) (4)**

W–P(11)	2.502 (2)	W–O(10)	2.038 (5)
W–O(20)	1.986 (5)	W–C(121)	2.190 (7)
W–C(122)	2.283 (8)	W–C(123)	2.301 (8)
W–C(124)	2.240 (8)	W–C(125)	2.299 (7)
W–C(126)	2.345 (7)		

P(11)–W–O(10)	79.9 (1)	W–O(10)–C(11)	119.0 (4)
P(11)–W–O(20)	81.0 (2)	W–O(20)–C(21)	127.0 (5)
O(10)–W–O(20)	116.8 (2)		

phorus of the dangling dppm ligand, in this case lacking any [183]W satellite peaks. An important spectroscopic tool for the detection of metal η^6-arene complexes in solution is the upfield shifting that takes place of the arene proton and carbon resonances upon π-bonding.[18] This results in the arene protons typically resonating in the δ 2–6 ppm region of the ^{1}H NMR spectrum. On the basis of the observed solid-state structures of 3 and 4, one would predict that the η^6-bound phenyl ring would give rise to five distinct proton resonances, due to the fact that there is no symmetry element present to make the two ortho and two meta protons equivalent. At ambient temperatures the ^{1}H NMR of 3 in toluene-d_8 solution shows no resolvable peaks in the η^6-arene part of the spectrum. However, in the case of 4, five broad equal intensity peaks in the δ 1.5–6.0 ppm region are resolvable, consistent with the observed solid-state structure. Cooling down solutions of 3 results in the building up of some similar peaks from the base line of the ^{1}H NMR spectrum. No sharp, limiting low-temperature ^{1}H NMR spectrum of 3 could be obtained, however. Due to their thermal instabilities (vide infra), high-temperature-limiting spectra of 3 and 4 are also unavailable. The observed temperature dependence of the ^{1}H NMR spectra of 3 and 4 could arise due to a number of possible processes. The use of spin magnetization transfer experiments at low temperatures for 3 and room temperature for 4 shows that there is exchange definitely taking place between the η^6-phenyl group and the other, nonbound aryloxide phenyl groups. This rules out fluxionality due to a simple "flip" of the unique, bound phenyl ring itself. Instead some process is causing exchange of the bound and all of the unbound aryl groups. This exchange may be occurring simply by a dissociative pathway involving a three-coordinate intermediate, "W(OAr-2,6-Ph$_2$)$_2$(L)", containing only terminally bound aryloxides. However, an intramolecular associative exchange in which an initially unbound aryl group attaches to the 16-electron metal center in an η^2-fashion can also be envisioned. Then a sequence of ring slippages allows for overall exchange of bound and unbound aryl groups. An alternative pathway involving mononuclear intermediates would be an exchange catalyzed by trace amounts of free phosphine ligand. Addition could lead to a four-coordinate compound, "W(OAr-2,6-Ph$_2$)$_2$(PMePh$_2$)$_2$", in the case of 3 which could then reassociate an aryl ring with displacement of one of the phosphine ligands. Arguing against this latter process is the sharp doublet observed for the bound P*Me*Ph$_2$ ligand even with added excess ligand at temperatures where facile phenyl exchange is taking place. Furthermore, the fact that the dppm compound 4 does not undergo phenyl exchange as fast as 3 despite the presence of a readily available, dangling phosphine center also implies that a phosphine catalyzed process is not operative. Hence it seems likely that facile bound, unbound arene exchange

Scheme III

OAr = 2,6-diphenylphenoxide; P = PMePh$_2$
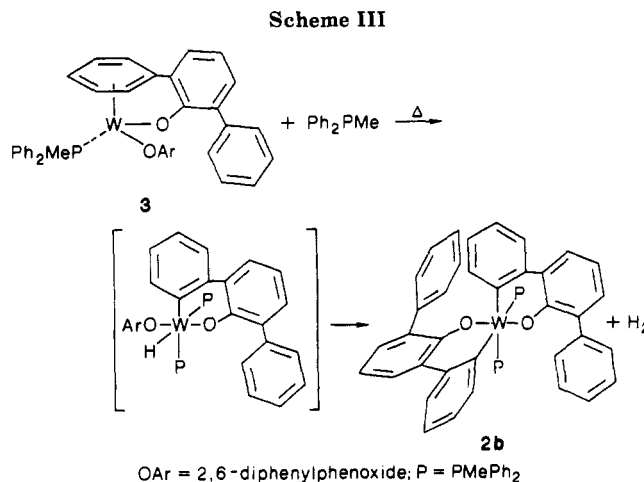
in 3 and 4 results from an intramolecular process which may be either associative or dissociative in nature.

The thermolysis (50 °C) of deep green 3 in toluene solution leads to the slow formation of dark brown mixtures that contain the bis-cyclometalated compound 2b along with other, unidentified products. The yields of 2b obtained from 3 in this fashion are estimated to be 20–30% by ^{1}H NMR integration. However, in the presence of an added equivalent of PMePh$_2$, deep green 3 converts smoothly and much more rapidly at 50 °C to orange solutions of 2b in almost quantitative yield. Analysis of the gasses above these solutions by gas chromatography showed the presence of dihydrogen. The reaction is most readily monitored by either ^{1}H or ^{31}P NMR. These results indicate that the direct conversion of 3 to 2b is a slow process that can be accelerated greatly by the addition of an extra equivalent of phosphine. The reactivity of 3 also contrasts with the great thermal stability of the 18-electron compounds M(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(H)(PMePh$_2$)$_2$ (M = Mo, W) and W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(Cl)(L)$_2$ (L = PMe$_2$Ph; L$_2$ = dppe). We interpret this data as showing that the conversion of 3 to 2b occurs via initial formation of an intermediate "W(OAr-2,6-Ph$_2$)$_2$(PMePh$_2$)$_2$". The steric requirements of two 2,6-diphenylphenoxide ligands in this intermediate should preclude any π-binding to the phenyl side groups. Hence, a four-coordinate W(II) species is produced. Previous work has shown that tungsten(II) compounds of the type X$_2$WL$_n$ are highly reactive and in particular can activate small molecules by oxidative addition pathways.[5,19,20] Hence, the cyclometalation of one of the 2,6-diphenylphenoxide groups in "W(OAr-2,6-Ph$_2$)$_2$(PMePh$_2$)$_2$" would generate a mono-cyclometalated, monohydride compound as shown (Scheme III). The product is then obtained by a second cyclometalation step involving a loss of H$_2$. The bis-cyclometalation observed within the group 5 metal d^2 compounds "M(OAr-2,6-Ph$_2$)$_3$" (M = Nb, Ta) has been shown to be very rapid, also leading to H$_2$ loss.[21] For the tungsten system of interest here, the second step may involve a second oxidative addition leading to a W(VI) dihydride intermediate or else take place via a multicenter, heterolytic pathway in which the formal oxidation state of the metal remains at +4 throughout the reaction. Previous work has shown hydride ligands to be excellent leaving groups for just such reactions.[9,10] However, given the absence of detection of in-

---

(18) 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.

(19) (a) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213. (b) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826.

(20) Sharp, P. R. *Organometallics* **1984**, *3*, 1217.

(21) Steffey, B. D.; Chesnut, R. W.; Kerschner, J. L.; Pellechia, P. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1989**, *111*, 378.

Table VII. Crystallographic Data

	2b	3	4
formula	$WP_2O_2C_{62}H_{50} \cdot \frac{1}{2}(C_7H_8)$	$WC_{49}H_{39}O_2P$	$WP_2O_2C_{61}H_{48}$
fw	1125.96	874.67	1058.86
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, Å	19.828 (8)	15.162 (6)	15.008 (2)
b, Å	26.214 (13)	14.096 (5)	39.449 (3)
c, Å	10.380 (4)	10.246 (4)	9.854 (2)
α, deg	90.00	61.25 (2)	90.00
β, deg	111.53 (2)	101.92 (2)	105.86 (1)
γ, deg	90.00	100.75 (2)	90.00
Z	4	2	4
V, Å^3	5018.62	1868.76	5612 (3)
d_{calcd}, g/cm^3	1.490	1.554	1.253
cryst size, mm	0.12 × 0.12 × 0.20	0.14 × 0.14 × 0.20	0.73 × 0.35 × 0.29
cryst color	orange	green	green
radiatn	Mo Kα (0.710 69 Å)	Mo Kα (0.710 69 Å)	Mo Kα (0.710 73 Å)
linear abs coeff, cm^{-1}	24.584	32.372	21.95
temp, °C	−140	−155	20
detector aperature	3.0 × 4.0	3.0 × 4.0	(1.5 + tan θ) mm × 4.00 mm
takeoff angle, deg	2.0	2.0	1.90
scan speed, deg/min	4.0	4.0	variable
scan width, deg	1.6 + dispersion	2.0 + dispersion	0.66 + 35 tan θ
bkgdcounts, s	8	8	50% of scan time
2θ range, deg	6–45	6–45	4.00–45.00
unique data	6587	4457	7458
unique data with $F_o > 3.00\sigma(F)$	3313 (>2.33σ)	4044	5247
$R(F)$	0.0615	0.0452	0.042
$R_w(F)$	0.0580	0.0438	0.068
goodness of fit	0.945	0.851	2.095
largest Δ/σ	0.134	0.05	0.10

termediates in this reaction the actual reaction pathway is unknown.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either in a Vacuum Atmospheres Dri-lab or by standard Schlenck techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone and stored under nitrogen. WCl$_4$(OAr-2,6-Ph$_2$)$_2$ (1) was obtained by a previously reported procedure.[22] ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Associates XL-200 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) or to 85% H$_3$PO$_4$ (^{31}P NMR). Microanalysis were obtained "in-house" at Purdue. Gas chromatograms were recorded on a Carle gas chromatograph.

W(OC$_6$H$_3$PhC$_6$H$_4$)$_2$(PMe$_2$Ph)$_2$ (2a). To a sodium amalgam containing Na metal (0.23 g, 10.0 mmol) in toluene (100 mL) was added W(OAr-2,6-Ph$_2$)$_2$Cl$_4$ (2.00 g, 2.45 mmol) and PMe$_2$Ph (0.71 g, 5.1 mmol). The mixture was then stirred vigorously at room temperature in a drybox for 24 h. The resulting orange suspension was allowed to settle for 1 h before the solution was decanted off the mercury pool and filtered. Concentration of the orange filtrate produced the crystalline product. Typical yield: 65%. Anal. Calcd for WC$_{52}$H$_{46}$O$_2$P$_2$: C, 65.69; H, 5.09; P, 6.52. Found: C, 65.31; H, 5.00; P, 5.89. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 0.68 (d), 0.71 (d, P*Me*$_2$Ph), 8.55 (d), 8.11 (d), 6–7.2 (aryl H's). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 187.5 (dd, W–C, cis-^2J (^{13}C–^{31}P) = 3.6 Hz; trans-^2J (^{13}C–^{31}P) = 60.5 Hz), 18.5 (d), 19.2 (d, P*Me*$_2$Ph). ^{31}P NMR (C$_6$D$_6$, 30 °C): δ −15.69 (^1J(^{183}W–^{31}P) = 179 Hz).

W(OC$_6$H$_3$PhC$_6$H$_4$)$_2$ (PMePh$_2$)$_2$ (2b). An identical procedure to that above, only using WCl$_4$(OAr-2,6-Ph$_2$)$_2$ (2.00 g, 2.45 mmol), Na (0.23 g, 10.0 mmol), and PMePh$_2$ (1.08 g, 5.4 mmol), yielded 2b as orange crystals in typical yields of 65%. Anal. Calcd for WC$_{62}$H$_{50}$O$_2$P$_2$: C, 69.28; H, 4.88; P, 5.76. Found: C, 69.72; H, 4.95; P, 5.49%. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 1.03 (d, P*Me*Ph$_2$), 8.00 (d), 8.46 (d), 6–7.1 (aryl H's). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 186.1 (dd, W–C, cis-^2J (^{13}C–^{31}P) = 3.1 Hz; trans-^2J (^{13}C–^{31}P) = 62.0 Hz), 16.7 (d, P*Me*Ph$_2$). ^{31}P NMR (C$_6$D$_6$, 30 °C): δ −36.9 ^1J (^{183}W–^{31}P) = 159 Hz.

W(OC$_6$H$_3$PhC$_6$H$_4$)$_2$(PMe$_3$)$_2$ (2c). An identical procedure to that above, only using W(OAr-2,6-Ph$_2$)$_2$Cl$_4$ (2.00 g, 2.45 mmol),

Na (0.13 g, 10.0 mmol), and PMe$_3$ (0.40 g, 5.3 mmol), yielded 2c as an orange crystalline solid in typical yields of 50%. Anal. Calcd for WC$_{42}$H$_{42}$O$_2$P$_2$: C, 61.18; H, 5.13; P, 7.51. Found: C, 60.71; H, 5.15; P, 7.94. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ .35 (P*Me*$_3$), 8.31 (d), 8.68 (d), 6–7.1 (aryl H's). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 192.39 (dd, W–C), 18.73 (d, P*Me*$_3$). ^{31}P NMR (C$_6$D$_6$, °C): δ −56.50 (^1J (^{183}W–^{31}P) = 188 Hz).

W(OC$_6$H$_3$PhC$_6$H$_4$)$_2$(dppe) (2d). An identical procedure to that above, only using W(OAr-2,6-Ph$_2$)$_2$Cl$_4$ (2.00 g, 2.45 mmol), Na (0.23 g, 10.0 mmol), and dppe (2.16 g, 5.4 mmol), produced orange crystals in typical yields of 60%. Anal. Calcd for WC$_{62}$H$_{48}$O$_2$P$_2$: C, 69.54; H, 4.52; P, 5.78. Found: C, 69.27; H, 4.94; P, 6.18. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 5.77 (d, d, P*CH$_2$CH$_2$*P), 8.13 (d), 8.71 (d), 6.1–7.5 (aryl H's). ^{31}P NMR (C$_6$D$_6$, 30 °C): δ −16.41 (^1J(^{183}W–^{31}P) = 160 Hz).

W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(PMePh$_2$) (3). Also isolated from the preparation of 2b was a small yield of the green crystalline product 3. Yield: 8%. ^{1}H NMR (C$_6$D$_5$CD$_3$, 30 °C): δ 1.45 (d, P*Me*Ph$_2$). At −35 °C two broad resonances at δ 3.61 and 3.09 ppm due to protons attached to the η^6-aryl ring begin to be resolved. ^{31}P NMR (C$_6$D$_6$, 30 °C): δ +49.9 (^1J(^{183}W–^{31}P) = 363 Hz).

W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(dppm) (4). To a sodium amalgam containing Na metal (0.17 g, 7.4 mmol) in toluene (100 mL) was added W(OAr-2,6-Ph$_2$)$_2$Cl$_4$ (1.50 g, 1.80 mmol) and dppm (0.76 g, 2.0 mmol). The mixture was stirred vigorously for 24 h at room temperature in a drybox. The resulting green suspension was allowed to settle for 1 h before the solution was decanted off the mercury pool and filtered. Green crystalline blocks were obtained from a saturated toluene solution. Anal. Calcd for WC$_{61}$H$_{49}$O$_2$P$_2$: C, 69.20; H, 4.57; P, 5.85. Found: C, 69.82; H, 5.25; P, 5.58. ^{1}H NMR (C$_6$D$_5$CD$_3$, 30 °C): δ 1.78 (t, P–*CH$_2$*–P), 1.71 (d), 2.77 (t), 3.14 (d), 3.38 (t), 4.62 (d, *p*-, *m*-, and *o*-H's attached to the η^6-C$_6$H$_5$ ring), 6.4–7.5 (other aromatics). ^{31}P NMR (C$_6$D$_6$, 30 °C): δ 55.22 (d, W–*P*), −24.75 (d, dangling P).

Crystallographic Studies

Two of the X-ray diffraction studies were obtained through the Indiana University Molecular Structure Center, while the third, that of 4, was completed in-house at Purdue. General operating procedures have been reviewed.[23] Some selected

(22) Quignard, F.; Leconte, M.; Bassett, J. M.; Hsu, L-Y; Alexander, J. J.; Schore, S. G. *Inorg. Chem.* **1987**, *26*, 4272.

(23) (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.

crystallographic data are collected in Table VII.

W(OC₆H₃PhC₆H₄)₂(PMePh₂)₂ (2b). An approximately equi-dimensional crystal was mounted by using silicone grease and was transferred to a goniostat where it was cooled to -140 °C for characterization and data collection. Space group P2₂/c was assigned based on systematic absences. Four standards measured every 300 data showed no significant trends. The residual for the averaging of redundant data was 0.11 for 799 intensities observed more than once. The data contained a large number of weak intensities, almost half of the 6587 unique data being less than 2.33σ.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. Following the location of the atoms in the molecule of interest, a difference map revealed four unique peaks near a crystallographic center of symmetry which formed an apparent molecule of *p*-xylene. These atoms did not refine well, but insofar as they could be refined, the occupancy of the terminal atom appears less than the atoms in the ring. Therefore the unit cell most likely contains ¹/₂ molecule of disordered toluene. No attempt was made to locate hydrogens on this molecule.

Attempts to refine all non-hydrogen atoms anisotropically were unsuccessful, probably due to the large amount of weak data. Tungsten, phosphorous, and oxygen atoms were refined aniso-tropically, and carbon atoms were refined isotropically. Hydrogens were placed in calculated positions prior to the final cycles of least-squares refinement which gave a final R = 0.0615 for 3313 unique data ≥2.33 σ. The final difference map had no additional peaks of significance. There were three residual peaks of 1.0–1.5 e/A³ in the vicinity of the tungsten atom, and all others were less than 1 e/A³.

W(OC₆H₃Ph-η⁶-C₆H₅)(OAr-2,6-Ph₂)(PMePh₂) (3). The particular sample consisted of two components, yellow crystals, which were the bulk of the sample (in the particular tube examined), and green crystals. The present study was undertaken on one of the green crystals. A suitable well-formed green crystal was located and transferred to the goniostat by using standard inert-atmosphere handling techniques employed by the IUMSC

and cooled to -155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences corresponding to one of the triclinic space groups. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, P1̄.

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 Patterson techniques and Fourier techniques. The positions of most of the hydrogen atoms were clearly visible in a difference Fourier phased on the non-hydrogen atoms and were included as fixed atom contributors in the final cycles of refinement.

A final difference Fourier was essentially featureless, with the largest peak being 0.85 e/A³.

W(OC₆H₃Ph-η⁶-C₆H₅)(OAr-2,6-Ph₂)(dppm) (4). A suitable crystal of compound 4 was examined under deoxygenated Nujol and mounted in a appropriate sized glass capillary surrounded by epoxy resin. The hydrogen atom positions were calculated after several cycles of anisotropic refinement assuming idealized geometries and a carbon–hydrogen bond distance of 0.95 Å. For the methyl groups, one hydrogen position was located in a difference Fourier map, this position idealized, and the other two hydrogen positions calculated. Hydrogens were drawn with an arbitrary radius and were not refined. No correction for extinction was applied.

Supplementary Material Available: Tables of anisotropic thermal parameters and full bond distances and angles for **2b**, **3**, and **4** (32 pages); listings of observed and calculated structure factor tables for **2b**, **3**, and **4** (57 pages). Ordering information is given on any current masthead page.

Thermodynamics for the Addition of [(OEP)Rh]₂ with Propene and Observation of a Facile Dyotropic 1,2 Exchange of (OEP)Rh Groups in (OEP)Rh–CH₂CH(CH₃)–Rh(OEP)

Bradford B. Wayland,* Yuping Feng, and Sujuan Ba

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323
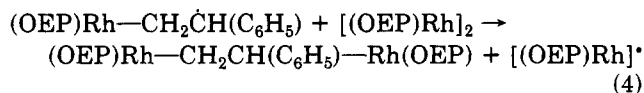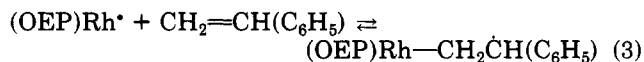
(Octaethylporphyrin)rhodium(II) dimer, [(OEP)Rh]₂ (1), reacts with propene to form (OEP)Rh–CH₂CH(CH₃)–Rh(OEP) (2). Thermodynamic values for the addition reaction were measured in benzene by NMR methods ($\Delta H° = -9.5 \pm 1.0$ kcal mol⁻¹; $\Delta S° = -20 \pm 5$ cal K⁻¹ mol⁻¹) and used in estimating an average Rh–C bond dissociation energy of ~45 kcal mol⁻¹ in **2**. Facile stereospecific 1,2 interchange of (OEP)Rh groups was observed for **2**, and the activation parameters for this dyotropic process were determined by NMR line-shape analysis ($\Delta H* = 12.4 \pm 0.5$ kcal mol⁻¹; $\Delta S* = -10.7 \pm 1.9$ cal K⁻¹ mol⁻¹).

Introduction

Addition reactions of (octaethylporphyrin)rhodium(II) dimer, [(OEP)Rh]₂ (1), with alkenes produce alkyl-bridged complexes (eq 1).[1,2] Both thermodynamic and kinetic studies for reaction 1 using styrene in benzene have been

$$[(OEP)Rh]_2 + CH_2{=}CH(X) \rightleftharpoons$$
$$(OEP)Rh{-}CH_2CH(X){-}Rh(OEP) \quad (1)$$
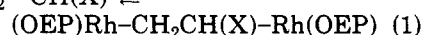
reported by Halpern.[2] Results from kinetic studies were used to implicate the metallo radical [(OEP)Rh]• in a radical chain mechanism described by eq 2-4.[2] This paper

$$[(OEP)Rh]_2 \rightleftharpoons 2[(OEP)Rh]• \quad (2)$$

$$(OEP)Rh• + CH_2{=}CH(C_6H_5) \rightleftharpoons$$
$$(OEP)Rh{-}CH_2\dot{C}H(C_6H_5) \quad (3)$$

$$(OEP)Rh{-}CH_2\dot{C}H(C_6H_5) + [(OEP)Rh]_2 \rightarrow$$
$$(OEP)Rh{-}CH_2CH(C_6H_5){-}Rh(OEP) + [(OEP)Rh]• \quad (4)$$

reports on the thermodynamic values for reaction 1 using

(1) (a) Ogoshi, H.; Setsume, J.; Yoshida, Z. *J. Am. Chem. Soc.* 1977, *99*, 3869. (b) Del Rossi, K. J.; Wayland, B. B *J. Chem. Soc., Chem. Commun.* 1986, 1653.

(2) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* 1985, *107*, 4333.