Reactivity of a tungsten(II) aryloxide with imines, ketones and aldehydes

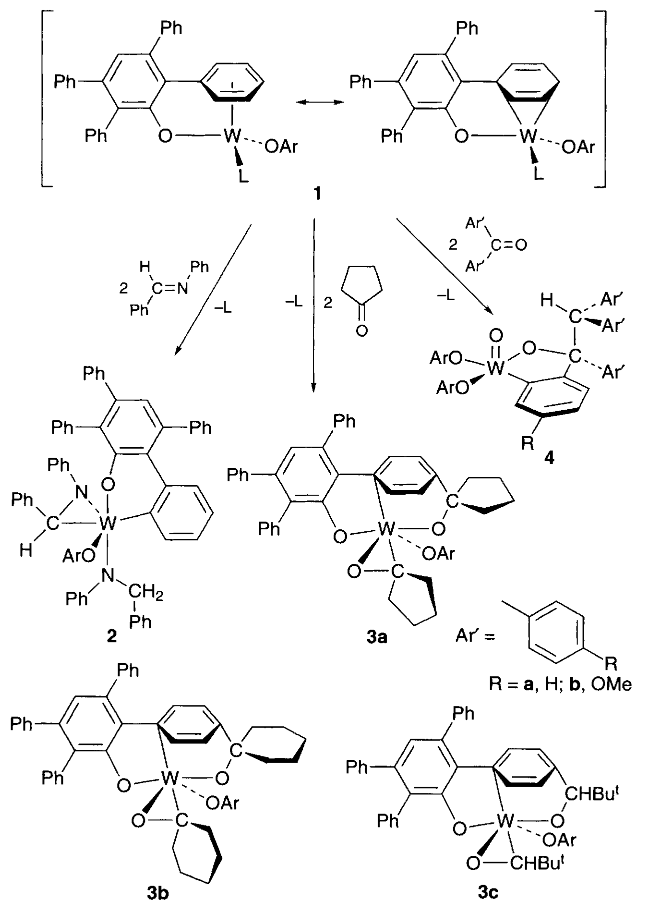
Mark A. Lockwood, Phillip E. Fanwick and Ian P. Rothwell*

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

The 16-electron complex [W(OC$_6$HPh$_3$-η^6-Ph)(OC$_6$HPh$_4$-2,3,5,6)(η^1-dppm)] reacts rapidly with imines, ketones and aldehydes to generate a variety of organometallic products.

We have recently demonstrated that the deep-green compound [W(OC$_6$HPh$_3$-η^6-Ph)(OC$_6$HPh$_4$-2,3,5,6)(L)] (OC$_6$HPh$_4$-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide, L = tertiary phosphine)[1] will carry out the four-electron reduction of dioxygen and azobenzene to produce the corresponding bis(oxo) and bis(phenylimido) derivatives.[2] This observation raises the possibility of converting **1** directly into Schrock type metathesis catalysts [(ArO)$_2$W(X)(=CR$_2$)] (X = NR',O)[3] by reaction with imino and keto substrates, a reaction established by Bryan and Mayer for mono-tungsten systems[4] and by Chisholm *et. al.* for ditungsten alkoxides.[5] We communicate here our initial investigation of reactions of this type.

Addition of PhCH=NPh to a suspension of the complex **1** (L = η^1-dppm) in C$_6$D$_6$ generates over minutes at 25 °C a dark orange mixture of free dppm (^{1}H, ^{31}P NMR) and a new organometallic product **2** (Scheme 1) which can be isolated as orange crystals upon dilution with hexane. The molecular structure of **2** was determined by single-crystal X-ray diffraction analysis (Fig. 1).† The geometry about the metal centre is best described as trigonal-bipyramidal with an η^2-imine (metalla–aziridine) ligand occupying an equatorial site. The two axial positions are occupied by the O-atom of a cyclometallated aryloxide ligand and the N-atom of a phenyl, benzyl amido ligand. The formation of **2** from **1** presumably occurs *via* cyclometallation of an aryloxide by a metalla–aziridine ligand generating the amido group, possibly within a bis(η^2-imine) species.



Scheme 1

The addition of either cyclopentanone, cyclohexanone or pivaldehyde (Bu^{t}CH=O) to C$_6$D$_6$ suspensions of **1** leads to dark orange solutions with many similar spectroscopic characteristics (see below). In the ^{1}H NMR spectrum of these products a large number of multiplets are present in the δ 3–7 region. Analysis of the molecular structure of the cyclopentanone product **3a** (Fig. 2) shows incorporation of two equivalents of ketone has occured in an unusual fashion. This product arises by insertion of one equivalent of ketone into a tungsten–carbon bond within a tungsta-norbornadiene resonance form that can be drawn for **1** (Scheme 1). The solid-state structure of **1** (L = PMePh$_2$) shows some distortion towards this form,[1] but not as dramatic as seen in some early d-block arene complexes.[6] The result of this insertion is to produce a 2,5-cyclohexadienyl ring which, besides being directly σ-bound to the metal at C-1, is also chelated *via* phenoxy and alkoxy linkages attached to C-1 and C-4. The second equivalent of cyclopentanone is η^2-bound to the metal centre.

Reaction of **1** with benzophenone in benzene solvent produces a suspension of a sparingly soluble orange product **4a**. The ^{1}H NMR spectrum of **4a** is very simple, consisting of a sharp singlet at δ 4.57 along with complex aromatic signals. Utilizing the substrate 4,4'-bis(methoxy)benzophenone was found to lead to an analogous product **4b** which, besides the presence of a singlet at δ 4.66, showed four non-equivalent

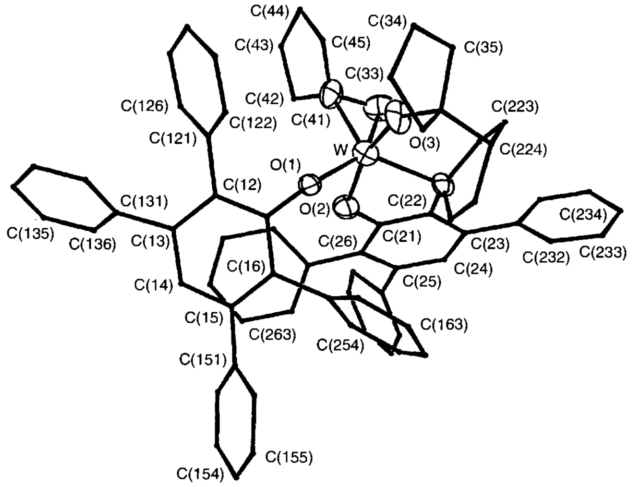


Fig. 1 Molecular structure of **2** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): W–O(1) 1.961(4), W–O(2) 1.922(4), W–N(30) 1.933(5), W–N(50) 1.971(5), W–C(40) 2.152(6), W–C(122) 2.119(6), N(30)–C(40) 1.429(8); O(1)–W–O(2) 82.0(2), O(1)–W–N(50) 164.4(2), O(1)–W–C(122) 81.6(2), W–O(1)–C(11) 130.6(4), W–O(2)–C(21) 166.0(4).

OMe signals in the ^{1}H NMR spectrum. Crystals of **4b** were obtained from benzene–hexane and the molecular structure is shown in Fig. 3. The compound can be seen to have incorporated two equivalents of ketone substrate (Scheme 1). The geometry about the tungsten atom is best described as square-pyramidal with the metal centre bound to an axial oxo group and two terminal aryloxide ligands. The remaining basal sites are occupied by the oxygen and carbon atoms of a metallacycle ring that is formally derived by metallation of an *o*-CH bond of a 1,1,2,2-tetraphenylethoxide ligand. Two possible pathways for the formation of **4** from **1** proceed *via* an intermediate 2,2,3,3-tetraphenyl oxametallacyclobutane which undergoes cyclometallation of a 3-phenyl substituent. The formation of this oxa-metallacyclobutane may occur either by C–O cleavage within a benzopinnacolate intermediate or *via* initial formation of an oxoalkylidene which adds the second equivalent of ketone.

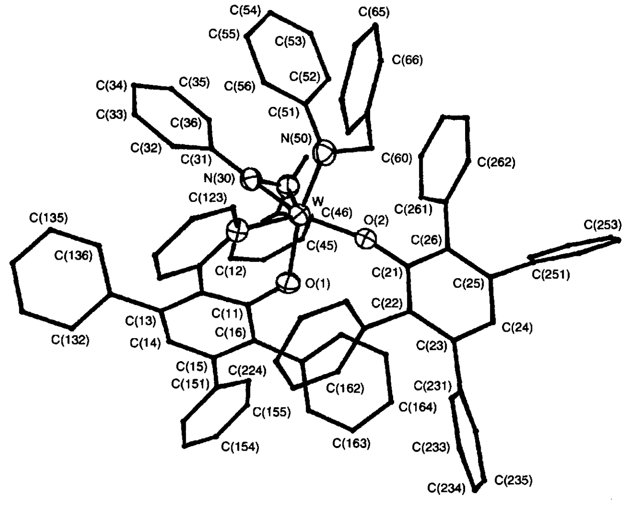


Fig. 2 Molecular structure of **3a** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): W–O(1) 1.942(9), W–O(2) 1.929(9), W–O(3) 1.819(9), W–O(4) 1.938(10), W–C(41) 2.07(2), W–C(221) 2.250(14), O(4)–C(41) 1.39(2), O(3)–C(31) 1.39(2); O(2)–W–O(3) 161.1(5), W–O(1)–C(11) 141.0(9), W–O(2)–C(21) 120.2(9), W–O(3)–C(31) 151.2(10).

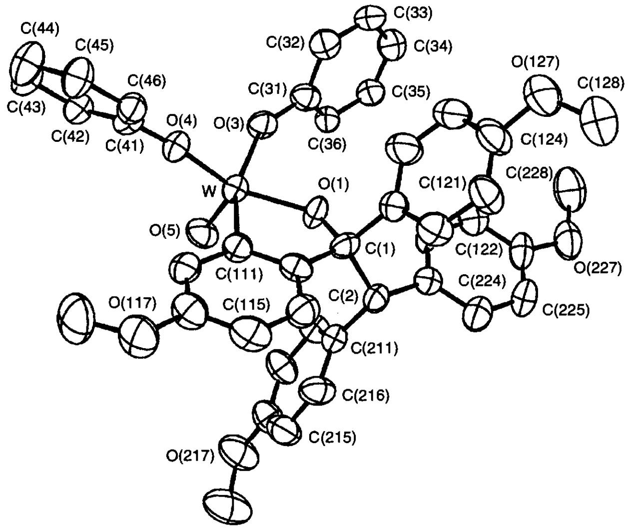


Fig. 3 Molecular structure of **4b** showing the atomic numbering scheme. The substituent phenyl rings attached to the tetraphenylphenoxide ligands have been removed for clarity. Selected bond lengths (Å) and angles (°): W–O(5) 1.691(5), W–O(3) 1.911(5), W–O(4) 1.845(4), W–O(1) 1.910(4), W–C(112) 2.143(7), O(5)–W–O(3) 107.7(2), O(5)–W–O(4) 107.1(2), O(5)–W–O(1) 108.2(2), O(5)–W–C(112) 98.0(3), W–O(3)–C(31) 149.4(5), W–O(4)–C(41) 172.4(4), W–O(1)–C(1) 128.1(4).

In order to more fully interrogate these reactions and to help with spectroscopic assignments we have reacted C_6D_6 solutions of **1** with the labelled substrates Ph^{13}CH$=$NPh, 1-^{13}C-cyclopentanone and Ph$_2$^{13}C$=$O, monitoring by ^{1}H and ^{13}C NMR spectroscopy. In the case of benzylideneaniline, two peaks assignable to **2**-$^{13}C_2$ were observed to rapidly build up at δ 59.2 [d, $^1J(^{13}C{-}^1H)$ 164.4, $^1J(^{13}C{-}^{183}W)$ 40.0 Hz] and δ 69.4 [t, $^1J(^{13}C{-}^1H)$ 140.0 Hz] in the ^{13}C NMR spectrum. These can be assigned to the η^2-PhCH$=$NPh and N(*C*H$_2$Ph)(Ph) carbon atoms respectively. The ^{1}H NMR spectrum of the pivaldehyde product **3c** shows a single set of well resolved resonances that were assigned using 2D COSY spectra. In the ^{1}H NMR spectrum of the cyclopentanone and cyclohexanone products **3a** and **3b** an isomeric mixture (60/40) appears to be present in solution. The addition of labelled cyclopentanone to **1** confirms this notion, showing two pairs of product signals at δ 105.0 [$^1J(^{13}C{-}^{183}W)$ 80.9 Hz], 107.7 (major isomer) and δ 115.9 [$^1J(^{13}C{-}^{183}W)$ 51.8 Hz], 103.1 (minor isomer). We assign the signals with well resolved ^{183}W satellites to the η^2-*c*-C$_4$H$_8$*C*$=$O carbon within each isomer of **3a**-$^{13}C_2$. One reasonable explanation for the presence of isomers is the adoption of two different conformations for the η^2-*c*-C$_4$H$_8$C$=$O cyclopentanone ligand. The addition of Ph$_2$^{13}C$=$O to **1** produces two signals at δ 66.4 [dd, $^1J(^{13}C{-}^1H)$ 122.2, $^1J(^{13}C{-}^{13}C)$ 34.5 Hz] and δ 106.3 [d, $^1J(^{13}C{-}^{13}C)$ 34.5, $^1J(^{13}C{-}^{183}W)$ 16.8 Hz] in the ^{13}C NMR spectrum. These can be assigned as the {O*C*(Ph)(η^1-C$_6$H$_4$)*C*HPh$_2$} carbon atoms (typical ^1J sp^3–sp^3 coupling constant) of **4a**-$^{13}C_2$ with the alkoxide carbon being to low field with resolved tungsten satellites. In the natural abundance spectrum of **4b** a peak at δ 222.4 can be assigned to the W–*C*(aryl) resonance.

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Footnote

† *Crystal data*: for **2**·0.5C$_6$H$_{14}$ at 295 K, $C_{89}H_{64}N_2O_2W$, M = 1384.42, space group $P\bar{1}$ (no. 2), a = 12.6198(15), b = 13.9301(15), c = 20.306(5) Å, α = 81.497(16), β = 88.136(15), γ = 73.063(9)°, U = 3377.1(13) Å^3, D_c = 1.361 g cm^{-3}, Z = 2. Of the 9052 unique reflections collected (5.16 < 2θ < 113.70°) with Cu-Kα (λ = 1.541 84 Å), the 5960 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield R = 0.038 and R_w = 0.044. For **3** at 295 K, $C_{70}H_{58}O_4W$, M = 1147.09, space group $P2_1/c$ (no. 14), a = 10.903(3), b = 22.732(7), c = 21.862(7) Å, β = 94.87(2)°, U = 5398(5) Å^3, D_c = 1.411 g cm^{-3}, Z = 4. Of the 7229 unique reflections collected (5.16 < 2θ < 113.70°) with Cu-Kα (λ = 1.541 84 Å), the 7229 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o)$ = 0.038 and $R_w(F_o^2)$ = 0.044. For **4b** at 296 K, $C_{90}H_{70}O_8W$, M = 1463.41, space group $P2_1/c$ (no. 14), a = 11.132(2), b = 20.5010(16), c = 31.555(4) Å, β = 97.192(13)°, U = 7144(3) Å^3, D_c = 1.360 g cm^{-3}, Z = 4. Of the 9611 unique reflections collected (5.46 < 2 θ < 112.16°) with Cu-Kα (λ = 1.541 84 Å), the 5002 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield R = 0.038 and R_w = 0.042. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/172.

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