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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 $[Mo(\mu\text{-}Cl)Cl(CO)_4]_2$ 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,

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TABLE 1

IR AND ^{1}H NMR DATA FOR [$MI_2(CO)_3\{P(OR)_3\}_2$]

M	R	ν(CO) (cm^{-1}) [a]	^{1}H NMR [b] (δ (ppm))
Mo	Me	1995(s), 1968(s) and 1903(s)	3.84 (d, $J(^{31}P—^1H)$ 5.86 Hz)
W	Me	1981(s), 1960(s) and 1888(s)	3.85 (d, $J(^{31}P—^1H)$ 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 [$MI_2(CO)_3\{P(OR)_3\}_2$] is dominated by loss of carbon monoxide. For example, refluxing the tungsten complex [$WI_2(CO)_3\{P(OMe)_3\}_2$] in chloroform for several hours affords the bright blue "16-electron" compound [$WI_2(CO)_2\{P(OMe)_3\}_2$], analogous to the phosphine complexes [$MX_2(CO)_2L_2$] (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 [$MI_2(CO)_3\{P(OR)_3\}_2$] complexes since the phosphine compounds [$MX_2(CO)_3L_2$] (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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