



COMMUNICATION

CONVERSION OF ARENE GROUPS TO η^2 -CYCLOHEXENE RINGS AT TUNGSTEN METAL CENTERS

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Abstract—The sodium amalgam (4Na per W) reduction of hydrocarbon solutions of $[\text{W}(\text{OC}_6\text{HPh}_4\text{-2,3,5,6})_2\text{Cl}_4]$ (**1**) ($\text{OC}_6\text{HPh}_4\text{-2,3,5,6}$ = 2,3,5,6 tetraphenylphenoxide) in the presence of phosphine ligands (L) leads to the deep-green complexes $[\text{W}(\text{OC}_6\text{HPh}_3\text{-}\eta^6\text{-C}_6\text{H}_5)(\text{OC}_6\text{PPh}_4\text{-2,3,5,6})(\text{L})]$ (**2a**, L = PMe_2Ph ; **2b**, L = PMePh_2). The solid state structure of **2a** shows one of the *ortho*-phenyl groups of an aryloxy ligand bound to the tungsten metal center. The η^6 -arene complex **2a** reacts very slowly with H_2 (1 atm, 25°C) in C_6D_6 solution to produce a dark-brown complex $[\text{W}(\text{OC}_6\text{HPh}_3\text{-}\eta^2\text{-C}_6\text{H}_9)(\text{OC}_6\text{HPh}_3\text{-}\eta^6\text{-C}_6\text{H}_5)(\text{PMe}_2\text{Ph})]$ (**3a**), the solid-state structure of which shows that one of the *ortho*-phenyl rings has undergone reaction with two equivalents of H_2 to produce a cyclohex-1-ene ring which is η^2 -bound to the metal center. The remaining aryloxy ligand in **3a** is chelated through an η^6 -interaction, leading to a formal 18-electron configuration at the metal.

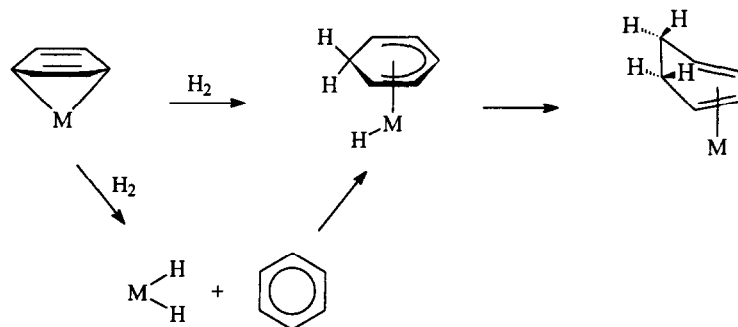
The demonstrated ability of mixed hydrido, aryloxy derivatives of niobium and tantalum to carry out the inter- and intramolecular hydrogenation of

arene rings raises many mechanistic questions.¹ One key problem concerns whether arene hydrogenation proceeds via reaction of a metal hydride with the arene substrate or whether arene coordination to a metal site precedes hydrogenation (Scheme 1).² We wish to communicate here on the intramolecular hydrogenation of the *ortho*-phenyl rings of aryloxy ligands by tungsten metal centers, the results of which highlight this mechanistic dilemma.

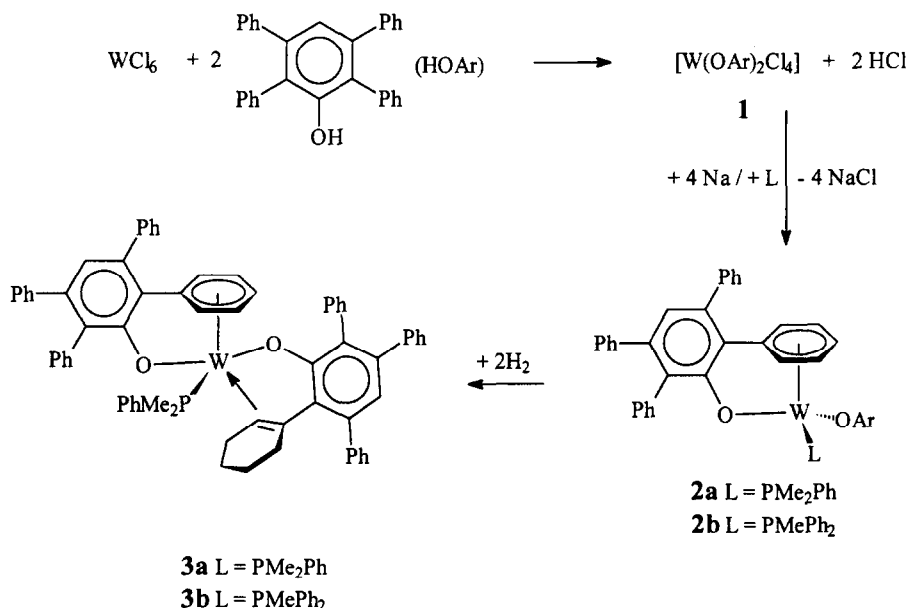
The ligand 2,3,5,6-tetraphenylphenol ($\text{HOC}_6\text{HPh}_4\text{-2,3,5,6}$) has been chosen for study because of its resistance to intramolecular CH bond activation (cyclometallation), a reaction that tends to dominate the early *d*-block organometallic chemistry of the related 2,6-diphenylphenoxide ligand.³ The reduction (4Na per W) of benzene solutions of the tungsten bis(aryloxy) $[\text{W}(\text{OCHPh}_4\text{-2,3,5,6})_2\text{Cl}_4]$ in the presence of phosphine ligands leads to the deep-green complexes $[\text{W}(\text{OC}_6\text{HPh}_3\text{-}\eta^6\text{-C}_6\text{H}_5)(\text{OC}_6\text{HPh}_4\text{-2,3,5,6})(\text{L})]$ (**2a**, L = PMe_2Ph ; **2b**, L = PMePh_2) as shown (Scheme 2).[†] The solid

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† Selected NMR data: ^{31}P NMR (C_6D_6 , 30°C), δ [$^1J(^{183}\text{W}\text{—}^{31}\text{P})$]: **2a**, 38.1 (367 Hz). **2b**, 49.1 (362 Hz). **3a**, -5.3 (324 Hz). **3b**, -4.6 (309 Hz). ^1H NMR (C_6D_6 , 30°C): **2a**, 1.13 (d), 1.22 (d, P—Me); 3.52 (m), 3.04 (m), 2.02 (m), 1.70 (m), 1.38 (m, $\eta^6\text{-C}_6\text{H}_5$); 6.8–7.7 (m, aromatic protons). **2b**, 1.26 (d, P—Me); 3.66 (m), 3.12 (m), 2.04 (m), 1.48 (m), 1.48 (m, $\eta^6\text{-C}_6\text{H}_5$); 6.8–7.7 (m, aromatic protons). **3a**, 1.02 (d), 1.16 (d, P—Me); 4.77 (d), 4.75 (t), 3.52 (d), 2.86 (t), 2.67 (t, $\eta^6\text{-C}_6\text{H}_5$); 3.10 (t, $\eta^2\text{-C}\equiv\text{CH}$); 3.60 (m), 3.14 (m), 2.48 (m), 2.22 (m, $\eta^2\text{-C}\equiv\text{CCH}_2$); 1.38 (m), 1.50 (m), 1.52 (m), 1.78 (m, $\eta^2\text{-C}\equiv\text{CCH}_2\text{CH}_2$); 6.8–7.7 (m, aromatic protons). **3b**, 1.57 (d, P—Me); 5.18 (d), 4.85 (t), 3.54 (d), 3.08 (t), 2.99 (t, $\eta^6\text{-C}_6\text{H}_5$); 3.10 (t, $\eta^2\text{-C}\equiv\text{CH}$); 3.40 (m), 2.98 (m), 2.43 (m), 2.15 (m, $\eta^2\text{-C}\equiv\text{CCH}_2$); 1.38 (m), 1.30 (m), 1.19 (m), 1.17 (m, $\eta^2\text{-C}\equiv\text{CCH}_2\text{CH}_2$); 6.8–7.7 (m, aromatic protons).



Scheme 1.



Scheme 2.

state structure of **2a** (Fig. 1)[‡] shows a three-legged piano-stool geometry about tungsten with an η^6 -interaction to one of the *ortho*-phenyl rings of an aryloxy ligand. The ^1H NMR spectra of **2a** and **2b** show five well resolved resonances for the non-

equivalent protons in the η^6 -bound arene ring. The W—C(arene) distances in 16-electron **2a** are among the shortest such parameters for any structurally characterized tungsten–arene complex.⁴ There is a definite distortion of the arene involving a bending of the two mutually *trans* carbon atoms C(121) and C(124) towards the tungsten metal center. This type of distortion has been well documented for other early *d*-block metal arene complexes and has been described in terms of approaching a metallanorbornadiene resonance structure.⁵ The distortion is, however, much less than in complexes such as $[\text{Ta}(\text{OAr})_2\text{Cl}(\eta^6\text{-C}_6\text{Me}_6)]$.⁵ When placed under an atmosphere of hydrogen, deep-green solutions of **2a** or **2b** in benzene are slowly converted over days into dark-brown solutions of new organometallic derivatives **3a** and **3b** (Scheme 2). The reactions are readily monitored in C_6D_6 solution by ^1H and ^{31}P NMR spectroscopy. For example, in the $[\text{H}]$ ^{31}P NMR spectrum the signals due to **2a** at $\delta 38.1$ ppm

[‡] Crystal data: **2a**, $\text{WPO}_2\text{C}_{74}\text{H}_{59}$: $M = 1195.12$, crystal size = $ca\ 0.13 \times 0.10 \times 0.08$ mm, triclinic space group $P\bar{1}$, $a = 12.179(1)$, $b = 13.839(1)$, $c = 19.399(2)$ Å, $\alpha = 101.100(6)^\circ$, $\beta = 97.950(8)^\circ$, $\gamma = 94.02(1)^\circ$, $V = 3041(1)$ Å³, $Z = 2$, $D_c = 1.305$ g cm⁻³, λ (Cu-K α) = 1.54184 Å; of the 8147 unique intensities measured the 4605 with $I > 3.0\sigma(I)$ yielded $R(F_o) = 0.056$, $R_w(F_o) = 0.028$. **3a**, $\text{WPO}_2\text{C}_{68}\text{H}_{57}$: $M = 1121.04$, crystal size = $ca\ 0.24 \times 0.14 \times 0.10$ mm, triclinic space group $P\bar{1}$, $a = 10.788(2)$, $b = 11.524(2)$, $c = 21.168(4)$ Å, $\alpha = 82.49(2)^\circ$, $\beta = 85.29(2)^\circ$, $\gamma = 83.01(2)^\circ$, $V = 2583(1)$ Å³, $Z = 2$, $D_c = 1.441$ g cm⁻³, λ (Cu-K α) = 1.5418 Å; of the 8186 unique intensities measured the 5440 with $I > 3.0\sigma(I)$ yielded $R(F_o) = 0.044$.

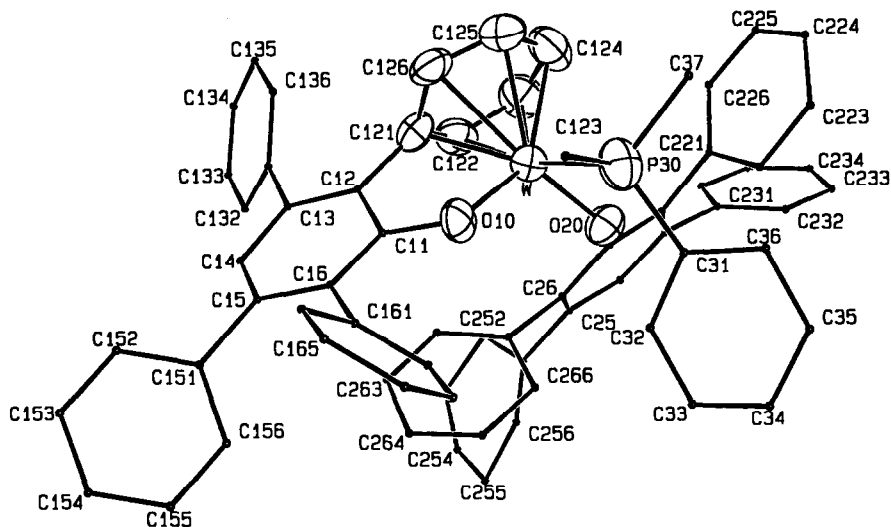


Fig. 1. Molecular structure of **2a**. Selected interatomic distances (Å) and angles (°): W—P(30) 2.478(4), W—O(10) 2.022(9), W—O(20) 1.966(9), W—C(121) 2.16(1), W—C(122) 2.27(1), W—C(123) 2.24(2), W—C(124) 2.18(1), W—C(125) 2.25(1), W—C(126) 2.35(1), C(121)—C(122) 1.41(2), C(121)—C(126) 1.46(2), C(122)—C(123) 1.39(2), C(123)—C(124) 1.43(2), C(124)—C(125) 1.44(2), C(125)—C(126) 1.36(2), P(30)—W—O(10) 80.2(3), P(30)—W—O(20) 85.6(3), O(10)—W—O(20) 115.3(4), W—O(10)—C(11) 119.5(8), W—O(20)—C(21) 130.8(9).

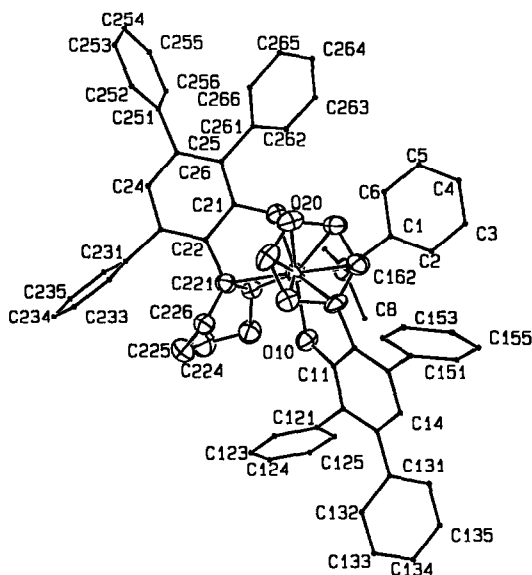
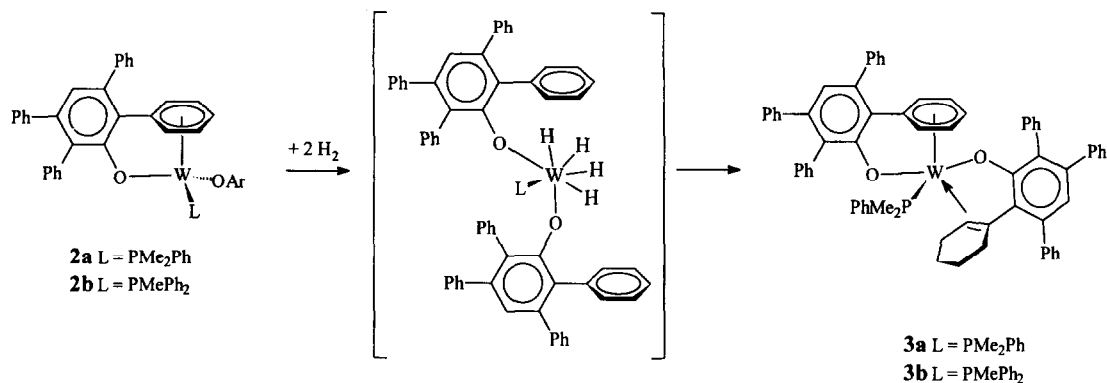


Fig. 2. Molecular structure of **3a**. Selected interatomic distances (Å) and angles (°): W—P 2.49(2), W—O(10) 2.130(4), W—O(20) 2.066(4), W—C(161) 2.367(7), W—C(162) 2.39(7), W—C(163) 2.274(7), W—C(164) 2.356(7), W—C(165) 2.368(7), W—C(166) 2.234(7), W—C(221) 2.267(7), W—C(222) 2.268(7), C(161)—C(162) 1.37(1), C(161)—C(166) 1.47(1), C(162)—C(163) 1.39(1), C(163)—C(164) 1.44(1), C(164)—C(165) 1.34(1), C(165)—C(166) 1.409(9), C(221)—C(222) 1.41(1), P—W—O(10) 80.71(1), P—W—O(20) 82.0(1), O(10)—W—O(20) 149.3(2), W—O(10)—C(11) 125.0(4), W—O(20)—C(21) 117.8(4).

(367 Hz ^{183}W satellites) are replaced by an upfield signal at δ -5.4 ppm (324 Hz) due to **3a**.† The molecular structure of **3a** (Fig. 2)‡ contains a 2-(cyclohex-1-enyl)-3,5,6-triphenylphenoxide and a 2,3,5,6-tetraphenylphenoxide ligand both chelated to the metal center. The η^6 -phenyl and η^2 -cyclohexene interactions result in a formal 18-electron configuration for **3a**. The W—O(aryloxide) and W—C(arene) distances in **3a** are significantly longer than those in 16-electron **2a**.

The strong interaction between the tungsten metal center and the arene ring in **2a** may lead to sufficient "tungstanorbornadiene" character such that hydrogenolysis of the incipient tungsten-carbon σ -bonds may be the initial step in the formation of **3a**. It may, however, be highly significant that the d^4 -W^{II} center in **2** leads, under H_2 , to the formation of a cyclohexene ring, while related work shows that a d^2 -Nb^{III} 2,6-diphenylphenoxide intermediate leads to a pendant cyclohexadiene ring. One possible rationalization of these results is that they represent the stoichiometric, intramolecular hydrogenation of an arene ring by the corresponding d^0 -metal hydride compounds⁶ (Scheme 3).

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Scheme 3.

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