gave phenyldimethylchlorogermane (**6**) quantitatively. As expected, photolysis of **1** in cyclohexane containing a large excess of 2,3-dimethylbutadiene gave the corresponding germylene trapped product 1,1,3,4-tetramethyl-1-germacyclopent-3-ene (**10**, 1%) together with **4** (11%) and **5** (17%).[15] These results are best rationalized by a diradical path described in Scheme I. A similar mechanism has been proposed for the photolysis of the silicon analogue aryldisilane.[1c,e] In contrast to the case of the disilane, we obtained no concrete evidence for the presence of a formal 1,3-germyl migration product, **9**, in the photolysis of **1**. As described above, the transient at 440 nm is more reasonably assigned to that from a germylene rather that from **9**.[17] These differences in photochemical behaviors between the phenylated digermane and disilane may be accounted for by following reasons. The bond dissociation energy of a Ge–C bond is less than that of a Si–C bond,[18] and π-bonding of carbon must be formed more effectively with a silicon atom than with germanium atom. In addition, germylene is virtually more thermodynamically stable than silylene. All these factors favor formation of germylene and **5** over that of **9** in the germanium analogue.

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(16) If the transient at 440 nm is due to **9**, this should be quenched by ethanol effectively.

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The Conversion of Chelated η^6-Arene to σ-Aryl Coordination at Tungsten Metal Centers

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

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

John C. Huffman and William E. Streib

Molecular Structure Center, Indiana University
Bloomington, Indiana 47405

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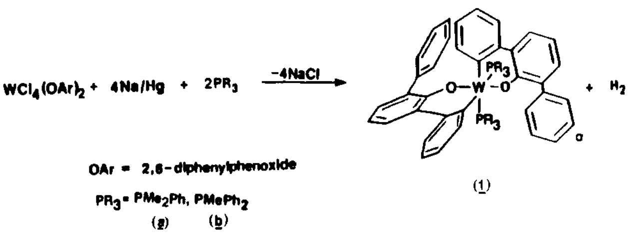
Summary: Reduction of the mixed chloro–aryloxide *cis*-W(OAr-2,6-Ph$_2$)$_2$Cl$_4$ (OAr-2,6-Ph = 2,6-diphenylphenoxide) with Na/Hg (4 equiv) in the presence of PMePh$_2$ leads to the green, η^6-arene compound W(OAr-2-Ph-6-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(PMePh$_2$) which converts smoothly on addition of PMePh$_2$ to the bis-cyclometalated compound W(OC$_6$H$_3$PhC$_6$H$_4$)$_2$(PMePh$_2$)$_2$ and H$_2$.

The homogeneous activation of aromatic CH bonds (both inter- and intramolecularly) by transition-metal compounds has received extensive synthetic study over the last 20 years.[2–4] An important mechanistic question that has been the focus of much attention involves the possible importance of η^2-arene intermediates prior to the oxidative addition of aromatic CH bonds at low-valent, electron-rich metal centers.[5–7] Although in some situations the activation of the CH bonds of benzene has been shown to proceed via an η^2-benzene complex,[5] the activation of CH bonds of ethylene has been shown to occur in related systems without prior π-coordination of the olefin.[7] Recently we had reported that the use of the ligand 2,6-diphenylphenoxide (OAr-2,6-Ph$_2$) attached to group 6 metal centers resulted in bonding modes in which the ligand could be chelated to the metal either via an η^6-interaction or else through a metal–carbon σ-bond to the arene side groups.[8,9] In this communication we wish to report our observation of the direct interconversion of these two types of bonding as well as some insights into the mechanism of this interconversion.

Scheme I



Reduction of toluene solutions of the bis(aryloxide) substrate *cis*-W(OAr-2,6-Ph$_2$)$_2$Cl$_4$[10] with sodium amalgam in the presence of added phosphine donor ligands can lead to a variety of mononuclear products (Scheme I).[11] In the presence of 4 equiv of Na/Hg and PMe$_2$Ph (2 equiv), the reaction proceeds to produce the orange bis-cyclometalated W(IV) compound **1a** in moderate yields.[11,12] The spectroscopic properties of **1a** are consistent with the geometry

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(11) Two intermediates in the reduction of stoichiometry W(OAr-2,6-Ph$_2$)$_2$Cl$_3$(PMe$_2$Ph) and W(OAr-2,6-Ph$_2$)$_2$Cl$_2$(PMe$_2$Ph)$_2$ have been identified and characterized (supplementary material). The reduction of mixed chloro–aryloxides of the type W(OAr)$_4$Cl$_2$ and W(OAr)$_3$Cl$_3$ in the absence of added ligand has been shown to lead to mononuclear and dinuclear compounds of stoichiometries [W(OAr)$_4$]$_n$ and [W(OAr)$_3$]$_n$; = 1 or 2 depending on the bulk of OAr; see: (a) Schavarien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (b) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2161.

(12) Anal. Calcd for WC$_{52}$O$_2$P$_2$H$_{46}$ (**1a**): C, 65.69; H, 5.09; P, 6.52. Found: C, 65.31; H, 5.00; P, 5.89.

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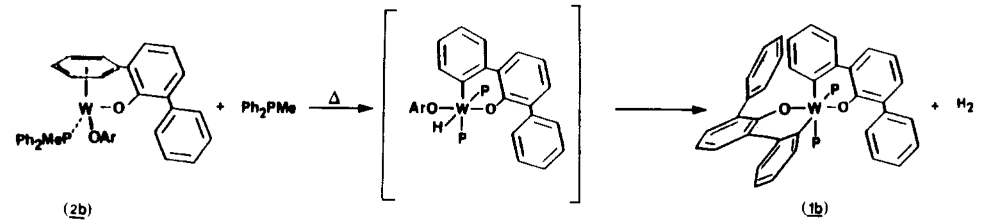
Scheme II



OAr = 2,6-diphenylphenoxide

P = $PMePh_2$

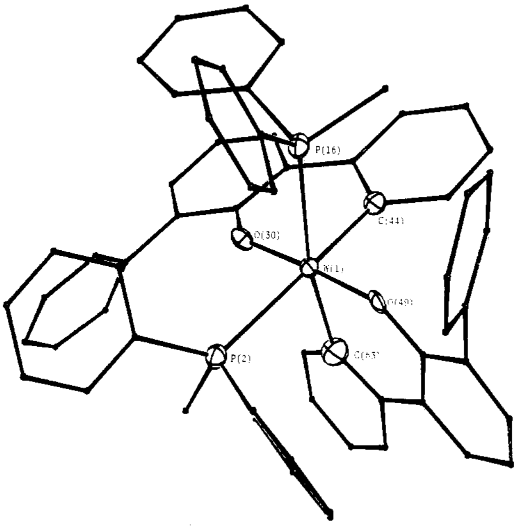


Figure 1. ORTEP view of **1b** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg): W(1)-P(2) = 2.622 (5), -P(16) = 2.653 (5), -O(3) = 1.879 (12), -O(49) = 1.877 (11), -C(44) = 2.138 (18), -C(63) = 2.180 (20), P(2)-W(1)-P(16) = 105.3 (1), -O(3) = 86.6 (3), -O(49) = 90.5 (4), -C(44) = 168.0 (5), -C(63) = 84.2 (5), P(16)-W(1)-O(30) = 88.8 (4), -O(49) = 92.4 (4), -C(44) = 83.0 (5), -C(63) = 169.7 (S5), O(30)-W(1)-O(49) = 177.0 (5), -C(44) = 85.0 (6), -C(63) = 83.3 (7), C(44)-W(1)-C(63) = 88.3 (7).

shown (Scheme I) containing cis phosphorus and trans oxygen atoms about the metal center.[13] Particularly informative are the diastereotopic methyl groups of the PMe_2Ph ligands (^1H and ^{13}C NMR) as well as the presence of the new W-C(ispso) carbon resonances as a doublet of doublets in the $\{^1H\}^{13}C$ NMR spectrum due to one cis and one trans phosphine ligand.[13]

Reduction of *cis*-$W(OAr\text{-}2,6\text{-}Ph_2)_2Cl_4$ with 4Na/Hg in the presence of the more bulky phosphine $PMePh_2$ also led to a bis-cyclometalated compound **1b** as the major product.[14] Spectroscopic data indicate identical structures for **1a** and **1b**,[13,15] and a single crystal X-ray diffraction study on **1b** confirmed the overall geometry (Figure 1).[16] The two six-membered metallacycles formed by the metalation of the side-chain phenyl groups can be seen to be very close to planar, maintaining an 85.0° and 83.3° bite at the metal. Large, 140.7° and 143.5° W-O-C angles help to accommodate the planar metallacycle ring. The most significant distortions from a pseudooctahedral environment about the tungsten metal center is the 105.3° angle between the bulky phosphine ligands.

Some insight into how the bis-cyclometalated derivatives **1** are formed is given by the isolation and characterization of the minor component formed when the reduction is carried out in the presence of $PMePh_2$. This emerald green, diamagnetic material of composition "$W(OAr\text{-}2,6\text{-}Ph_2)_2(PMePh_2)$" (**2b**) was shown by single-crystal X-ray diffraction to indeed be a mononuclear, 16-electron W(II) species containing an η^6-bound aryl side chain (Figure 2).[17] The coordination about the tungsten atom in **2b** can best be described as a "three-legged piano stool" with the six carbon atoms of the arene ring being almost equally bound to the metal.[18] The phosphorus atom of the $PMePh_2$ group makes equal angles to the chelated and terminal aryloxide oxygen atoms. The ^1H NMR spectrum of **2b** under ambient conditions does not show the five sharp sets of resonances of the η^6-aryl group expected on the basis of the observed solid-state structure. However, on cooling toluene-d_8 solutions of **2b**, broad resonances can begin to be resolved in the δ 3–5 region of the spectrum.[19] The use of spin magnetization experiments (^1H) lead us to interpret this fluxionality as arising from a rapid exchange of the bound and unbound aryl side groups of the two 2,6-diphenylphenoxide ligands.[18] The thermolysis of green **2b** in hydrocarbon solvents results in the slow formation of brown solutions that contain **1b** as well as other, as yet unidentified, components. However, in the presence of an added equivalent of $PMePh_2$, **2b** undergoes the mild (50 °C) quantitative conversion to the bis-cyclometalated compound **1b** with the elimination of H_2 (identified by gc analysis), (Scheme II).[20] The conversion of **2b** to **1b** presumably takes place via an undetected intermediate,

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[13] Selected spectroscopic data for **1a**: ^1H NMR (C_6D_6, 30 °C) δ 0.68 (d), 0.71 (d, PMe_2Ph), 8.55 (d), 8.11 (d, H atoms on metalated ring), 6–7.2 (other aromatics); ^{13}C NMR (C_6D_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, PMe_2Ph); ^{31}P NMR (C_6D_6, 30 °C) δ -15.69 ($^1J(^{183}W-^{31}P)$ = 179 Hz).

[14] Anal. Calcd for $WC_{62}O_2P_2H_{50}$ (**1b**): C, 69.28; H, 4.88; P, 5.76. Found: C, 69.72; H, 4.95; P, 5.99.

[15] Selected spectroscopic data for **1b**: ^1H NMR (C_6D_6, 30 °C) δ 1.03 (d, $PMePh_2$), 8.00 (d), 8.46 (d, H's attached to metalated ring), 6–7.1 (other aromatics); ^{13}C NMR (C_6D_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, $PMePh_2$); ^{31}P NMR (C_6D_6, 30 °C) δ -36.9 ($^1J(^{183}W-^{31}P)$ = 159 Hz).

[16] Crystal data for **1b** at -140 °C: a = 19.828 (8), b = 26.214 (13), c = 10.380 (4) Å, β = 111.53 (2)°; Z = 4; d_{calcd} = 1.490 g cm^{-3} in space group $P2_1/a$. A total of 6587 unique intensities were collected by using Mo Kα radiation, 6° $\le 2\theta \le$ 45°, of which 3313 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are R = 0.0615 and R_w = 0.0580.

[17] Crystal data for **2b** at -155 °C: a = 15.162 (6), b = 14.096 (5), c = 10.246 (4) Å, α = 61.25 (2), β = 101.92 (2), γ = 100.75 (2)°; Z = 2; d_{calcd} = 1.554 in space group $P\bar{1}$. Of the 4457 unique intensities measured with Mo Kα, 6° $\le 2\theta \le$ 45°, the 4044 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are R = 0.0452 and R_w = 0.0438.

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[19] Selected spectroscopic data for **2b**: ^1H NMR ($C_6D_5CD_3$, 30 °C) δ 1.45 (d, $PMePh_2$); ^{31}P NMR (C_6D_6, 30 °C) δ +49.9 ($^1J(^{183}W-^{31}P)$ = 363 Hz). At -35 °C two broad resonances at δ 3.61 and 3.09 due to protons attached to the η^6-aryl ring begin to be resolved.

[20] The conversion of **2b** to **1b** could be conveniently followed by using either ^1H or ^{31}P NMR. The signals due to the $PMePh_2$ groups in **2b** and the free ligand (initially of equal intensity) drop simultaneously to zero with a concomitant build up of intensity of the phosphine signals of **1b**.

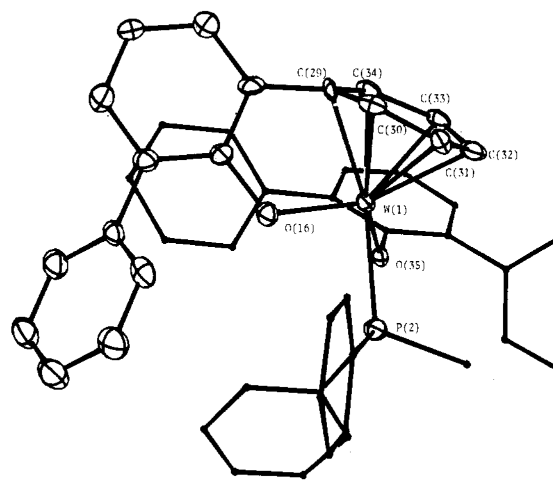

Figure 2. ORTEP view of **2b**. Selected bond distances (Å) and angles (deg): W(1)–P(2) = 2.481 (3), –O(16) = 2.033 (6), –O(35) = 2.001 (6), –C(29) = 2.202 (8), –C(30) = 2.357 (8), –C(31) = 2.292 (a), –C(32) = 2.227 (a), –C(33) = 2.296 (8), –C(34) = 2.286 (a), P(2)–W(1)–O(16) = 79.1 (1), –O(35) = 79.0 (2), O(16)–W(1)–O(35) = 117.1 (2), W(1)–O(16)–C(17) = 117.5 (5), W(1)–O(35)–C(36) = 127.4 (5).

mono-cyclometalated hydride compound that then undergoes a second CH bond activation to generate the observed H_2 gas (Scheme II).[21,22] Addition of the smaller phosphine PMe_2Ph to solutions of **2b** also results in the rapid formation of bis-cyclometalated **1a** along with H_2.

These results taken along with the high thermal stability of the 18-electron complexes $W(OAr\text{-}2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5)(PMePh_2)_2(H)$[8] and $W(OAr\text{-}2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5)(PMe_2Ph)_2(Cl)$[23] strongly indicate the lack of facile, direct conversion of an η^6-bound arene group into a σ-bound aryl function via oxidative addition at these W(II) centers. Instead the dislodging of the η^6-arene group appears to be necessary to initiate CH bond activation. Hence in the case of **2b**, steric congestion caused by the added phosphine would displace the η^6-arene leading to a highly reactive "$W(OAr)_2(PR_3)_2$" intermediate.[21] Further mechanistic study of this reactivity is underway.

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Supplementary Material Available: Tables of positional parameters, general temperature fractions, bond distances, and bond angles for **1b** and **2b** and also analytical data on intermediates mentioned in text (23 pages); listings of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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[21] The chlorophosphine compounds of W(II) of stoichiometry $WCl_2(PR_3)_4$ have been shown to be highly reactive toward oxidative addition; see: Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808 and references therein.

[22] The double metalation of 2,6-diphenylphenoxide at Ta(III) metal centers has also been demonstrated although no intermediates could be detected; see ref 9b. However, intramolecular oxidative addition of an aliphatic CH bond to Ta(III) has been shown to yield a hydrido–alkyl compound: Lubben, T. V.; Wolczarski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 414.

[23] Formed by the reduction of toluene solutions of $W(OAr\text{-}2,6\text{-}Ph_2)Cl_5$ with Na/Hg (4 equiv) in the presence of PMe_2Ph (2 equiv); see supplementary material.

Stereocontrolled Bifacial Complexation of the Isodicyclopentadienyl Ligand to Cyclopentadienyltitanium Dichloride Fragments[1]

Leo A. Paquette,*,† Kevin J. Moriarty,† Philippe Meunier,‡ Bernard Gautheron,*,‡ and Véronique Crocq‡

Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210, and
Laboratoire de Synthèse et d'Electrosynthèse
Organométalliques associe au CNRS (UA 33)
Faculté des Sciences, 6 bd Gabriel
21000 Dijon, France

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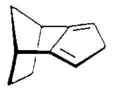
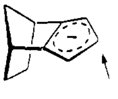
Summary: Reaction of the isodicyclopentadienide anion with $(RCp)TiCl_3$ (R = H, CH_3) and $Cp''TiCl_3$ is shown to proceed under conditions presumed to be kinetically controlled with complete bifacial stereoselectivity depending upon temperature. While endo complexation materializes at −78 °C, exo coordination operates exclusively at room temperature and above, as ascertained by X-ray analysis. The isomeric complexes can also be easily distinguished spectroscopically.

The plane-nonsymmetric nature of isodicyclopentadiene (isodiCp, **1**) has served admirably for examination of the relevance of π-facial selectivity in a wide range of cycloaddition reactions.[2] The remarkable predilection of this system for stereoselective dienophile capture from the sterically more congested endo direction (in the absence of overriding steric effects) is mirrored in its anion (**2**), which captures electrophiles predominantly, if not exclusively, from its endo surface to deliver C_s-symmetric products.[3,4] In a previous paper,[5] we demonstrated that **2** is complexed uniquely from its sterically less crowded exo face when allowed to react with tri- or tetrachloride salts of the group 4 transition metals. The symmetrical complexes represented by **3** (M = Ti, Zr, Hf) result.


1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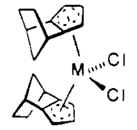

3

Like the situation in **1**, the π-facial course of isodicyclopentadienide anion reactions is believed to be governed by a complex interplay of electronic[6] and steric factors.[7] One may immediately inquire whether the crossover in stereoselectivity that materializes in the course of the **2** → **3** conversions, when compared to the reaction

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† The Ohio State University.

‡ Faculté des Sciences Dijon.

[1] Part 40 in the series dealing with isodicyclopentadienes and related molecules. (a) For part 39, see: Paquette, L. A.; Gugelchuk, M. *J. Org. Chem.*, in press. (b) For part 38, consult: Paquette, L. A.; Gugelchuk, M.; McLaughlin, M. L. *Ibid.* **1987**, *52*, 4732.

[2] An extensive listing of literature citations can be found in ref 1b.

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