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SYNTHESIS, SPECTRAL PROPERTIES AND REACTIONS OF THE NOVEL ACETONITRILE DIIODOTRICARBONYLTRIPHENYL PHOSPHINE, ARSINE AND ANTIMONY COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

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Abstract—The bisacetonitrile complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with L (L = PPh_3, $AsPh_3$ or $SbPh_3$) to give the novel compounds $[MI_2(CO)_3(NCMe)L]$, which undergo acetonitrile displacement reactions to afford a variety of new mixed complexes.

The complexes $[MX_2(CO)_3L_2]$ (M = Mo or W, L = PPh_3 or $AsPh_3$, X = Cl or Br) are currently under investigation as catalysts for the ring-opening polymerization of norbornene,[1,2] and it is proposed that it is the ease of phosphine or arsine dissociation in these complexes which is the rate-determining step in the mechanism. Although a wide variety of bisphosphine complexes of the type $[MX_2(CO)_3L_2]$ (L = phosphine) have been prepared,[3] until now no mixed seven-coordinate complexes of this type have been reported with a labile ligand such as acetonitrile attached to the metal which should enhance the catalytic activity of these complexes in view of the work of Bencze *et al.*[1,2] In this communication the synthesis of the new mixed compounds $[MI_2(CO)_3(NCMe)L]$ (M = Mo or W; L = PPh_3, $AsPh_3$ or $SbPh_3$) and preliminary studies of their reactivity are reported.

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$,[4] and L (L = PPh_3, $AsPh_3$ or $SbPh_3$) react in CH_2Cl_2 to afford high yields of the crystalline compounds $[MI_2(CO)_3(NCMe)L]$, which have been fully characterized by elemental analysis (C, H and N) and IR spectroscopy (Table 1) and ^1H NMR spectroscopy.† All the complexes are stable in the solid state when stored under argon, but decompose rapidly in solution when exposed to air. Several X-ray crystal structures of the known seven-coordinate bisphosphine compounds $[MX_2(CO)_3L_2]$ have been carried out,[5–16] all having capped octahedral geometry. Since the spectral properties of $[MI_2(CO)_3(NCMe)L]$ closely resemble those of the analogous bisphosphine compounds it is likely that they will have a similar geometry.

It is interesting to note that $[MoI_2(CO)_3(NCMe)_2]$ reacts with $SbPh_3$ to initially afford $[MoI_2(CO)_3(NCMe)(SbPh_3)]$, which rapidly loses acetonitrile to afford the iodide-bridged dimer $[Mo(\mu\text{-}I)I(CO)_3(SbPh_3)]_2$, whereas the other complexes $[MI_2(CO)_3(NCMe)L]$ are fairly stable to loss of acetonitrile. We are currently investigating the electronic and steric effects of different phosphine and phosphite ligands on the rate of dimerization of the complexes $[MI_2(CO)_3(NCMe)L]$ (L = phosphine or phosphite). The chemistry of these complexes is dominated by acetonitrile displacement (Scheme 1).

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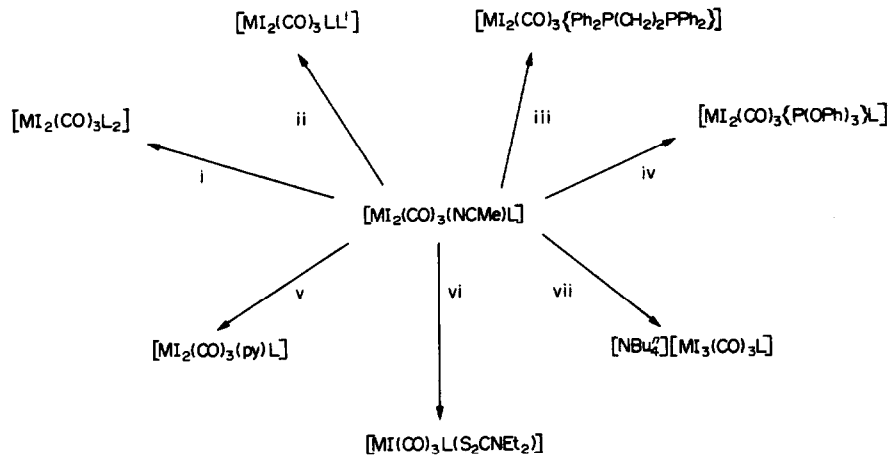
† ^1H NMR spectra (δ) of **1–6** (see Table 1) all recorded in $CDCl_3$ referenced to tetramethylsilane. (**1**) 7.72 (m, 15H, Ph), 2.02 (*s*, 3H, NCMe). (**2**) 7.47 (*m*, 15H, Ph), 1.9 (*s*, 3H, NCMe). (**3**) 7.48 (*m*, 15H, Ph), 1.99 (*s*, 3H, NCMe). (**4**) 7.52 (*m*, 15H, Ph), 1.96 (*s*, 3H, NCMe). (**5**) 7.50 (*m*, 15H, Ph), 1.94 (*s*, 3H, NCMe). (**6**) 7.53 (*m*, 15H, Ph), 2.01 (*s*, 3H, NCMe).

Table 1. Analytical (C, H and N)[a] and IR[b] data of $[MI_2(CO)_3(NCMe)L]$

	M	L	C	H	N	ν(CO) (cm^{-1})	ν(CN) (cm^{-1})
1	Mo	PPh_3	37.3 (37.5)	2.2 (2.5)	1.9 (2.2)	2045(s), 1965(s), 1930(s)	2320(w)
2	Mo	$AsPh_3$	35.6 (35.4)	2.5 (2.3)	2.0 (1.8)	2049(s), 1985(s), 1921(m)	2315(w)
3	Mo	$SbPh_3$	33.5 (33.4)	2.4 (2.2)	1.2 (1.7)	2049(s), 1990(s), 1919(s)	2310(w)
4	W	PPh_3	33.7 (33.5)	2.3 (2.2)	1.7 (1.5)	2040(s), 1950(s), 1918(s)	2325(w)
5	W	$AsPh_3$	32.0 (31.8)	2.3 (2.1)	1.5 (1.6)	2040(s), 1970(s), 1909(s)	2325(w)
6	W	$SbPh_3$	30.3 (30.2)	2.2 (2.0)	1.3 (1.5)	2035(s), 1975(s), 1905(s)	2315(w)

[a] Calculated values in parentheses.
[b] Spectra recorded in $CHCl_3$ unless stated: s = strong, m = medium, w = weak.



Scheme 1. M = Mo or W; L = PPh_3, $AsPh_3$ or $SbPh_3$. Reagents: L, L^1 = PPh_3, $AsPh_3$ or $SbPh_3$ in CH_2Cl_2 [(i) and (ii)]; $Ph_2P(CH_2)_2PPh_2$ in CH_2Cl_2 (iii); $P(OPh)_3$ in CH_2Cl_2 (iv); pyridine in CH_2Cl_2 (v); $NaS_2CNEt_2 \cdot 3H_2O$ in CH_2Cl_2 (vi); and $[NBu^n_4]I$ in CH_2Cl_2 (vii).

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