Dalton Communications

The Synthesis of the First Examples of Water-soluble Seven-co-ordinate Complexes of Tungsten(II)

Paul K. Baker,*[a] **Alyn E. Jenkins,**[a] **Aidan J. Lavery,***[b] **David J. Muldoon**[a] **and Andrew Shawcross**[b]
[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b] *ZENECA Specialities, PO Box 42, Hexagon House, Blackley, Manchester M9 3DA, UK*

Reaction of the seven-co-ordinate complex $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of $4\text{-}HO_2CC_5H_4N$ in methanol at room temperature gave the bis(pyridine-4-carboxylic acid) complex $[WI_2(CO)_3(4\text{-}HO_2CC_5H_4N)_2]$ **1** in good yield, which, upon treatment with two equivalents of NaOH in ethanol, afforded the completely water-soluble complex $[WI_2(CO)_3(4\text{-}NaO_2CC_5H_4N)_2]$ **2** in good yield; reaction of the latter with an equimolar amount of $3\text{-}NaO_3SC_5H_4N$ yielded $[WI_2(CO)_3(4\text{-}NaO_2CC_5H_4N)(3\text{-}NaO_3SC_5H_4N)]$, which represents the first room-temperature ligand-substitution reaction in water of a metal carbonyl complex.

Since the report in 1958 by Chatt and co-workers[1] of the first water-soluble phosphine, namely sodium 3-(diphenylphosphino)benzenesulfonate, the importance of such compounds and their transition-metal complexes has become very important in catalytic processes.[2,3] Although a number of water-soluble organotransition-metal complexes have been prepared,[4] very few molybdenum and tungsten complexes have been described. In 1991, Darensbourg *et al.*[5] reported the preparation and characterisation of the zero-valent tungsten complex $[W(CO)_5\{P(C_6H_4SO_3Na\text{-}3)_3\}]$. In 1993,[6] they extended this work to the molybdenum analogue $[Mo(CO)_5\{P(C_6H_4SO_3Na\text{-}3)_3\}]$ and the water-soluble bis(ligand) complexes *cis*-$[M(CO)_4\{P(C_6H_4SO_3Na\text{-}3)_3\}_2]$ (M = Mo or W). Owing to the difficulties in preparing these water-soluble phosphines,[4] we considered the possibility that the easily prepared sodium salts of pyridine-4-carboxylate ($4\text{-}NaO_2CC_5H_4N$) and pyridine-3-sulfonate ($3\text{-}NaO_3SC_5H_4N$) when co-ordinated to an organotransition-metal centre might induce water solubility in these complexes. The only ligand of this type to have been previously used to prepare water-soluble metal carbonyl complexes is sodium 2-(2′-pyridyl)pyridine-5-sulfonate described by Herrmann and co-workers.[7,8] In this communication we describe the synthesis of the first examples of completely water-soluble seven-co-ordinate complexes, $[WI_2(CO)_3(4\text{-}NaO_2CC_5H_4N)_2]$ and $[WI_2(CO)_3(4\text{-}NaO_2CC_5H_4N)(3\text{-}NaO_3SC_5H_4N)]$.

The starting material $[WI_2(CO)_3(NCMe)_2]$ was prepared by treating the zero-valent complex *fac*-$[W(CO)_3(NCMe)_3]$ (prepared *in situ*) with an equimolar amount of I_2 at 0 °C.[9] Reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of $4\text{-}HO_2CC_5H_4N$ in methanol at room temperature gave the seven-co-ordinate complex $[WI_2(CO)_3(4\text{-}HO_2CC_5H_4N)_2]$ **1** in 39% yield.† Complex **1** is soluble in acetone and dimethyl sulfoxide, but only sparingly soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. The complex was also only slightly soluble in water, however upon addition of alkali to the aqueous solution complex **2** was generated and observed to be completely soluble at a pH > 7.

In order to increase the water solubility of **1**, the complex was suspended in ethanol and two equivalents of NaOH were added to afford the completely water-soluble complex $[WI_2(CO)_3(4\text{-}NaO_2CC_5H_4N)_2]$ **2** in 61% yield.‡ This complex is the first example of a completely water-soluble seven-co-ordinate complex of tungsten(II). It has as expected three $\nu(C\equiv O)$ bands (KBr disc) at 2064, 2009 and 1920 cm^{-1}, and a band due to the carboxy group at 1730 cm^{-1}. The ^1H NMR spectrum (25 °C, D_2O) showed the expected two doublets at δ 8.77 and 8.12 for the pyridine protons. In view of these observations a weak acid (complex **1**)–strong base (NaOH) titration was carried out, and a typical plot was obtained by monitoring the pH change on addition of NaOH.

The reaction of complex **2** with one equivalent of $3\text{-}NaO_3SC_5H_4N$ in water at room temperature gave the pale green ligand-exchanged complex $[WI_2(CO)_3(4\text{-}NaO_2CC_5H_4N)(3\text{-}NaO_3SC_5H_4N)]$ **3** in 85% yield.§ We believe this to be the first example of a room-temperature ligand-substitution reaction of a metal carbonyl derivative carried out in water. Complex **3** is completely soluble in water, and reasonably air-stable in solution and in the solid state. Many unsuccessful attempts have been made to grow single crystals for X-ray structural studies of complexes **1**–**3**, however, since the majority of seven-co-ordinate complexes of the type $[MX_2(CO)_3L_2]$ have capped-octahedral geometries,[10,11] it is likely that these complexes have similar configurations.

We are currently exploring the wider applicability of the easily prepared water-soluble ligands $4\text{-}NaO_2CC_5H_4N$, 3-

---

† Complex **1** (Found: C, 23.1; H, 1.7; N, 3.6. $C_{15}H_{10}I_2N_2O_7W$ requires C, 23.4; H, 1.3; N, 3.6%). IR (KBr): $\nu(C\equiv O)$ 2069s, 2006s, 1910s; $\nu(C{=}O)$ 1733s cm^{-1}. ^1H NMR [25 °C, $(CD_3)_2CO$]: δ 9.32 (d, J = 8.33, 4 H, C_5H_4N), 8.13 (d, J = 6.67 Hz, 4 H, C_5H_4N), 5.75 (s, 2 H, CO_2H).

‡ Complex **2** (Found: C, 21.9; H, 1.5; N, 3.4. $C_{15}H_8I_2N_2Na_2O_7W$ requires C, 22.1; H, 1.0; N, 3.4%). IR (KBr): $\nu(C\equiv O)$ 2064s, 2009m, 1920s (br); $\nu(C{=}O)$ 1730s (br) cm^{-1}. ^1H NMR (25 °C, D_2O): δ, 8.77 (d, J = 4.61, 4 H, C_5H_4N), 8.12 (d, J = 5.00 Hz, 4 H, C_5H_4N).

§ Complex **3** (Found: C, 19.2; H, 1.2; N, 3.3. $C_{14}H_8I_2N_2Na_2O_8SW$ requires C, 19.8; H, 1.0; N, 3.3%). IR (KBr): $\nu(C\equiv O)$ 2066m, 1922s, 1894s; $\nu(C{=}O)$ 1718s; $\nu(S{=}O)$ 1229 cm^{-1}. ^1H NMR (25 °C, D_2O): δ 8.76 (br m, 4 H, $4\text{-}NaO_2CC_5H_4N$, $4\text{-}NaO_3SC_5H_4N$), 8.11 (s, 2 H, $4\text{-}NaO_2CC_5H_4N$), 7.83 (d, J = 5.00 Hz, 2 H, $4\text{-}NaO_3SC_5H_4N$).

$NaO_2CC_5H_4N$ and 3-$NaO_3SC_5H_4N$ for attachment to other transition-metal centres and the potential catalytic activity of these complexes.

Acknowledgements

D. J. M. thanks ZENECA Specialities and the SERC for a CASE Studentship.

References

1 S. Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.*, 1958, 264.
2 E. G. Kuntz, *Chemtech.*, 1987, **17**, 570.
3 A. F. Borowski, D. J. Cole-Hamilton and G. Wilkinson, *New J. Chem.*, 1978, **2**, 137.
4 M. Barton and J. D. Atwood, *J. Coord. Chem.*, 1991, **24**, 43 and refs. therein.
5 D. J. Darensbourg, C. J. Bischoff and J. H. Reibenspies, *Inorg. Chem.*, 1991, **30**, 1144.
6 D. J. Darensbourg and C. J. Bischoff, *Inorg. Chem.*, 1993, **32**, 47.
7 W. A. Herrmann, W. R. Thiel and J. G. Kuchler, *Chem. Ber.*, 1990, **123**, 1953.
8 W. A. Herrmann, W. R. Thiel, J. G. Kuchler, J. Behm and E. Herdtweck, *Chem. Ber.*, 1990, **123**, 1963.
9 P. K. Baker, S. G. Fraser and E. M. Keys, *J. Organomet. Chem.*, 1986, **309**, 319.
10 M. G. B. Drew, *Prog. Inorg. Chem.*, 1977, **23**, 67, and refs. therein.
11 C. W. Haigh and P. K. Baker, *Polyhedron*, 1994, **13**, 417, and refs. therein.

Received 21*st February* 1995; *Communication* 5/01040C