3574 *Organometallics* **1997,** *16,* 3574−3575

Reactivity of a Tungsten(II) Aryloxide with Isocyanides and Isocyanates

Mark A. Lockwood, Phillip E. Fanwick, and Ian P. Rothwell*

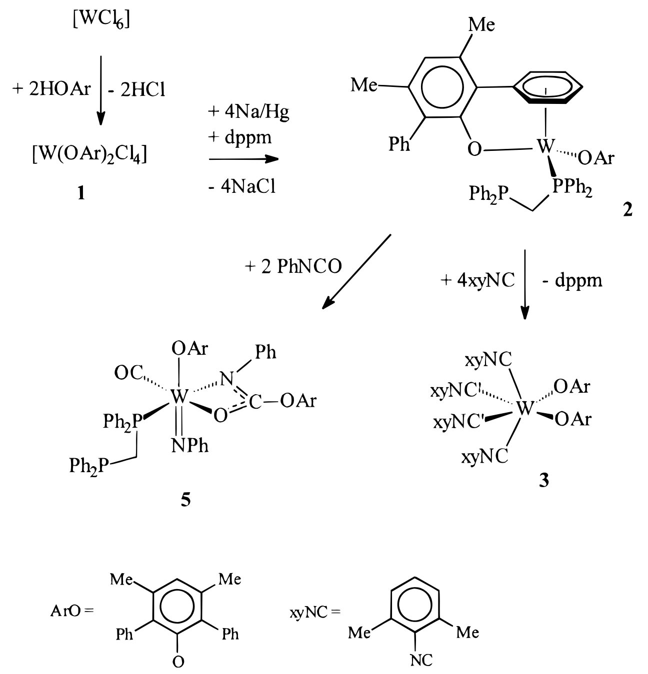
Department of Chemistry, 1393 Brown Building, Purdue University,
West Lafayette, Indiana 47907-1393

Received March 28, 1997⊗

Summary: The 16-electron W(II) aryloxide [W(OC$_6$HPhMe$_2$-η^6-C$_6$H$_4$)(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)(η^1-dppm)] (**2**)*; OC$_6$HPh$_2$-2,6-Me$_2$-3,5 = 2,6-diphenyl-3,5-dimethylphenoxide) reacts with 2,6-dimethylphenyl isocyanide (xyNC) to produce the structurally distorted compounds cis-[W(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$(xyNC)$_4$]* (**3**)*. The addition of PhNCO to* **2** *produces a product* (**5**) *in which both cleavage of an isocyanate C═N double bond and insertion of an isocyanate into a W—OAr bond has occurred.*

Low-valent halide,[1] alkoxide,[2,3] and aryloxide[4] derivatives of tungsten sometimes exhibit reactivity in which heteroatom−heteroatom, carbon−heteroatom, and carbon−carbon multiple bonds can be cleaved. Recently we have demonstrated the reduction of a variety of substrates by a W(II) aryloxide compound. In all of the reactions reported so far the products are formally d^0 W(VI) species in which substrate molecules have been reduced by four electrons.[4] We wish to communicate here related reactivity with isocyanide and isocyanate substrates leading to structurally interesting mid-valent aryloxides of tungsten containing π-acceptor ligands.

Scheme 1



The bis(aryloxide) compound [W(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$Cl$_4$] (**1**; OC$_6$HPh$_2$-2,6-Me$_2$-3,5 = the metalation-resistant 2,6-diphenyl-3,5-dimethylphenoxide[5]) undergoes sodium amalgam (4/1 Na/W) reduction in the presence of dppm to produce the emerald green, 16-electron compound [W(OC$_6$HPhMe$_2$-η^6-C$_6$H$_5$)(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)(η^1-dppm)] (**2**).[6] The spectroscopic data for **2** confirm the η^6 bonding of one of the *ortho* phenyl rings of an aryloxide and the monodentate coordination of the dppm ligand.[6] A solution of **2** in C$_6$D$_6$ reacts rapidly (^{1}H NMR) with 2,6-dimethylphenyl isocyanide (CNxy) to produce a dark brown mixture from which crystals of [W(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$(CNxy)$_4$] (**3**) can be isolated.[7] Analysis by ^{31}P NMR of the reaction mixture showed only free dppm to be present. The molecular structure of **3** (Figure 1)[8] shows a six-coordinate tungsten atom bound to two aryloxide and four isocyanide ligands. The literature abounds with numerous examples of six-coordinate, d^4 transition-metal compounds

---

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298.

(2) (a) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 602. (b) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 607.

(3) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(4) (a) Lockwood, M. A.; Fanwick, P. E.; Eisenstein, O.; Rothwell, I. P. *J. Am. Chem. Soc.* **1996**, *118*, 2762. (b) Lockwood, M. A.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1996**, 2013.

(5) Lockwood, M. A.; Clark, J. R.; Parkin, B. C.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1996**, 1973.

(6) Selected data for [W(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$Cl$_4$] (**1**): Anal. Calcd for C$_{40}$H$_{34}$O$_2$Cl$_4$W: C, 56.88; H, 4.14; Cl, 15.47. Found: C, 56.93; H, 4.14; Cl, 15.56. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 7.0−7.4 (m, 20H, aromatics), 6.34 (s, 2H, *para* proton), 1.83 (s, 12H, *meta* Me). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 127−140 (aromatics), 20.8 (*meta* Me). Selected data for [W(OC$_6$HPh-η^6-C$_6$H$_5$-Me$_2$-3,5)(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)(η^1-dppm)] (**2**): ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 6.6−7.6 (m, 20H, aromatics), 6.57 (s, 1H, *para* H), 6.46 (s, 1H, *para* H), 4.34 (m, 1H), 3.36 (m, 1H), 3.07 (m, 1H), 2.47 (m, 1H), 1.73 (m, 1H, *ortho*, *meta*, and *para* protons of the η^6-C$_6$H$_5$ group), 2.72 (m, 2H, PCH_2P), 2.29, 2.22, 2.05, 2.02, 1.94, 1.92 (*meta* Me). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 177.6 (d, W−O−C, $^3J(^{31}P-^{13}C) = 10.1$ Hz), 164.9 (d, W−O−C, $^3J(^{31}P-^{13}C) = 5.6$ Hz), 139.0, 135.3, 134.8, 133.9, 133.7, 133.6, 133.5, 133.3, 133.2, 133.0, 132.9, 132.7, 132.6, 132.5, 131.8, 129.2, 127.8, 127.3, 126.5, 125.6, 124.1 (d, $^1J(^{31}P-^{13}C) = 5.5$ Hz), 99.1, 98.9, 98.8, 98.6, 92.6, 92.4 (η^6-C$_6$H$_4$), 26.6 (m, PCH$_2$P), 24.6, 20.6, 19.2 (*meta* Me). ^{31}P NMR (C$_6$D$_6$, 30 °C): δ 57.0 (d, $^2J(^{31}P-^{31}P) = 56.3$ Hz, $^1J(^{183}W-^{31}P) = 357.2$ Hz), −24.73 (d, $^2J(^{31}P-^{31}P) = 56.3$ Hz).

(7) Selected data for *cis*-[W(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$(CNxy)$_4$] (**3**): Anal. Calcd for C$_{76}$H$_{70}$N$_4$O$_2$W: C, 72.74; H, 5.58; N, 4.47. Found: C, 69.23; H, 5.57; N, 4.37. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 7.43 (d, 8H), 7.17 (s, 4H), 7.09 (t, 8H), 6.75 (t, 4H), 6.96 (s, 2H), 6.66 (s, 8H), 2.18 (s, 12H), 1.87 (s, 24H). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 192.3 (W−CNxy, unable to resolve ^{183}W satellites), 162.5 (W−O−C), 140.8, 135.7, 132.6, 132.1, 131.9, 130.75, 130.69, 126.2, 125.6, 122.9, 122.7, 22.3 (xylyl methyl), 18.2 (*meta* Me). IR (Nujol mull): 2120, 2035, 1973 cm^{-1} (ν(CN)).

(8) Crystal data for **3** at 295 K: WO$_2$N$_4$C$_{76}$H$_{70}$, $M_r = 1255.28$, space group $P2_1/c$ (No. 14), $a = 23.369(5)$ Å, $b = 12.326(2)$ Å, $c = 22.135(4)$ Å, $\beta = 91.97(2)°$, $V = 6372(4)$ Å^3, $d_{calcd} = 1.308$ g cm^{-3}, $Z = 4$. Of the 8940 unique reflections collected ($5.12 \leq 2\theta \leq 45.34°$) with Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å), the 4668 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield $R(F_o) = 0.035$ and $R_W(F_o) = 0.038$. Crystal data for **4** at 295 K: WN$_6$C$_{60}$H$_{60}$, $M_r = 1049.04$, space group $P2_1/c$ (No. 14), $a = 11.815(2)$ Å, $b = 18.915(5)$ Å, $c = 23.941(5)$ Å, $\beta = 90.39(2)°$, $V = 5350(3)$ Å^3, $d_{calcd} = 1.302$ g cm^{-3}, $Z = 4$. Of the 7376 unique reflections collected ($5.32 \leq 2\,\theta \leq 45.34°$) with Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å), the 4984 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield $R(F_o) = 0.033$ and $R_w(F_o) = 0.042$. Crystal data for **5**·2.5C$_6$H$_6$ at 203 K: WP$_2$O$_4$N$_2$C$_{94}$H$_{81}$, $M_r = 1548.50$, space group $P\bar{1}$ (No. 2), $a = 12.226(2)$ Å, $b = 15.372(3)$ Å, $c = 22.151(9)$ Å, $\alpha = 107.39(2)°$, $\beta = 92.91(2)°$, $\gamma = 103.46(2)°$, $V = 3831(4)$ Å^3, $d_{calcd} = 1.342$ g cm^{-3}, $Z = 2$. Of the 10 189 unique reflections collected ($5.52 \leq 2\theta \leq 45.34°$) with Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å), the 9446 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield $R(F_o) = 0.024$ and $R_W(F_o) = 0.034$.

S0276-7333(97)00239-2 CCC: $14.00

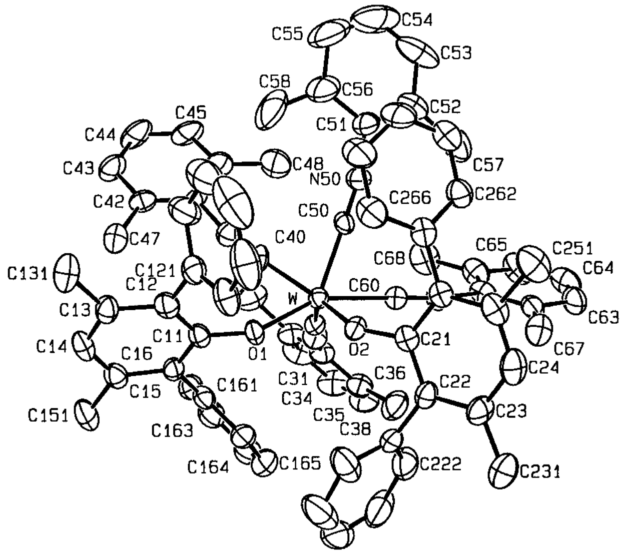
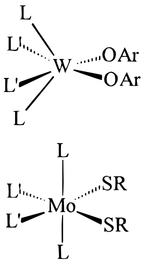


Figure 1. Molecular structure of **3** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (deg): W−O(1), 2.012(4); W−O(2), 2.005(5); W−C(30), 1.984(9); W−C(40), 2.018(8); W−C(50), 1.975(8); W−C(60), 2.067(8); O(1)−W−O(2), 77.0(2); C(30)−W−C(50), 104.9(3); C(40)−W−C(60), 120.3(3); O(1)−W−C(30), 107.1(2); O(1)−W−C(40), 83.4(2); O(1)−W−C(50), 132.3(2); O(1)−W−C(60), 153.4(3); O(2)−W−C(30), 132.5(3); O(2)−W−C(40), 152.6(2); O(2)−W−C(50), 105.4(2); O(2)−W−C(60), 83.8(2); W−O(1)−C(11), 142.9(4); W−O(2)−C(21), 142.9(4).

Chart 1



ArO-W-OAr = 77
L-W-L = 105
L'-W-L' = 120

RS-Mo-SR = 115
L-Mo-L = 174
L'-Mo-L' = 74

which are distorted away from octahedral geometry. Theoretical analysis by Hoffman et al. has accounted for many of these structures by focusing on the π-donor/acceptor properties of the ligation.[9] The structure adopted by **3** appears to be unprecedented. The structural parameters cannot be readily referenced to ideal octahedral geometry with the two phenoxides occupying half of the coordination sphere and the four isocyanides squeezed together on the other side of the molecule (Chart 1; L, L′ = isocyanide). The situation contrasts markedly with that reported for *cis*-[Mo(SBu^t)$_2$(CNBu^t)$_4$] (Chart 1).[10] The observed geometry may very well be controlled by the steric influence of the aryloxide ligands. It can be seen (Figure 1) that the *ortho* phenyl rings (conformationally locked by the *meta* methyl groups) appear to block out half of the coordination sphere. Attempts to generate **3** by reduction of **1** in the presence of xyNC led to formation of both **3** and the homoleptic isocyanide [W(CNxy)$_6$] (**4**), whose molecular structure (regular octahedral) is described in the Supporting Information.[11]

Treatment of **2** with phenyl isocyanate (PhNCO, >2 equiv) led to the rapid formation of a new product, **5**, that still contained an η^1-dppm ligand (^{31}P NMR) and a carbonyl group (infrared).[12] The molecular structure of **5** was determined by X-ray diffraction and is shown in Figure 2.[8] It can be seen that cleavage of an isocyanate C═N double bond has led to carbonyl and phenylimido ligands, while a second equivalent of isocyanate has inserted into one of the metal aryloxide bonds to produce an η^2(O,N)-bound carbamate group. The coordination sphere of the formally W(IV) metal center consists of a terminal aryloxide (*trans* to the imido ligand) and the η^1-dppm phosphorus atom (*cis* to the carbonyl). An analogous cleavage of the C═N bond of isocyanates by W(II) chlorides has been reported by Mayer et al.[1] Related future work will focus on the reactivity of molecules such as **2** toward CO and CO$_2$.

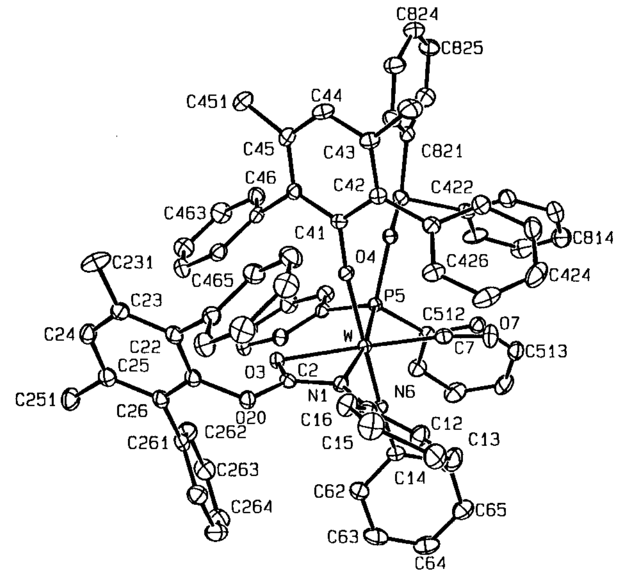


Figure 2. Molecular structure of **5** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (deg): W−P(5), 2.5029(5); W−O(3), 2.254(1); W−O(4), 1.985(1); W−N(1), 2.153(2); W−N(6), 1.768(2); W−C(7), 1.990(2); O(4)−W−N(1), 90.83(6); O(4)−W−N(6), 174.90(6); O(4)−W−C(7), 94.08(7); O(4)−W−O(3), 81.28(5); O(4)−W−P(5), 86.76(4); P(5)−W−C(7), 86.55(6); P(5)−W−O(3), 110.90(4); P(5)−W−N(1), 170.60(5); P(5)−W−N(6), 88.21(6); O(3)−W−C(7), 161.49(7); W−O(4)−C(41), 174.1(1); W−N(6)−C(61), 176.0(2); W−C(7)−O(7), 172.8(2).

Acknowledgment. We thank the National Science Foundation (Grant CHE-9321906) for financial support of this research.

Supporting Information Available: A figure giving an ORTEP view of **4** and text giving descriptions of the experimental procedures for X-ray diffraction studies and tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and multiplicities for **3**−**5** (54 pages). Ordering information is given on any current masthead page.

OM970239X

---

(9) Kubacek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

(10) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772.

(11) Selected data for [W(CNxy)$_6$]·C$_6$H$_6$ (**4**): Anal. Calcd for C$_{54}$H$_{54}$N$_6$W·C$_6$H$_6$: C, 68.70; H, 5.77; N, 7.98. Found: C, 67.81; H, 5.87; N, 7.34. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 7.09 (br s, 6H), 6.72 (br. s, 12H), 2.41 (s, 36H). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 179.9 (W−*C*Nxy, ^1J(W−C) = 122.9 Hz), 133.9, 131.7, 127.8, 124.9, 19.5. IR (Nujol mull): 1940 cm^{-1} (ν(CN)).

(12) Selected data for [W(CO)(NPh)(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)(η^1-dppm){η^2-OC(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)N(C$_6$H$_5$)}·2C$_6$H$_6$ (**5**): Anal. Calcd for C$_{79}$H$_{66}$N$_2$O$_4$P$_2$W·2C$_6$H$_6$): C, 72.42; H, 5.17; N, 1.86. Found: C, 71.80; H, 5.13; N, 1.67. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 6.0−8.0 (m, aromatics), 3.26 (broad doublet, Ph$_2$PC*H*$_2$PPh$_2$), 2.29, 2.14, 2.05, 1.87 (s, *meta* Me). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 248 (d very weak, *C*O), 120−165 (aromatics), 29 (broad multiplet, Ph$_2$P*C*H$_2$PPh$_2$), 21.9, 21.7, 21.0, 20.5 (*meta* Me). ^{31}P NMR (C$_6$D$_6$, 30 °C): δ 26.8 (br multiplet, W−*P*(Ph$_2$)CH$_2$PPh$_2$), −25.8 (br multiplet, W−P(Ph$_2$)CH$_2$*P*Ph$_2$). IR (Nujol mull): 1952 cm^{-1}, 1652 cm^{-1} (ν(CO)).