J. Chem. Research (S), 1998, 379
J. Chem. Research (M), 1998, 1461–1482

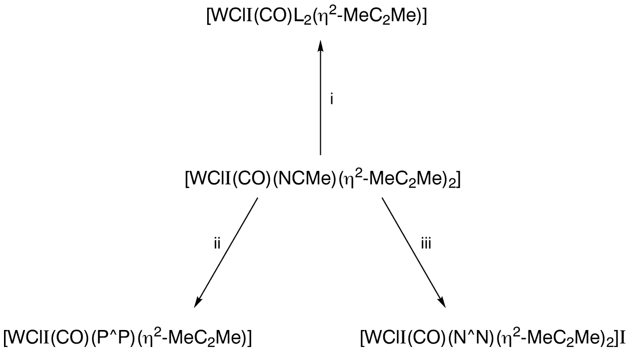
Seven-coordinate and Alkyne Complexes of Tungsten(II) containing both Chloride and Iodide Ligands. Crystal Structure of $[WCl(CO)(2,2'\text{-bipy})(\eta^2\text{-MeC}_2\text{Me})_2]I$

Paul K. Baker,*[a] Michael G. B. Drew,[b] Margaret M. Meehan,[a] Hitesh K. Patel[a] and Alison White[a]

[a]*Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b]*Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*

Reaction of $[WClI(CO)(NCMe)(\eta^2\text{-MeC}_2\text{Me})_2]$ with an equimolar amount of 2,2′-bipy gives the crystallographically characterised iodide displaced product $[WCl(CO)(2,2'\text{-bipy})(\eta^2\text{-MeC}_2\text{Me})_2]I$, which proves definitively that iodide is displaced in preference to chloride for the first time in these mixed halide complexes.

Reaction of *fac*-$[W(CO)_3(NCMe)_3]$ (prepared *in situ*)[15] with an equimolar amount of ICl gives the seven-coordinate complex $[WClI(CO)_3(NCMe)_2]$ (**1**) in high yield. Equimolar quantities of **1** and PhC_2Ph react in CH_2Cl_2 at room temperature to eventually give the dimeric complex $[\{W(\mu\text{-I})Cl(CO)(NCMe)(\eta^2\text{-PhC}_2\text{Ph})\}_2]$ (**2**),[11] whereas reaction of **1** with two equivalents of RC_2R (R = Me and Ph) in CH_2Cl_2 at room temperature yields the bis(alkyne) complexes $[WClI(CO)(NCMe)(\eta^2\text{-RC}_2\text{R})_2]$ (**3** and **4**).[12] The reactions of **3** (R = Me) are shown in the Scheme.



Scheme *Reagents*: i, 2L (L = PPh_3, PPh_2Cy); ii, P^P $\{P^\wedge P = Ph_2P(CH_2)_nPPh_2\}$ (*n* = 1–6); iii, N^N (N^N = 2,2′-bipy, 1.10-phen, CyN=CHCH=NCy)

The most important reaction described in the full paper is between equimolar quantities of **3** and 2,2′-bipy to give the crystallographically characterised complex $[WCl(CO)(2,2'\text{-bipy})(\eta^2\text{-MeC}_2\text{Me})_2]I$ (**13**).[25] The structure of **13** is shown in Fig. 5, together with the atom numbering scheme. This structure shows for the first time that iodide is displaced in preference to chloride in mixed halide carbonyl complexes of tungsten(II).

Techniques used: Elemental analysis, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy, X-ray crystallography

Appendix: Crystal data for **13**

References: 30

Table 1: Physical, analytical and IR data for complexes **1**–**15**

Table 2: Proton NMR data for complexes **1**–**15**

Table 3: Bond lengths and angles in the atomic coordination sphere of **13**

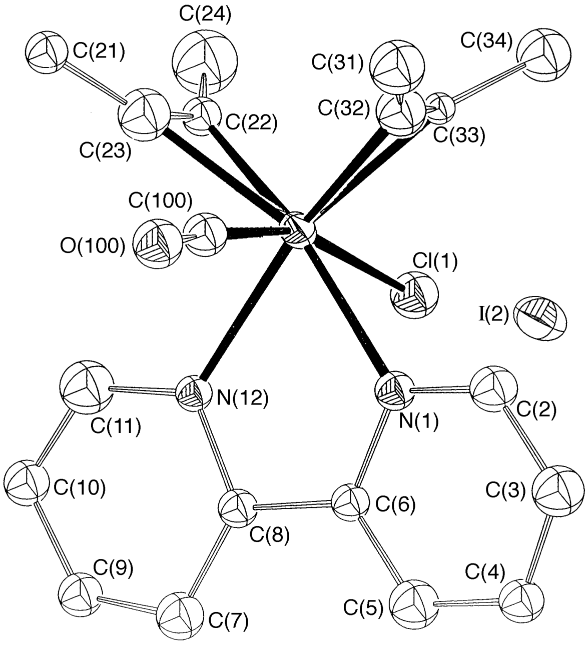


Fig. 5 Structure of $[WCl(CO)(2,2'\text{-bipy})(\eta^2\text{-MeC}_2\text{Me})_2]I$ (**13**). Thermal ellipsoids are drawn at 30% probability

Table 4: Crystal data and structure refinement for **13**

Figure 1: Proposed structure of **1**

Figure 2: Proposed structure of **3** and **4**

Figure 3: Proposed structure of **5** and **6**

Figure 4: Proposed structure of **9**

Received, 6th February 1998; Accepted, 17th March 1998
Paper E/8/01074I

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*To receive any correspondence (*e-mail:* chs018@bangor.ac.uk).