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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 $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_4]$ (**1**) (OC_6HPh_4-2,3,5,6 = 2,3,5,6 tetraphenylphenoxide) in the presence of phosphine ligands (L) leads to the deep-green complexes $[W(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(OC_6PHh_4\text{-}2,3,5,6)(L)]$ (**2a**, L = PMe_2Ph; **2b**, L = $PMePh_2$). The solid state structure of **2a** shows one of the *ortho*-phenyl groups of an aryloxide 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 $[W(OC_6HPh_3\text{-}\eta^2\text{-}C_6H_9)(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(PMe_2Ph)]$ (**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 aryloxide 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, aryloxide 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 aryloxide ligands by tungsten metal centers, the results of which highlight this mechanistic dilemma.

The ligand 2,3,5,6-tetraphenylphenol (HOC_6HPh_4-2,3,5,6) 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(aryloxide) $[W(OCHPh_4\text{-}2,3,5,6)_2Cl_4]$ in the presence of phosphine ligands leads to the deep-green complexes $[W(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(OC_6HPh_4\text{-}2,3,5,6)(L)]$ (**2a**, L = PMe_2Ph; **2b**, L = $PMePh_2$) as shown (Scheme 2).† The solid

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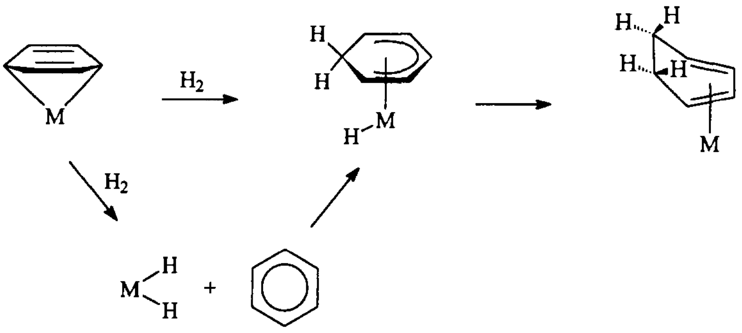
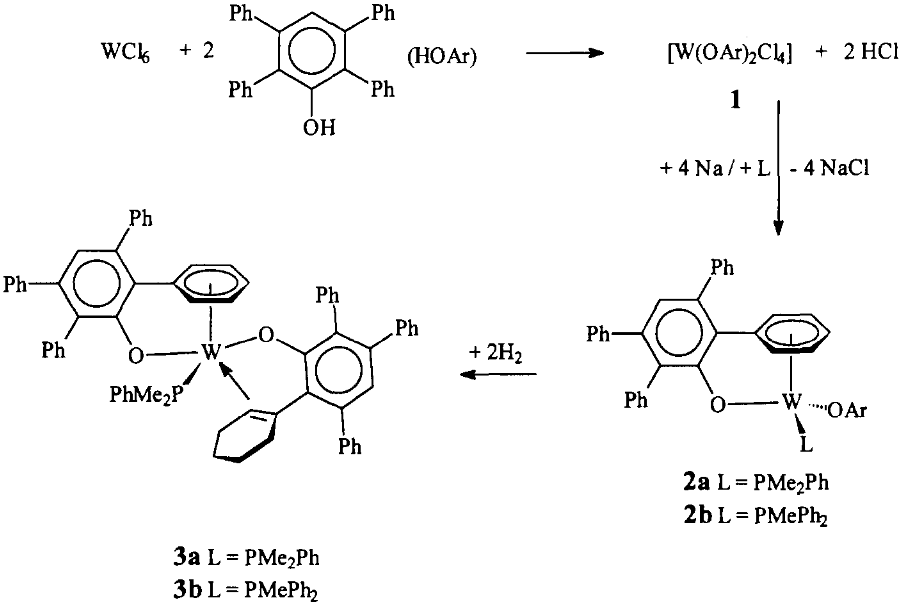
† *Selected NMR data*: ^{31}P NMR (C_6D_6, 30°C), δ $[^1J(^{183}W\text{—}^{31}P)]$: **2a**, 38.1(367 Hz). **2b**, 49.1(362 Hz). **3a**, −5.3(324 Hz). **3b**, −4.6(309 Hz). ^1H NMR (C_6D_6, 30°C): **2a**, 1.13 (d), 1.22 (d, P—*Me*); 3.52 (m), 3.04 (m), 2.02 (m), 1.70 (m), 1.38 (m, $\eta^6\text{-}C_6H_5$); 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, $\eta^6\text{-}C_6H_5$); 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, $\eta^6\text{-}C_6H_5$) ; 3.10 (t, $\eta^2\text{-}C{=}CH$); 3.60 (m), 3.14 (m), 2.48 (m), 2.22 (m, $\eta^2\text{-}C{=}CCH_2$); 1.38 (m), 1.50 (m), 1.52 (m), 1.78 (m, $\eta^2\text{-}C{=}CCH_2CH_2$); 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, $\eta^6\text{-}C_6H_5$); 3.10 (t, $\eta^2\text{-}C{=}CH$); 3.40 (m), 2.98 (m), 2.43 (m), 2.15 (m, $\eta^2\text{-}C{=}CCH_2$); 1.38 (m), 1.30 (m), 1.19 (m), 1.17 (m, $\eta^2\text{-}C{=}CCH_2CH_2$); 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 aryloxide 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 $[Ta(OAr)_2Cl(\eta^6\text{-}C_6Me_6)]$.[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 $[^1H]$ ^{31}P NMR spectrum the signals due to **2a** at $\delta 38.1$ ppm

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‡ *Crystal data*: **2a**, $WPO_2C_{74}H_{59}$: M = 1195.12, crystal size = *ca* 0.13 × 0.10 × 0.08 mm, triclinic space group $P\bar{1}$, a = 12.179(1), b = 13.839(1), c = 19.399 (2) Å, α = 101.100(6), β = 97.950(8), γ = 94.02(1)°, V = 3041(1) Å^3, 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**, $WPO_2C_{68}H_{57}$: M = 1121.04, crystal size = *ca* 0.24 × 0.14 × 0.10 mm, triclinic space group $P\bar{1}$, a = 10.788(2), b = 11.524(2), c = 21.168(4) Å, α = 82.49(2), β = 85.29(2), γ = 83.01(2)°, V = 2583(1) Å^3, 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.

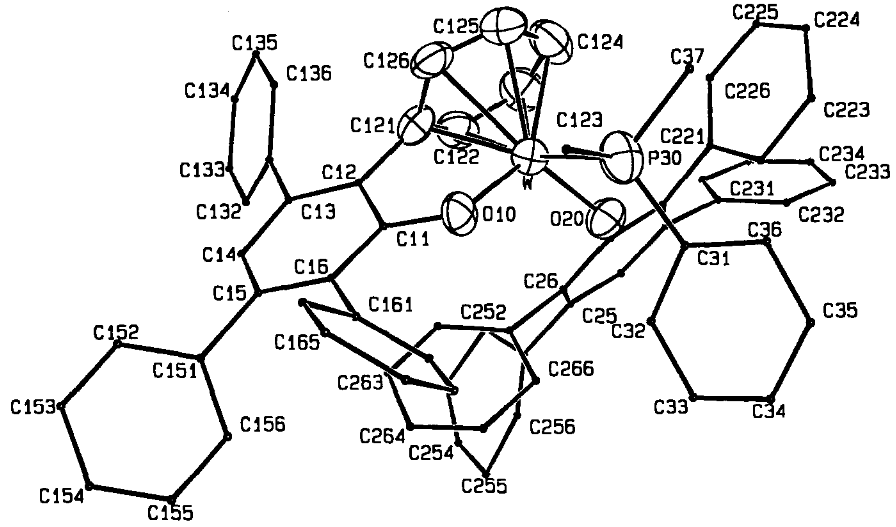

Fig. 1. Molecular structure of **2a**. Selected interatomic distances (Å) and angles (°): W—P(30) 2.478(4), W—O(10) 2.022(9), W—O(20) 1.966(9), W—C(121) 2.16(1), W—C(122) 2.27(1), W—C(123) 2.24(2), W—C(124) 2.18(1), W—C(125) 2.25(1), W—C(126) 2.35(1), C(121)—C(122) 1.41(2), C(121)—C(126) 1.46(2), C(122)—(123) 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).

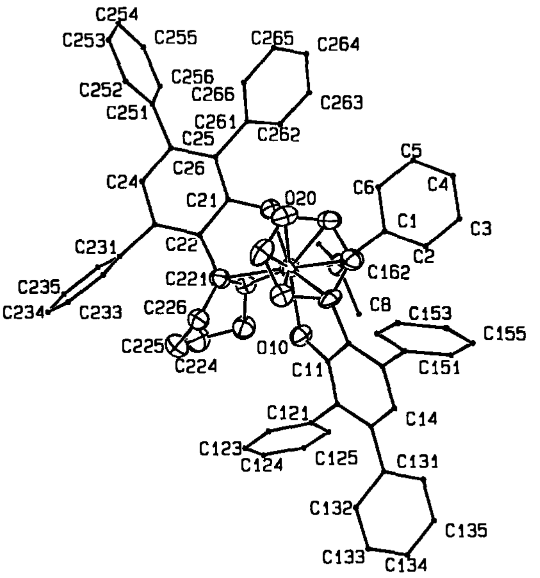

Fig. 2. Molecular structure of **3a**. Selected interatomic distances (Å) and angles (°): W—P 2.49(2), W—O(10) 2.130(4), W—O(20) 2.066(4), W—C(161) 2.367(7), W—C(162) 2.39(7), W—C(163) 2.274(7), W—C(164) 2.356(7), W—C(165) 2.368(7), W—C(166) 2.234(7), W—C(221) 2.267(7), W—C(222) 2.268(7)0, C(161)—C(162) 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 compounds[6] (Scheme 3).

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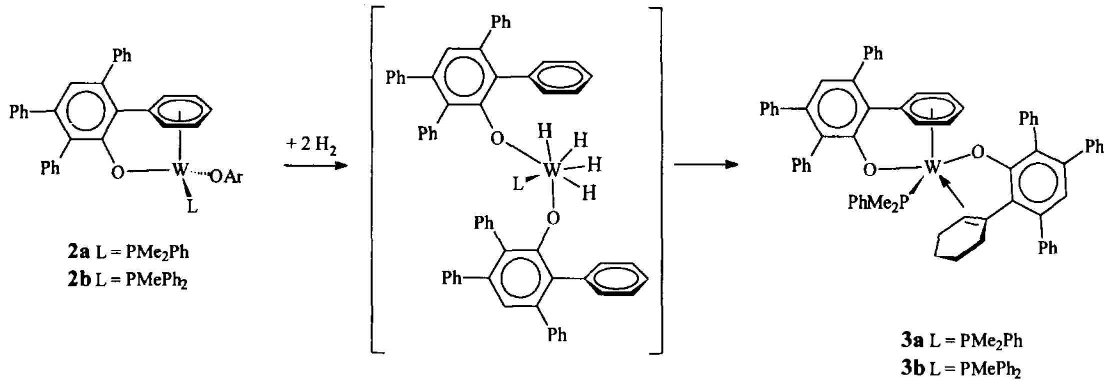

Scheme 3.

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