

## Carbonyl Insertion and Reductive Elimination Chemistry of Tungsten(II) Alkoxides and Aryloxides

Brian P. Buffin, Atta M. Arif and Thomas G. Richmond\*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

Carbonyl insertion into the W–O bond in a series of novel W<sup>II</sup> alkoxides and aryloxides, containing a tridentate monoanionic [C,N,N'] ligand, results in the generation of alkoxy carbonyl- and aryloxy carbonyl-groups, which readily reductively eliminate to form new C–C bonds; in contrast, carbon dioxide insertion into the W–OMe alkoxide bond generates an  $\eta^1$ -carbonate ligand, which retains coordination to the metal centre.

The activation of small molecules by transition metal alkoxides has received renewed attention in recent years owing, in part, to their proposed role in several important homogeneous reactions including the catalytic carbonylation of methanol by tungsten hexacarbonyl/potassium methoxide<sup>1</sup> and the reduction of organic carbonyls.<sup>2</sup> Although the chemistry of group 6 metal alkoxides has been extensively studied in d<sup>6</sup> anionic complexes of [M(CO)<sub>5</sub>OR]<sup>−</sup>,<sup>3</sup> bimetallic d<sup>3</sup>–d<sup>3</sup> systems,<sup>4</sup> and higher oxidation state complexes,<sup>5</sup> little has been reported on d<sup>4</sup> M<sup>II</sup> alkoxides and aryloxides.<sup>6</sup> The stabilization of hard ligands such as fluoride by monoanionic [C,N,N'] chelating ligands at tungsten(II)<sup>7</sup> suggests that related metal alkoxides could be prepared.† In this work we report the synthesis and reactivity of a series of novel W<sup>II</sup> alkoxides and aryloxides, which are found to be stable to decomposition pathways such as  $\beta$ -hydrogen elimination and exhibit interesting insertion chemistry.

As shown in Scheme 1,‡ treatment of the tungsten(II) bromide **1**, which can be readily prepared by the room

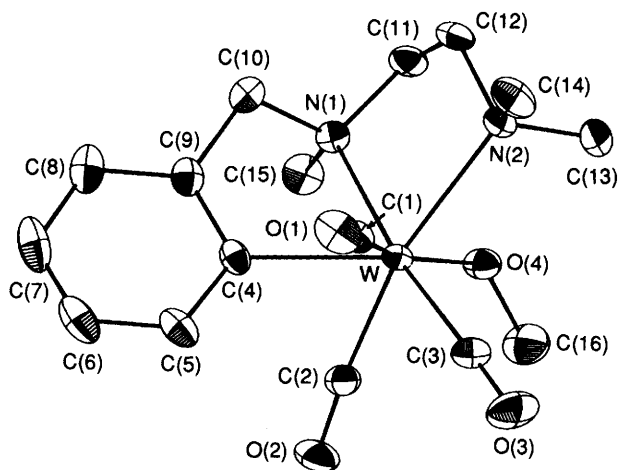
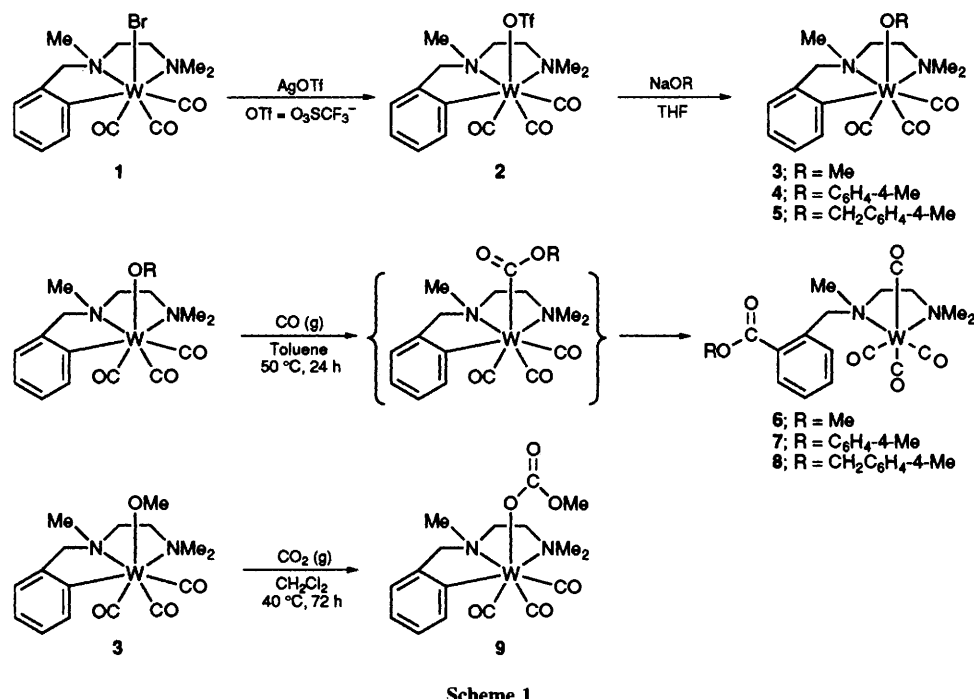
temperature oxidative addition reaction of the chelating arylbromide ligand with W(CO)<sub>5</sub>(EtCN)<sub>3</sub>,<sup>8</sup> with silver trifluoromethanesulfonate results in quantitative spectroscopic conversion to the tungsten(II) triflate **2**, which can be isolated as an air-stable yellow solid in 86% yield from CH<sub>2</sub>Cl<sub>2</sub>. The increase in IR carbonyl stretching frequencies upon halide exchange is indicative of the weak donor ability of the trifluoromethanesulfonate anion. Addition of sodium alkoxide or aryloxide salts to a tetrahydrofuran (THF) solution of **2** results in displacement of the labile triflate ligand and a quantitative spectroscopic conversion to the corresponding tungsten(II) alkoxides **3,5** and aryloxide **4**, which were isolated as air-stable, yellow solids in 70–84% yields. The methoxide complex **3** was further characterized by X-ray crystallography§ as illustrated in Fig. 1. The geometry about the seven-coordinate tungsten atom is best described as capped octahedral with the *ipso*-carbon C(4) of the phenyl ring capping the trigonal face comprised of N(1), C(1), and C(2). The bent methoxide ligand has a W–O(4)–C(16) bond angle of 125.6(5)° as expected with a W–O(4) distance of 2.033(5) Å, which is intermediary between that observed for the d<sup>6</sup> [W(CO)<sub>5</sub>OPh]<sup>−</sup> anion of 2.18(2) Å<sup>3a</sup> and that of the d<sup>2</sup>

† To our knowledge Group 6 d<sup>4</sup> complexes such as CpM(CO)<sub>3</sub>OR (where M = Cr, Mo, or W and R = Me, Et, or Ph) have yet to be prepared.

‡ All new compounds were characterized by IR, <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopic methods and satisfactory elemental analyses (C,H,N) were obtained. Selected spectroscopic data: **2**: IR  $\nu_{\text{CO}}$  2020m, 1931s, 1895m cm<sup>−1</sup>. **3**: IR  $\nu_{\text{CO}}$  1991m, 1895s, 1860m cm<sup>−1</sup>; <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  COs 227.0, *ipso*-C 150.8, OCH<sub>3</sub> 64.33. **6**: IR  $\nu_{\text{CO}}$  2007m, 1873s, 1863vs, 1837s, 1722w cm<sup>−1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  COs 213.3, 213.1, 206.2, 206.1, C(O)OMe 168.3, OCH<sub>3</sub> 52.65. **9**: IR  $\nu_{\text{CO}}$  2010m, 1917s, 1881m, 1694w, 1276w cm<sup>−1</sup>; <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  COs 224.9, *ipso*-C 147.0, OC(O)OMe 159.8, OCH<sub>3</sub> 53.94. All IR data obtained in THF.

§ Crystallographic data for **3** (C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>W): Monoclinic space group P2<sub>1</sub>/c, a = 13.568(3), b = 8.655(3), c = 15.746(3) Å,  $\beta$  = 105.90(2)°, V = 1778.3 Å<sup>3</sup>, and Z = 4 based on 2724 observations at 18°C (Mo-K $\alpha$ , 4° < 2 $\theta$  < 50°,  $\mu$  = 66.544 cm<sup>−1</sup>, empirical absorption correction applied) with I > 3 $\sigma$ (I) and 208 variables to yield R = 0.0259, R<sub>w</sub> = 0.0327, and GOF = 1.17.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 1** ORTEP representation of **3** illustrating the atom labelling scheme. Selected bond distances (Å) and angles (°): W–O(4) 2.033(5); W–N(1) 2.320(5); W–N(2) 2.404(5); W–C(4) 2.305(7); W–O(4)–C(16) 125.6(5); O(4)–W–N(1) 78.3(2); N(1)–W–C(4) 73.9(2); N(2)–W–C(4) 124.0(2); O(4)–W–C(1) 159.9(3); N(1)–W–C(3) 171.0(3); N(2)–W–C(2) 164.5(3).

$W(OCH_2-Bu^t)_4(py)(\eta^2-OCPh_2)$  complex in which the W–O bond distances average 1.92 Å.<sup>9</sup> Surprisingly, both of the tungsten(II) alkoxides **3** and **5** are stable in solution and fail to decompose by a  $\beta$ -elimination pathway even under conditions where CO dissociation is possible.

As illustrated in Scheme 1, placement of toluene solutions of **3**, **4** or **5** under an atmosphere of CO (g) and heating to ca. 50 °C affords the tungsten(0) tetracarbonyl complexes **6**, **7** or **8** in which an ester functional group has been placed on the aryl ring. Presumably CO insertion into the W–O bond results in the formation of putative tungsten(II) alkoxy-carbonyl- and aryloxy-carbonyl-complexes<sup>10</sup> (see Scheme 1), which then readily reductively eliminate to give the tungsten(0) com-

plexes in 50–64% yields.<sup>11</sup> The presence of the ester carbonyl is clearly evident in the solution IR spectra appearing as a weak absorbance at ca. 1730 cm<sup>-1</sup> for all three complexes, and a signal at ca.  $\delta$  167 in the <sup>13</sup>C{<sup>1</sup>H} NMR is also diagnostic for these ester carbonyls. In addition, a static spectrum is observed in the carbonyl region of the <sup>13</sup>C{<sup>1</sup>H} NMR as expected for these octahedral d<sup>6</sup> complexes in contrast to the seven-coordinate tungsten(II) compounds, which all exhibit fluxional behaviour on the NMR timescale at room temperature.

We have also examined the reactivity of **3** with carbon dioxide. As shown in Scheme 1, placement of a CH<sub>2</sub>Cl<sub>2</sub> solution of **3** under an atmosphere of CO<sub>2</sub> (g) and heating to 40 °C for ca. 72 h results in the formation of the tungsten(II)  $\eta^1$ -carbonate complex **9**, which can be isolated as an air-stable yellow solid in 24% yield from CH<sub>2</sub>Cl<sub>2</sub>/pentane.<sup>†</sup> As reported in other systems,<sup>12</sup> IR absorptions at 1694 and 1276 cm<sup>-1</sup> are indicative of an  $\eta^1$ -bound carbonate ligand when compared with the three band pattern which is observed for  $\eta^2$ -coordinated carbonates. In contrast to the alkoxy-carbonyl and aryloxy-carbonyl ligands in which a second carbon atom has been attached to the tungsten metal atom and reductive elimination of a C–C bond occurs, the  $\eta^1$ -carbonate ligand retains coordination to the metal centre. Regeneration of **3** when either a THF solution or a solid sample of **9** is placed under vacuum (with some heating necessary for the solution) demonstrates the reversible nature of this carbon dioxide insertion reaction.

Insertion of CO into W–O bonds results in the formation of new C–C bonds by reductive coupling with the carbon of the [C,N,N'] ligand. Isolation of the  $\eta^1$ -carbonate ligand from CO<sub>2</sub> insertion into the W–OMe bond suggests that CO also inserts into the alkoxide bond rather than the W-phenyl bond. The mechanism of these transformations is under further study.

<sup>†</sup> The low isolated yield of **9** is attributed to an as yet unidentified unstable red product which is formed during the reaction.

We acknowledge the support of this work by the National Science Foundation through a PYI award to T. G. R. (CHE-895845) and through funds for the X-ray diffractometer (CHE-8811363). T. G. R. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1991–1993).

Received, 10th May 1993; Com. 3/02652C

## References

- 1 D. J. Darensbourg, R. L. Gray and C. Ovalles, *J. Mol. Catal.*, 1987, **41**, 329.
- 2 P. L. Gaus, S. C. Kao, K. Youngdahl and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1985, **107**, 2428.
- 3 (a) D. J. Darensbourg, K. M. Sanchez, J. H. Reibenspies and A. L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 7094; (b) D. J. Darensbourg, B. L. Mueller, J. H. Reibenspies and C. J. Bischoff, *Inorg. Chem.*, 1990, **29**, 1789; (c) D. J. Darensbourg, B. L. Mueller, C. J. Bischoff, S. S. Chojnacki and J. H. Reibenspies, *Inorg. Chem.*, 1991, **30**, 2418. For d<sup>6</sup> Re<sup>I</sup> alkoxides see: R. D. Simpson and R. G. Bergman, *Organometallics*, 1993, **12**, 781; S. K. Mandal, D. M. Ho and M. Orchin, *Organometallics*, 1993, **12**, 1714.
- 4 M. H. Chisholm, *Acc. Chem. Res.*, 1990, **23**, 419; M. H. Chisholm, *J. Organomet. Chem.*, 1990, **400**, 235; M. H. Chisholm, C. E. Hammond, V. J. Johnston, W. E. Streib and J. C. Huffman, *J. Am. Chem. Soc.*, 1992, **114**, 7056. The chemistry of dimeric Mo compounds with bridging thiolate ligands has also been extensively studied by M. R. DuBois. See: M. R. DuBois, *Chem. Rev.*, 1989, **89**, 1.
- 5 R. R. Schrock, *Acc. Chem. Res.*, 1990, **23**, 158; P. A. van der Schaaf, R. A. T. M. Abbenhuis, D. M. Grove, W. J. J. Smeets, A. L. Spek and G. van Koten, *J. Chem. Soc., Chem. Commun.*, 1993, 504.
- 6 The air-sensitive d<sup>4</sup> complex Mo(O-Bu<sup>t</sup>)<sub>2</sub>(CO)<sub>2</sub>(py)<sub>2</sub> has been crystallographically characterized: M. H. Chisholm, J. C. Huffman and R. L. Kelly, *J. Am. Chem. Soc.*, 1979, **101**, 7615. Reviews: R. C. Mehrotra, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 269; H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163.
- 7 T. G. Richmond, C. E. Osterberg and A. M. Arif, *J. Am. Chem. Soc.*, 1987, **109**, 8091; C. E. Osterberg, M. A. King, A. M. Arif and T. G. Richmond, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 888; T. G. Richmond, *Coord. Chem. Rev.*, 1990, **105**, 221; B. Lucht, M. J. Poss, M. A. King and T. G. Richmond, *J. Chem. Soc., Chem. Commun.*, 1991, 400.
- 8 B. P. Buffin, M. J. Poss, A. M. Arif and T. G. Richmond, *Inorg. Chem.*, 1993, **32**, in the press.
- 9 M. H. Chisholm, K. Foltling and J. A. Klang, *Organometallics*, 1990, **9**, 607.
- 10 Carbonyl insertion into M-O bonds to form stable alkoxycarbonyl complexes has been reported in several metal systems. See: G. D. Smith, B. E. Hanson, J. S. Merola and F. J. Waller, *Organometallics*, 1993, **12**, 568; W. M. Rees, M. R. Churchill, J. C. Fettinger and J. D. Atwood, *Organometallics*, 1985, **4**, 2179; H. E. Bryndza, *Organometallics*, 1985, **4**, 1686.
- 11 An intramolecular metalloester in which Cp is bound to W and no reductive elimination of the ester occurs has been reported: T. S. Coolbaugh, B. D. Santarsiero and R. H. Grubbs, *J. Am. Chem. Soc.*, 1984, **106**, 6310.
- 12 WH(η<sup>1</sup>-OCO<sub>2</sub>Me)(CO)(dppe)<sub>2</sub> has been prepared recently: IR (Nujol mull) ν/cm<sup>-1</sup> 1790 (CO), 1671 and 1293 (OCO<sub>2</sub>). T. Ishida, T. Hayashi, Y. Mizobe and M. Hidai, *Inorg. Chem.*, 1992, **31**, 4481.