

Preliminary communication

THE REACTIONS OF $[MI_2(CO)_3(NCMe)_2]$ (M = Mo AND W)

I. THE PREPARATION OF BIS-PHOSPHITEDIIODOTRICARBONYL COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

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Summary

The phosphites, $P(OMe)_3$ and $P(OPh)_3$ react with $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) to afford the new seven-coordinate complexes $[MI_2(CO)_3\{P(OR)_3\}_2]$. The tungsten complex $[WI_2(CO)_3\{P(OMe)_3\}_2]$ loses carbon monoxide on refluxing in chloroform to afford the "16-electron" compound $[WI_2(CO)_2\{P(OMe)_3\}_2]$.

Although a wide range of bis-phosphine complexes of the type $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl, Br and I; L = phosphines) [1] are known, no examples of the simple seven-coordinate bis-phosphite complexes have hitherto been reported. Reaction of the halide bridged dimer $[Mo(\mu-Cl)Cl(CO)_4]_2$ with $P(OMe)_3$ gave the unexpectedly complicated product $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^{n+}$ $[Mo\{O(P(OMe)_2)Cl_4(O)\}]^{n-}$ [2], whereas reaction of the halide-bridged dimer with phosphines invariably affords the seven-coordinate bis-phosphine compounds $[MX_2(CO)_3L_2]$ [1]. We now wish to report the synthesis of the new complexes $[MI_2(CO)_3\{P(OR)_3\}_2]$ (M = Mo and W; R = Me and Ph), and preliminary studies of their reactivity.

Two molar equivalents of $P(OR)_3$ (R = Me and Ph) react with $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) [3] in CH_2Cl_2 to give the yellow crystalline compounds $[MI_2(CO)_3\{P(OR)_3\}_2]$ in high yield via displacement of acetonitrile ligands. The phosphite complexes are stable in the solid state when stored under argon and have been fully characterised by elemental analysis (C, H and N) and by IR, and 1H NMR spectroscopy (Table 1).

In view of the X-ray crystal structures of seven-coordinate bis-phosphine complexes $[MX_2(CO)_3L_2]$ [4], all of which have capped octahedral geometry,

TABLE 1

IR AND ^1H NMR DATA FOR $[\text{Ml}_2(\text{CO})_3\{\text{P}(\text{OR})_3\}_2]$

M	R	$\nu(\text{CO}) (\text{cm}^{-1})^a$	^1H NMR b (δ (ppm))
Mo	Me	1995(s), 1968(s) and 1903(s)	3.84 (d, $J(^{31}\text{P}-^1\text{H})$ 5.86 Hz)
W	Me	1981(s), 1960(s) and 1888(s)	3.85 (d, $J(^{31}\text{P}-^1\text{H})$ 4.1 Hz)
Mo	Ph	2044(m), 1976(s) and 1920(s)	7.27 (o-H) 7.18 (m-H) 7.02 (p-H)
W	Ph	2051(m), 1978(s) and 1928(s)	7.27 (o-H) 7.19 (m-H) 7.04 (p-H)

a Spectra recorded in CHCl_3 , m, medium; s, strong. b Spectra recorded in CDCl_3 (+25°C) and referenced to SiMe_4 .

it is likely that the bis-phosphite compounds have a similar geometry since their spectral properties closely resemble those of the bis-phosphine complexes.

The chemistry of $[\text{Ml}_2(\text{CO})_3\{\text{P}(\text{OR})_3\}_2]$ is dominated by loss of carbon monoxide. For example, refluxing the tungsten complex $[\text{Wl}_2(\text{CO})_3\{\text{P}(\text{OME})_3\}_2]$ in chloroform for several hours affords the bright blue "16-electron" compound $[\text{Wl}_2(\text{CO})_2\{\text{P}(\text{OME})_3\}_2]$, analogous to the phosphine complexes $[\text{MX}_2(\text{CO})_2\text{L}_2]$ (M = Mo and W; X = Cl, Br and I; L = PPh_3 and PET_3) which have been reported [5]. We are currently investigating the catalytic activity of these $[\text{Ml}_2(\text{CO})_3\{\text{P}(\text{OR})_3\}_2]$ complexes since the phosphine compounds $[\text{MX}_2(\text{CO})_3\text{L}_2]$ (M = Mo and W; X = Cl and Br; L = PPh_3 and AsPh_3) have recently been discovered to be catalysts in the ring opening polymerisation of norbornene [6].

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References

- (a) A.D. Westland and N. Muriithi, *Inorg. Chem.*, **12** (1973) 2356; (b) R. Colton and C.J. Rix, *Aust. J. Chem.*, **22** (1969) 305; (c) J. Lewis and R. Whyman, *J. Chem. Soc. A*, (1967) 77; (d) W.S. Tsang, D.W. Meek and A. Wojcicki, *Inorg. Chem.*, **7** (1968) 1263; (e) J.A. Bowden and R. Colton, *Aust. J. Chem.*, **22** (1969) 905; (f) R. Colton, G.P. Scollary and I.B. Tomkins, *Aust. J. Chem.*, **21** (1968) 15; (g) R. Colton and I.B. Tomkins, *Aust. J. Chem.*, **19** (1966) 1143; (h) R. Colton and G.P. Scollary, *Aust. J. Chem.*, **21** (1968) 1435; (i) J.R. Moss and B.L. Shaw, *J. Chem. Soc. A*, (1970) 595; (j) F.A. Cotton and B.F.G. Johnson, *Inorg. Chem.*, **3** (1964) 1609; (k) B.F.G. Johnson, *J. Chem. Soc. A*, (1967) 475; (l) R. Colton, *Coord. Chem. Rev.*, **6** (1971) 269.
- M.G.B. Drew and J.D. Wilkins, *J. Chem. Soc., Dalton Trans.*, (1975) 1984.
- P.K. Baker, S.G. Fraser, and E.M. Keys, *J. Organomet. Chem.*, to be submitted.
- (a) A. Mawby and G.E. Pringle, *J. Inorg. Nucl. Chem.*, **34** (1972) 517; (b) M.G.B. Drew, *J. Chem. Soc. Dalton*, (1972) 1329; (c) M.G.B. Drew and J.D. Wilkins, *ibid.*, (1973) 2664; (d) M.G.B. Drew, *ibid.*, (1972) 626; (e) (1975) 1984; (f) M.G.B. Drew, I.B. Tomkins and R. Colton, *Aust. J. Chem.*, **23** (1970) 2517; (g) G. Schmid, R. Boese and E. Weiz, *Chem. Ber.*, **108** (1975) 260; R. Boese and U. Müller, *Acta Crystallogr.*, **B 32** (1976) 582; (h) M.G.B. Drew and J.D. Wilkins, *J. Chem. Soc. Dalton Trans.*, (1977) 557; (i) M.G.B. Drew, A.P. Wolter and I.B. Tomkins, *ibid.*, (1977) 974; (j) M.G.B. Drew and J.D. Wilkins, *ibid.*, (1977) 194; (k) J.C. Dewan, K. Henrick, D.L. Kepert, K.R. Trigwell, A.H. White, and S.B. Wild, *ibid.*, (1975) 546.
- (a) R. Colton and I.B. Tomkins, *Aust. J. Chem.*, **19** (1966) 1143; (b) 19 (1966) 1519; (c) M.W. Anker, R. Colton, and I.B. Tomkins, *ibid.*, **20** (1967) 9. (d) R. Colton and C.J. Rix, *ibid.*, **22** (1969) 305; (e) J.R. Moss and B.L. Shaw, *J. Chem. Soc. A*, (1970) 595.
- (a) L. Bencze and A. Kraut-Vass, *J. Mol. Catal.*, **28** (1985) 369; (b) L. Bencze, A. Kraut-Vass, and L. Prokai, *J. Chem. Soc., Chem. Commun.*, (1985) 911.