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Triphenylphosphineoxide and Triphenylphosphinesulfide Seven-coordinate Complexes of Molybdenum(II) and Tungsten(II)

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Abstract

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with one equivalent of $OPPh_3$ in CH_2Cl_2 at room temperature to rapidly afford the iodo-bridged dimers $[M(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ in good yield. By contrast reaction of equimolar quantities of $SPPh_3$ and $[MI_2(CO)_3(NCMe)_2]$ react in CH_2Cl_2 at room temperature to give the monoacetonitrile monomers $[MI_2(CO)_3(NCMe)(SPPh_3)]$. The monomers $[MI_2(CO)_3(NCMe)(SPPh_3)]$ dimerise very slowly on stirring at room temperature in CH_2Cl_2 for 24 h to eventually give the iodo-bridged dimers $[M(\mu\text{-}I)I(CO)_3(SPPh_3)]_2$. The molybdenum iodo-bridged compound $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ reacts with two equivalents of L (L = PPh_3, $AsPh_3$ or $P(OPh)_3$) to rapidly give the bridged cleaved products $[MoI_2(CO)_3L(OPPh_3)]$. The monoacetonitrile complexes $[MI_2(CO)_3(NCMe)(SPPh_3)]$ react *in situ* with an equimolar quantity of $[NBu^n_4]I$ in CH_2Cl_2 at room temperature to give the expected anionic compounds $[NBu^n_4][MI_3(CO)_3(SPPh_3)]$ in good yield. The bis-acetonitrile compounds $[MI_2(CO)_3(NCMe)_2]$ react with two equivalents of L (L = $OPPh_3$ or $SPPh_3$) in CH_2Cl_2 to afford the bis-ligand compounds $[MI_2(CO)_3L_2]$ in high yield. However, one equivalent of L (L = $OPPh_3$ or $SPPh_3$) reacts with $[MI_2(CO)_3L_2]$ to give the monocationic complexes $[MI(CO)_3L_3]I$. The ionic nature of these complexes was confirmed by the formulation of the complex $[MoI(CO)_3(SPPh_3)_3][BPh_4]$ by iodide exchange with $Na[BPh_4]$. The reaction of $[MI_2(CO)_3L_2]$ with two equivalents of L (L = $OPPh_3$ (for M = W only) or $SPPh_3$) give the dicationic compounds $[M(CO)_3L_4]2I$. The bis-tetraphenylborate complex $[Mo(CO)_3(SPPh_3)_4][BPh_4]_2$ was also prepared in the normal manner. Three equivalents of $OPPh_3$ react with $[MI_2(CO)_3(OPPh_3)_2]$ to give the dicarbonyl compounds $[M(CO)_2(OPPh_3)_5]2I$ in high yield. The mixed ligand complexes $[MI_2(CO)_3L'L]$ (M = Mo or W; L = $OPPh_3$ or $SPPh_3$; L′ = PPh_3, $AsPh_3$ or $SbPh_3$) were synthesised by reaction of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of L′ in CH_2Cl_2, followed by an *in situ* reaction with one equivalent of L. The triphenylphosphine complex $[MoI_2(CO)_3(PPh_3)(OPPh_3)]$ on stirring in CH_2Cl_2 for 18 h gave the anionic complex $[PPh_3H][MoI_3(CO)_3(OPPh_3)]$. Low temperature ^{13}C NMR spectra (carbonyl region) for several seven-coordinate complexes are interpreted to suggest structures for these compounds.

Introduction

Seven-coordinate complexes of molybdenum(II) and tungsten(II) containing group 5B donor ligands have received considerable attention over the past two decades [1–12]. The importance of this type of compound has been recently highlighted by the catalytic activity of $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$) for the ring-opening polymerisation of norbornene and norbornadiene [13, 14]. Although many seven-coordinate complexes containing anionic group 6B donor ligands such as dithiocarbamates, xanthates and piconalines have been reported [15–21], very few complexes of molybdenum(II) and tungsten(II) containing neutral oxygen and sulfur donor ligands are known. Some examples include $[MX_2(CO)_3(dth)]$ (M = Mo or W; X = Br or I; dth = 2,5-dithiahexane) reported by Mannerskantz and Wilkinson in 1962 [22], and recently the first selenium seven-coordinate compounds $[MX_2(CO)_3LL']$ (M = Mo or W; X = Cl or Br; LL′ = $Ph_2P(CH_2)P(Se)Ph_2$; M = Mo, X = Cl or Br, LL′ = $Ph_2As(CH_2)_2P(Se)Ph_2$) and $[MoX_2(CO)_2(LL')_2]$ (X = Cl or Br; LL′ = $Ph_2P(CH_2)P(Se)Ph_2$ or $Ph_2As(CH_2)_2P(Se)Ph_2$ or $[MoX_2(CO)_3\{Ph_2As(CH_2)_2P(Se)Ph_2\}_2]$ (X = Cl or Br) described by Colton and Panagiotidou [23].

In recent years we have been studying the chemistry of the seven-coordinate bis-acetonitrile compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) which are prepared in quantitative yield by reaction of the zero valent complexes $[M(CO)_3(NCMe)_3]$ with an equimolar quantity of I_2 at 0 °C [24]. In this paper

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we describe full details of the reactions of the complexes $[MI_2(CO)_3(NCMe)_2]$ with the monodentate neutral oxygen and sulfur donor ligands $OPPh_3$ and $SPPh_3$. Preliminary results of this work have been described in an earlier communication [25].

Experimental

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen using vacuum/Schlenk line techniques. Dichloromethane was dried over P_2O_5 and distilled before use. The compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were synthesised by the literature method [24], and all chemicals were purchased from commercial sources. Elemental analyses (C, H and N) were determined by using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas) by Mr E. Lewis of the Department of Chemistry, University of Wales, Bangor. IR spectra were recorded on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer. ^1H NMR spectra were recorded on a Jeol FX 60 NMR spectrometer. Low temperature ^{13}C NMR spectra were recorded on a Bruker WH 400 NMR spectrometer (all spectra were calibrated against tetramethylsilane). Molecular weights of the dimeric complexes were determined using Rasts' method [26]. Magnetic susceptibilities were determined using a Johnson-Matthey magnetic susceptibility balance.

Preparation of $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ (1)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $OPPh_3$ (0.269 g, 0.969 mmol). The mixture was stirred for 30 s, followed by filtration, and removal of the solvent *in vacuo* gave the brown crystalline complex $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ (1) which was recrystallised from CH_2Cl_2 (yield of pure product = 0.57 g, 83%). Molecular weight for $C_{42}H_{30}I_4O_8Mo_2P_2$: calc. 1424; found, 1292.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L (L = $OPPh_3$ (reaction time = 30 s); and L = $SPPh_3$ (reaction time = 24 h)) afforded the new compounds $[M(\mu\text{-}I)I(CO)_3L]_2$ (2, 5 and 6) which were recrystallised from CH_2Cl_2 (see Table 1 for physical and analytical data). Molecular weight for $[Mo(\mu\text{-}I)I(CO)_3(SPPh_3)]_2$, $C_{42}H_{30}I_4O_6Mo_2P_2S_2$: calc. 1456, found 1382.

Preparation of $[MoI_2(CO)_3(NCMe)(SPPh_3)]$ (3)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $SPPh_3$ (0.285 g, 0.969 mmol). After stirring the mixture for 30 s, followed by filtration, removal of the solvent *in vacuo* gave the brown complex $[MoI_2(CO)_3(NCMe)(SPPh_3)]$ (3), which was recrystallised from CH_2Cl_2 (yield of pure product = 0.37 g, 50%).

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with an equimolar amount of $SPPh_3$ in CH_2Cl_2 (for 30 s) gave $[WI_2(CO)_3(NCMe)(SPPh_3)]$ (4) (see Table 1 for physical and analytical data).

Reactions of $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ with Two Equivalents of L (L = PPh_3, $AsPh_3$ and $P(OPh)_3$)

To $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ (0.500 g, 0.351 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added PPh_3 (0.184 g, 0.702 mmol). After stirring the mixture for 18 h, followed by filtration, removal of the solvent *in vacuo* gave the brown complex $[MoI_2(CO)_3(PPh_3)(OPPh_3)]$, which was recrystallised from CH_2Cl_2 (yield of pure product = 0.41 g, 66%). *Anal.* Found: C, 48.1; H, 3.1. Calc. for $C_{39}H_{30}I_2MoO_4P_2$: C, 48.1; H, 3.0%). IR ($CHCl_3$, NaCl plates): ν(CO) 2005(m), 1975(m), 1935(s) and 1895(m) cm^{-1}.

A similar reaction of $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ with two equivalents of $AsPh_3$ in CH_2Cl_2 gave the bridge-cleaved product $[MoI_2(CO)_3(AsPh_3)(OPPh_3)]\cdot CH_2Cl_2$ in 81% yield of pure product. *Anal.* Found: C, 43.4; H, 2.7. Calc. for $C_{40}H_{32}I_2MoO_4AsPCl_2$: C, 43.6; H, 2.9%. IR ($CHCl_3$, NaCl plates): ν(CO) 2005(s), 1940(s) and 1895(s).

A similar reaction of $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ with two equivalents of $P(OPh)_3$ in CH_2Cl_2 gave the bridge-cleaved product $[MoI_2(CO)_3\{P(OPh)_3\}(OPPh_3)]$ in 53% yield of pure product. *Anal.* Found: C, 44.9; H, 3.0. Calc. for $C_{39}H_{30}I_2MoO_7P_2$: C, 45.8; H, 3.0%. IR ($CHCl_3$, NaCl plates) ν(CO) 2010(s), 1960(s) and 1905(s).

Reaction of $[MoI_2(CO)_3(NCMe)(SPPh_3)]$ with $[NBu^n_4]I$

To $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $SPPh_3$ (0.285 g, 0.969 mmol). After stirring for 1 min $[NBu^n_4]I$ (0.358 g, 0.969 mmol) was added and the solution was stirred for a further 45 min. Filtration, followed by removal of the solvent *in vacuo* gave the brown complex $[NBu^n_4][MoI_3(CO)_3(SPPh_3)]$ (0.83 g, 78%) which was recrystallised from CH_2Cl_2. *Anal.* Found: C, 40.6; H, 5.2; N, 1.1. Calc. for $C_{37}H_{51}NMoI_3PSO_3$: C, 40.5; H, 4.7; N, 1.3. IR ($CHCl_3$, NaCl plates) 2060(s), 2000(s) and 1940(s) cm^{-1}.

A similar reaction of $[WI_2(CO)_3(NCMe)(SPPh_3)]$ with one equivalent of $[NBu^n_4]I$ gave the anionic seven-coordinate complex $[NBu^n_4][WI_3(CO)_3(SPPh_3)]$ in 68% yield. *Anal.* Found: C, 38.2; H, 4.5; N, 1.0. Calc. for $C_{37}H_{51}I_3NMoO_3PS$: C, 37.5; H, 4.3; N, 1.2%. IR ($CHCl_3$, NaCl plates) 2060(s), 1995(s) and 1925(s) cm^{-1}.

Preparation of [$MoI_2(CO)_3(OPPh_3)_2$]·CH_2Cl_2 (7)

To [$MoI_2(CO)_3(NCMe)_2$] (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $OPPh_3$ (0.538 g, 1.938 mmol). The mixture was stirred for 18 h. After filtration, removal of the solvent *in vacuo* gave the brown crystalline complex [$MoI_2(CO)_3(OPPh_3)_2$]·CH_2Cl_2 (7) (0.94 g, 75%) which was recrystallised from CH_2Cl_2.

Similar reactions of [$MI_2(CO)_3(NCMe)_2$] with two equivalents of L (L = $OPPh_3$ and $SPPh_3$) gave the new compounds [$MI_2(CO)_3L_2$] (**8–10**).

Preparation of [$MoI(CO)_3(OPPh_3)_3$]I (11)

To [$MoI_2(CO)_3(NCMe)_2$] (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $OPPh_3$ (0.538 g, 1.938 mmol). After stirring for 2 h $OPPh_3$ (0.269 g, 0.969 mmol) was added, and the mixture was stirred for a further 18 h. After filtration, removal of the solvent *in vacuo* gave a golden brown crystalline solid, [$MoI(CO)_3(OPPh_3)_3$]I (**11**) (yield of pure product = 1.05 g, 85%), which was recrystallised from CH_2Cl_2.

Similar reactions of [$MI_2(CO)_3(NCMe)_2$] with three equivalents of L (L = $OPPh_3$ or $SPPh_3$) gave the new compounds [$WI(CO)_3(OPPh_3)_3$]I (**12**) and [$MI(CO)_3(SPPh_3)_3$]I (**13** and **15**). The complex [$MoI_2(CO)_3(SPPh_3)_2$] reacted *in situ* with one equivalent of $SPPh_3$ and Na[BPh_4] for 18 h in CH_2Cl_2 to afford the anion exchanged complex [$MoI(CO)_3(SPPh_3)_3$][BPh_4] (**14**).

Preparation of [$W(CO)_3(OPPh_3)_4$]2I (16)

To [$WI_2(CO)_3(NCMe)_2$] (0.500 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of nitrogen, was added $OPPh_3$ (0.461 g, 1.656 mmol). After stirring the solution for 2 h $OPPh_3$ (0.461 g, 1.656 mmol) and CH_2Cl_2 (10 cm^3) was added and the mixture was stirred for a further 18 h. After filtration, removal of the solvent *in vacuo* gave a brown crystalline solid [$W(CO)_3(OPPh_3)_4$]2I (**16**) (1.00 g, 74%) which was recrystallised from CH_2Cl_2.

Similar reactions of [$MI_2(CO)_3(NCMe)_2$] (M = Mo and W) with $SPPh_3$ gave [$M(CO)_3(SPPh_3)_4$]2I (**17** and **18**). [$Mo(CO)_3(SPPh_3)_4$]2I also reacts *in situ* with two equivalents of Na[BPh_4] in CH_2Cl_2 to give [$Mo(CO)_3(SPPh_3)_4$][BPh_4]$_2$ (**19**).

Preparation of [$Mo(CO)_2(OPPh_3)_5$]2I (20)

To [$MoI_2(CO)_3(NCMe)_2$] (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of nitrogen, was added $OPPh_3$ (0.538 g, 1.938 mmol). After stirring for 2 h $OPPh_3$ (0.807 g, 2.907 mmol) and CH_2Cl_2 (10 cm^3) were added and the mixture was stirred for a further 18 h. After filtration, removal of the solvent *in vacuo* gave a golden brown crystalline solid [$Mo(CO)_2(OPPh_3)_5$]2I (**20**) (1.30 g, 75%) which was recrystallised from CH_2Cl_2.

Similarly, reaction of [$WI_2(CO)_3(NCMe)_2$] with $OPPh_3$ afforded the new complex [$W(CO)_2(OPPh_3)_5$]2I (**21**).

Preparation of [$MoI_2(CO)_3(PPh_3)(OPPh_3)$] (22)

To [$MoI_2(CO)_3(NCMe)_2$] (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of nitrogen, was added PPh_3 (0.254 g, 0.968 mmol). After stirring the solution for 1 min, $OPPh_3$ (0.269 g, 0.969 mmol) was added and the mixture was stirred for a further 18 h. Filtration, followed by removal of the solvent *in vacuo* gave the brown crystalline complex [$MoI_2(CO)_3(PPh_3)(OPPh_3)$] (22) (yield of pure product = 0.84 g, 89%), which was recrystallised from CH_2Cl_2.

Similar reactions of [$MI_2(CO)_3(NCMe)_2$] with L′ (L′ = PPh_3, $AsPh_3$ or $SbPh_3$) followed by an *in situ* reaction with L (L = $OPPh_3$ or $SPPh_3$) gave the new compounds [$MI_2(CO)_3LL'$] (23–33). Reaction times for [$MI_2(CO)_3(NCMe)_2$] + L′ → [$MI_2(CO)_3(NCMe)L'$] + NCMe and [$MI_2(CO)_3(NCMe)L'$] + L → [$MI_2(CO)_3L'L$] + NCMe at 25 °C are:

23: M = W, L′ = PPh_3, 1 min; L = $OPPh_3$, 18 h
24: M = Mo, L′ = $AsPh_3$, 3 min; L = $OPPh_3$, 18 h
25: M = W, L′ = $AsPh_3$, 3 min; L = $OPPh_3$, 18 h
26: M = Mo, L′ = $SbPh_3$, 5 min; L = $OPPh_3$, 18 h
27: M = W, L′ = $SbPh_3$, 5 min; L = $OPPh_3$, 18 h

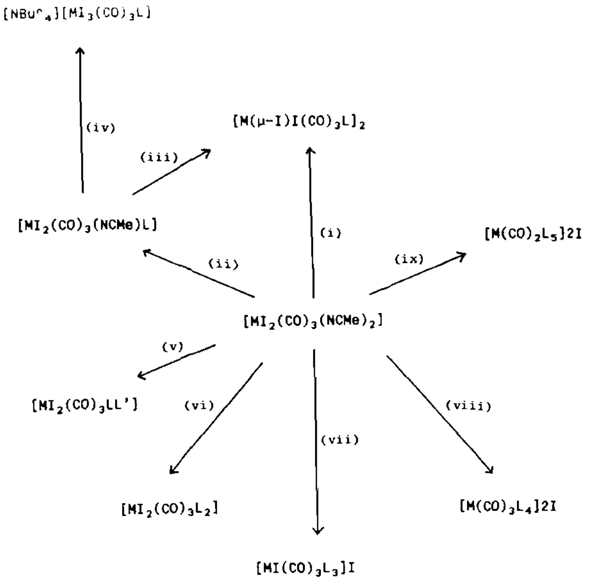
Similar times were recorded for the $SPPh_3$ complexes 28–33.

Reaction of [$MoI_2(CO)_3(PPh_3)(OPPh_3)$] in CH_2Cl_2 to Give [PPh_3H][$MoI_3(CO)_3(OPPh_3)$] (34)

The compound [$MoI_2(CO)_3(PPh_3)(OPPh_3)$] (0.500 g, 0.513 mmol) was dissolved in CH_2Cl_2 (20 cm^3) with continuous stirring under a stream of nitrogen. The mixture was stirred for 18 h, after which time [PPh_3H][$MoI_3(CO)_3(OPPh_3)$] (34) precipitated from the solution. The yellow precipitate was filtered off and dried under vacuum, yield of pure product = 0.087 g, 15%.

Results and Discussion

The phosphorus(V) ligands, triphenylphosphineoxide and triphenylphosphinesulfide react with the seven-coordinate [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) or [$MI_2(CO)_3(NCMe)L'$] (L′ = PPh_3, $AsPh_3$ or $SbPh_3$) complexes to give a wide range of new seven-coordinate compounds. The variety of reactions described in this paper are summarised in Scheme 1. All the new seven-coordinate complexes containing $OPPh_3$ and $SPPh_3$ as attached ligands (**1–34**) have been fully characterised by elemental analyses (C, H



Scheme 1. All reactions carried out in CH_2Cl_2 at room temperature. For (i) → (vii) and (ix), M = Mo or W. Reagents: (i) L = $OPPh_3$ for 30 s. (ii) L = $SPPh_3$ for 30 s. (iii) Stirring in CH_2Cl_2 for 24 h. (iv) L = $SPPh_3$; $[NBu_4{}^n]I$ for 45 min. (v) L' = PPh_3 (1 min), $AsPh_3$ (3 min) or $SbPh_3$ (5 min) followed by an *in situ* reaction with L = $OPPh_3$ or $SPPh_3$ for 18 h. (vi) 2L = $OPPh_3$ or $SPPh_3$ for 18 h. (vii) 2L = $OPPh_3$ or $SPPh_3$ for 2 h, followed by one further equivalent of L added *in situ* for 18 h. (viii) M = Mo, 2L = $SPPh_3$ for 2 h followed by two further equivalents of L added *in situ* for 18 h. M = W, 2L = $OPPh_3$ or $SPPh_3$ for 2 h followed by two further equivalents of L added *in situ* for 18 h. (ix) 2L = $OPPh_3$ for 2 h followed by three further equivalents of L added *in situ* for 18 h.

and N) (Table 1) and IR spectroscopy (Table 2). The complexes 7 and 24 were confirmed as CH_2Cl_2 solvates by repeated elemental analyses and ^1H NMR spectroscopy (Table 3). The products derived from reactions of $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ and $[MI_2(CO)_3(NCMe)(SPPh_3)]$ were also fully characterised (see 'Experimental'). Magnetic susceptibility measurements of the seven-coordinate complexes showed them to be diamagnetic, which was expected since the complexes 1–34 obey the 18-electron rule.

Equimolar quantities of the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $OPPh_3$ react in CH_2Cl_2 at room temperature for 30 s to rapidly afford the iodo-bridged complexes $[M(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ in good yield. It is likely that these complexes were formed via the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)(OPPh_3)]$ which rapidly lose acetonitrile to give the dimers $[M(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ (1 and 2). Attempts were made to isolate the monomeric compounds $[MI_2(CO)_3(NCMe)(OPPh_3)]$ by carrying out the reactions at 0 °C without success. However, reaction of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of $SPPh_3$ in CH_2Cl_2 at room temperature gave the monoacetonitrile monomers $[MI_2(CO)_3(NCMe)(SPPh_3)]$ (3 and 4) which were isolated and fully characterised (see Tables 1–3). We have previously observed that the ease of the dimerisation of the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)L]$ was $L = PPh_3 < AsPh_3 < SbPh_3$, i.e. in order of donor atom size, hence it might be expected that the monoacetonitrile $SPPh_3$ complexes would dimerise more readily than their $OPPh_3$ counterparts which were not observed. The most likely explanation for this behaviour is that the sulfur atom on $SPPh_3$ has empty $d\pi$-orbitals which can accept electron density synergistically which cannot happen with $OPPh_3$. This synergic bonding decreases the electron density at the metal and strengthens the M–N bond since acetonitrile is mainly a σ-donor ligand. The dimeric $SPPh_3$ complexes $[M(\mu\text{-}I)I(CO)_3(SPPh_3)]_2$ complexes (5 and 6) are obtained by stirring $[MI_2(CO)_3(NCMe)(SPPh_3)]$ in CH_2Cl_2 at room temperature for 24 h. These dimeric complexes (1, 2, 5 and 6) were not very stable but could be stored under nitrogen in the dark for several weeks. They are soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, but insoluble in diethylether and hydrocarbon solvents. The dimeric nature of these compounds was confirmed by molecular weight measurements using Rasts' method [26] (see 'Experimental'). Other dimeric complexes of the type $[M(\mu\text{-}X)X(CO)_4]_2$ (M = Mo or W; X = Cl, Br or I) [27–29] and $[M(\mu\text{-}X)X(CO)_3L]_2$ [30, 31] have been previously described. The structure of the bromo-bridged compound $[W(\mu\text{-}Br)Br(CO)_4]_2$ has been determined by Cotton and co-workers [32], which showed each tungsten atom to be in a capped octahedral environment, with a carbonyl ligand in the unique capping position. It is likely that the structure of the dimeric complexes $[M(\mu\text{-}I)I(CO)_3L]_2$ will be similar. The molybdenum iodo-bridged dimer $[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ (1) reacts with two equivalents of L' (L' = PPh_3, $AsPh_3$ and $P(OPh)_3$) in CH_2Cl_2 at room temperature to give the bridge-cleaved products $[MoI_2(CO)_3L'(OPPh_3)]$. These complexes were fully characterised (see 'Experimental'). Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) with an equimolar quantity of $SPPh_3$ in CH_2Cl_2 at room temperature to give $[MI_2(CO)_3(NCMe)(SPPh_3)]$, followed by an *in situ* reaction with one equivalent of $[NBu^n{}_4]I$, affords the new anionic seven-coordinate compounds $[NBu^n{}_4][MI_3(CO)_3(SPPh_3)]$ (see 'Experimental'). These $[NBu^n{}_4][MI_3(CO)_3(SPPh_3)]$ complexes are quite stable and very soluble in CH_2Cl_2 and $CHCl_3$. The low temperature ^{13}C NMR spectra (–70 °C, CD_2Cl_2) of $[NBu^n{}_4][MI_3(CO)_3(SPPh_3)]$ showed resonances at δ = 207.82 and 239.67 ppm for M = Mo and δ = 200.72 and 227.95 ppm for M = W both with an intensity ratio of 2:1. The spectrum of $[NBu^n{}_4][WI_3(CO)_3(SPPh_3)]$ is shown in Fig. 1. In view of the work of Colton and Kevekordes [33] on the low

TABLE 1. Physical and analytical[a] data for the seven-coordinate triphenylphosphineoxide and triphenylphosphinesulfide complexes of molybdenum(II) and tungsten(II)

Complex	Colour	Yield (%)	Analysis (%)[a]		
			C	H	N
$[Mo(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ (**1**)	brown	83	35.3	2.6	
			(35.4)	(2.1)	
$[W(\mu\text{-}I)I(CO)_3(OPPh_3)]_2$ (**2**)	brown	49	32.3	2.0	
			(31.5)	(1.9)	
$[MoI_2(CO)_3(NCMe)(SPPh_3)]$ (**3**)	brown	50	35.2	2.7	1.6
			(35.9)	(2.4)	(1.8)
$[WI_2(CO)_3(NCMe)(SPPh_3)]$ (**4**)	brown	60	32.7	2.3	1.9
			(32.2)	(2.1)	(1.6)
$[Mo(\mu\text{-}I)I(CO)_3(SPPh_3)]_2$ (**5**)	brown	51	34.1	2.5	
			(34.6)	(2.1)	
$[W(\mu\text{-}I)I(CO)_3(SPPh_3)]_2$ (**6**)	green	37	30.7	2.0	
			(30.9)	(1.9)	
$[MoI_2(CO)_3(OPPh_3)_2]\cdot CH_2Cl_2$ (**7**)	brown	75	44.6	3.1	
			(44.7)	(3.0)	
$[WI_2(CO)_3(OPPh_3)_2]$ (**8**)	golden brown	75	43.3	2.8	
			(43.4)	(2.8)	
$[MoI_2(CO)_3(SPPh_3)_2]$ (**9**)	brown	84	46.2	3.3	
			(45.8)	(3.0)	
$[WI_2(CO)_3(SPPh_3)_2]$ (**10**)	green	90	42.7	3.0	
			(42.2)	(3.7)	
$[MoI(CO)_3(OPPh_3)_3]I$ (**11**)	golden brown	85	53.1	3.6	
			(54.0)	(3.6)	
$[WI(CO)_3(OPPh_3)_3]I$ (**12**)	brown	60	50.0	3.6	
			(50.5)	(3.3)	
$[MoI(CO)_3(SPPh_3)_3]I$ (**13**)	brown	91	53.5	3.3	
			(52.0)	(3.4)	
$[MoI(CO)_3(SPPh_3)_3][BPh_4]$ (**14**)	brown	77	65.0	4.7	
			(64.5)	(4.3)	
$[WI(CO)_3(SPPh_3)_3]I$ (**15**)	brown	69	48.3	3.5	
			(48.7)	(3.2)	
$[W(CO)_3(OPPh_3)_4]2I$ (**16**)	brown	74	54.7	3.8	
			(55.1)	(3.7)	
$[Mo(CO)_3(SPPh_3)_4]2I$ (**17**)	brown	81	55.2	3.6	
			(55.9)	(3.8)	
$[W(CO)_3(SPPh_3)_4]2I$ (**18**)	green	87	52.1	3.8	
			(53.0)	(3.6)	
$[Mo(CO)_3(SPPh_3)_4][BPh_4]_2$ (**19**)	brown	71	73.8	4.9	
			(74.0)	(5.1)	
$[Mo(CO)_2(OPPh_3)_5]2I$ (**20**)	golden brown	75	60.9	4.5	
			(61.5)	(4.2)	
$[W(CO)_2(OPPh_3)_5]2I$ (**21**)	golden brown	68	58.1	4.4	
			(58.6)	(4.0)	
$[MoI_2(CO)_3(PPh_3)(OPPh_3)]$ (**22**)	brown	89	47.7	3.0	
			(48.1)	(3.1)	
$[WI_2(CO)_3(PPh_3)(OPPh_3)]$ (**23**)	golden brown	86	43.8	3.1	
			(44.1)	(2.9)	
$[MoI_2(CO)_3(AsPh_3)(OPPh_3)]\cdot CH_2Cl_2$ (**24**)	brown	73	43.1	3.0	
			(43.6)	(2.9)	
$[WI_2(CO)_3(AsPh_3)(OPPh_3)]$ (**25**)	brown	71	41.8	2.4	
			(42.4)	(2.7)	
$[MoI_2(CO)_3(SbPh_3)(OPPh_3)]$ (**26**)	brown	85	44.1	3.2	
			(44.0)	(2.8)	
$[WI_2(CO)_3(SbPh_3)(OPPh_3)]$ (**27**)	brown	81	41.0	2.7	
			(40.6)	(2.6)	

(continued)

TABLE 1. *(continued)*

Complex	Colour	Yield (%)	Analysis (%)[a]		
			C	H	N
$[MoI_2(CO)_3(PPh_3)(SPPh_3)]$ (**28**)	brown	81	47.7 (47.3)	3.3 (3.1)	
$[WI_2(CO)_3(PPh_3)(SPPh_3)]$ (**29**)	golden yellow	89	43.3 (43.4)	3.0 (2.8)	
$[MoI_2(CO)_3(AsPh_3)(SPPh_3)]$ (**30**)	brown	76	44.8 (45.3)	3.3 (2.9)	
$[WI_2(CO)_3(AsPh_3)(SPPh_3)]$ (**31**)	olive green	82	41.2 (41.7)	2.7 (2.7)	
$[MoI_2(CO)_3(SbPh_3)(SPPh_3)]$ (**32**)	brown	74	43.3 (43.3)	3.2 (2.8)	
$[WI_2(CO)_3(SbPh_3)(SPPh_3)]$ (**33**)	brown	74	40.0 (40.1)	3.0 (2.6)	
$[PPh_3H][MoI_3(CO)_3(OPPh_3)]$ (**34**)	yellow	15	42.0 (42.5)	3.0 (2.7)	

[a]Calculated values in parentheses.

TABLE 2. IR data[a] for the triphenylphosphineoxide and triphenylphosphinesulfide seven-coordinate complexes of molybdenum(II) and tungsten(II)

Complex	ν(CO) (cm^{-1})
1	2055(s), 1995(s), 1935(s)
2	2050(s), 1990(s), 1920(s)
3[b]	2020(s), 1995(s), 1955(s)
4[c]	2060(m), 2000(s), 1940(s)
5	2050(s), 1995(s), 1920(s)
6	2055(s), 1990(s), 1925(s)
7	2050(s), 1995(s), 1935(s)
8	2055(s), 1990(s), 1905(s)
9	2070(s), 2015(s), 1890(s)
10	2070(s), 2015(s), 1930(s)
11	1995(s), 1980(m), 1935(s)
12	2050(s), 1985(s), 1915(s)
13	2055(s), 2000(s), 1940(s)
14	2020(w)*[d], 1980(m)*, 1940(s)
15	2055(s), 1990(s), 1930(s)
16	2050(m), 1995(s), 1905(s)
17	2050(m), 2000(s), 1940(m)
18	2050(s), 1990(s), 1920(s)
19	2060(w)*, 1980(s), 1935(s)
20	2000(s), 1920(s)
21	1985(s), 1890(s)
22	1995(s), 1925(s), 1890(s)
23	1995(s), 1930(s), 1905(s)
24	2005(s), 1940(s), 1895(s)
25	2000(s), 1990(s), 1945(s)*, 1920(s), 1895(s)
26	2005(s), 1950(s), 1880(s)
27	2000(s), 1935(s), 1895(s)
28	2030(s), 1962(s), 1925(s)
29	2020(m), 1962(s), 1915(s)
30	2025(m), 1975(s), 1915(m)
31	2025(m), 1980(s), 1905(s)
32	2020(m), 1955(s), 1915(m)*
33	2010(m), 1945(s), 1915(s)
34	2005(m), 1925(s), 1900(m)

(continued)

TABLE 2. *(continued)*

[a]Spectra recorded as thin films between NaCl plates in $CHCl_3$; w, weak; m, medium, s, strong. [b]ν(C≡N) = 2300(w) cm^{-1}. [c]ν(C≡N) = 2320(w) cm^{-1}. [d]Starred item = shoulder.

TABLE 3. ^{1}H NMR data[a] for selected seven-coordinate triphenylphosphineoxide and triphenylphosphinesulfide complexes of molybdenum(II) and tungsten(II)

Complex	^{1}H NMR (δ) (ppm)
3	2.19 (s, 3H, Me), 7.52, 7.72 (m, 15H, Ph)
4	2.02 (s, 3H, Me), 7.48, 7.7, 7.9 (m, 15H, Ph)
7	5.3 (s, 2H, CH_2), 7.54 (m, 30H, Ph)
24	5.29 (s, 2H, CH_2), 7.31 (m, 30H, Ph)

[a]Spectra recorded in $CDCl_3$ (+25 °C) referenced to Me_4Si.

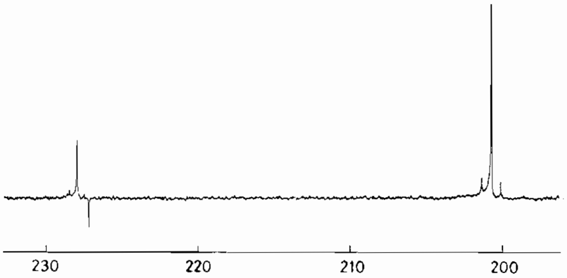


Fig. 1. Low temperature (−70 °C, CD_2Cl_2) ^{13}C NMR spectrum (carbonyl region) of $[NBu^n{}_4][WI_3(CO)_3(SPPh_3)]$.

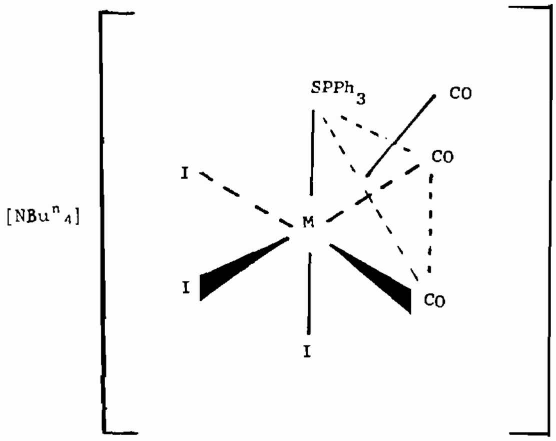


Fig. 2. Proposed structure for the complexes $[NBu^n_4][MI_3(CO)_3(SPPh_3)]$.

temperature ^{13}C NMR spectra of seven-coordinate complexes of molybdenum(II) and tungsten(II) it is highly likely that the very low field resonances at $\delta = 239.67$ and 227.95 ppm for M = Mo and W, respectively are likely to be due to a carbonyl ligand in the unique capping position in these complexes. Ganscow and Vernon [34] have suggested that the low field resonances for carbonyl ligands in the capping position is due to π-backdonation and the carbonyl resonance occurs at lower field compared to an octahedral carbonyl resonance. The most likely structure of these seven-coordinate anions $[NBu^n_4][MI_3(CO)_3(SPPh_3)]$ is shown in Fig. 2. The three iodide ligands are on the face opposite to the capped face and the two octahedral carbonyl ligands are in the same environment. This proposed geometry is the same as the triiodide anion $[PPh_2CyH][WI_3(CO)_3(SbPh_3)]$ previously described [35]. It should be noted that the ^{13}C NMR spectrum (–70 °C, CD_2Cl_2) of $[NBu^n_4][WI_3(CO)_3(SbPh_3)]$ has resonances at $\delta = 209.68$ and 235.50 ppm with an intensity ratio of 2:1 [35].

The complexes $[MI_2(CO)_3(NCMe)_2]$ react with two equivalents of L (L = $OPPh_3$ and $SPPh_3$) in CH_2Cl_2 at room temperature to give the seven-coordinate compounds $[MI_2(CO)_3L_2]$ (**7–10**) in good yield by the substitution of the labile acetonitrile ligands. It is likely that these reactions and other acetonitrile displacement reactions described in this paper go via dissociative substitutions of acetonitrile ligands since the seven-coordinate complexes of molybdenum(II) and tungsten(II) are coordinatively saturated. Evidence to support these dissociative mechanisms comes from work by Tripathi and co-workers [36]. They reacted $[Mo(CO)_5L]$ with one equivalent of X_2 (X = Cl, Br or I) in hexane to give the coordinatively unsaturated compounds $[MoX_2(CO)_3L]$ which are very similar to our proposed intermediates formed by loss of acetonitrile from $[MI_2(CO)_3(NCMe)_2]$.

The complexes $[MI_2(CO)_3L_2]$ (M = Mo and W) react with one equivalent of L (L = $OPPh_3$ and $SPPh_3$) in CH_2Cl_2 to give the monocationic compounds $[MI(CO)_3L_3]I$ (**11–13** and **15**) in high yield. The cationic nature of these complexes was confirmed by preparing the tetraphenylborate salt $[MoI(CO)_3(SPPh_3)_3][BPh_4]$ (**14**) by reaction of $[MoI(CO)_3(SPPh_3)_3]I$ with $Na[BPh_4]$ in CH_2Cl_2. Two equivalents of $OPPh_3$ and $SPPh_3$ react in CH_2Cl_2 with $[MI_2(CO)_3L_2]$ to afford the dicationic complexes $[M(CO)_3L_4]2I$ (**16–18**). Again the ionic nature was shown by reacting $[Mo(CO)_3(SPPh_3)_4]2I$ with two equivalents of $Na[BPh_4]$ in CH_2Cl_2 to give the compound $[Mo(CO)_3(SPPh_3)_4][BPh_4]_2$ (**19**). The compounds $[MI_2(CO)_3L_2]$ react with three equivalents of $OPPh_3$ in CH_2Cl_2 to give the dicarbonyl complexes $[M(CO)_2(OPPh_3)_5]2I$ (**20** and **21**). Attempts to prepare the analogous $SPPh_3$ complexes were unsuccessful probably due to the larger size of the $SPPh_3$ ligand. These tris, tetrakis and pentakis ligand complexes (**11–21**) are much less stable than either the bis-ligand or mixed ligand complexes, hence good quality low temperature NMR spectra of these complexes were difficult to obtain. Many attempts were made to grow crystals of several of these complexes without success. Surprisingly heating complexes of the types $[M(CO)_3L_4]2I$ and $[M(CO)_2(OPPh_3)_5]2I$ in $CHCl_3$ did not appear to afford the monocationic complexes $[MI(CO)_2L_4]I$ or $[MI(CO)(OPPh_3)_5]I$. Only decomposition products were obtained from these reactions. Reactions of $[MI_2(CO)_3(NCMe)_2]$ with six- and seven-equivalents of $OPPh_3$ were also attempted to afford complexes of the type $[MI(OPPh_3)_6]I$ or $[M(OPPh_3)_7]2I$. However, these were unsuccessful, even after refluxing in $CHCl_3$ for 24 h only $[M(CO)_2(OPPh_3)_5]2I$ and decomposition products were observed. It should be noted that isonitrile complexes of the types $[MI(CNR)_6]I$ and $[M(CNR)_7]2I$ have been previously reported by Lippard and co-workers [37] and Walton and co-workers [38].

The mixed ligand complexes $[MI_2(CO)_3L'L]$ (M = Mo or W; L = $OPPh_3$ or $SPPh_3$; L$'$ = PPh_3, $AsPh_3$ or $SbPh_3$) (**22–33**) were prepared by reacting $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L$'$ in CH_2Cl_2 at room temperature to give $[MI_2(CO)_3(NCMe)L']$ which have been previously described [39]. These monoacetonitrile complexes $[MI_2(CO)_3(NCMe)L']$ react *in situ* with one equivalent of L to give the new compounds $[MI_2(CO)_3L'L]$ (**22–33**). Apart from our work the only mixed ligand seven-coordinate complexes of type $[MX_2(CO)_3LL']$ to be reported are $[WX_2(CO)_3L'L]$ (X = Cl, Br or I; L, L$'$ = PMe_3, $AsMe_2H$, $P(OMe)_3$ or py] in 1982 [40]. The complexes $[WX_2(CO)_3L'L]$ were prepared by reaction of $[WX_2(CO)_4L]$ with L$'$. The mixed ligand complexes $[MI_2(CO)_3L'L]$ (**22–33**) described herein are considerably more stable than the bis-ligand com-

TABLE 4. Low temperature ^{13}C NMR data (δ/ppm)^a ($C{\equiv}O$) for selected seven-coordinate triphenylphosphineoxide and triphenylphosphinesulfide complexes of molybdenum(II) and tungsten(II)

Complex	δ (ppm)
$[NBu^n_4][MoI_3(CO)_3(SPPh_3)]$	207.8, 239.67
$[NBu^n_4][WI_3(CO)_3(SPPh_3)]$	200.72, 227.95
$[MoI_2(CO)_3(PPh_3)(OPPh_3)]$ (22)	206.65, 238.79
$[MoI_2(CO)_3(AsPh_3)(OPPh_3)]\cdot CH_2Cl_2$ (24)	206.87, 238.99
$[MoI_2(CO)_3(SbPh_3)(OPPh_3)]$ (26)	216.98, 245.17
$[MoI_2(CO)_3(PPh_3)(SPPh_3)]$ (28)	206.80, 238.61

^{a}Spectra recorded in CD_2Cl_2 (−70 °C) and referenced to Me_4Si.

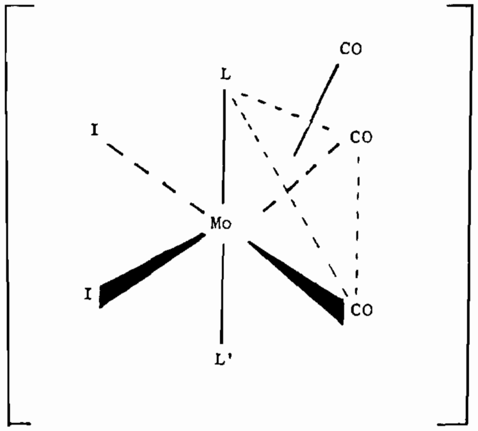


Fig. 3. Proposed structure for the complexes $[MoI_2(CO)_3LL']$ ($L = OPPh_3$, $L' = PPh_3$, $AsPh_3$ or $SbPh_3$, $L = SPPh_3$, $L' = PPh_3$).

plexes etc. described in the previous section, however they must be stored under nitrogen. The complexes are soluble in chlorinated solvents such as $CHCl_3$ and CH_2Cl_2, but are insoluble in hydrocarbon solvents. The geometry of most seven-coordinate complexes of the type $[MX_2(CO)_3L_2]$ have been shown to have capped octahedral geometry [41], and hence in view of the similar spectral properties of $[MI_2(CO)_3LL']$ (22–33) to the complexes $[MX_2(CO)_3L_2]$ with capped octahedral geometry it is likely that 22–33 have this geometry. Low temperature ^{13}C NMR (−70 °C, CD_2Cl_2) studies (carbonyl region) were obtained for several of these mixed ligand complexes (22, 24, 26 and 28) (see Table 4). The mixed ligand molybdenum complexes 22, 24, 26 and 28 all showed two carbonyl resonances with an intensity ratio of 2:1 for the high field:low field resonances (see Table 4). Using the observations of Colton and Kevekordes [33] the lower field resonances at δ = 238.79, 238.99, 245.17 and 238.61 for 22, 24, 26 and 28 are due to the carbonyl ligand in the unique capping position. Hence the most likely geometry for these complexes is shown in Fig. 3, i.e. with two equivalent octahedral carbonyl ligands. It is difficult to distinguish between L and L′ in these complexes, however it is more likely that the most bulky donor ligand will be further away from the capped face. The mixed ligand complex $[MoI_2(CO)_3(PPh_3)(OPPh_3)]$ (22) upon stirring in CH_2Cl_2 for 18 h affords a yellow precipitate which after purification was confirmed as the new phosphonium salt $[PPh_3H][MoI_3(CO)_3(OPPh_3)]$ (34). This type of rearrangement has been previously observed for the bis-triphenylphosphine complexes $[MI_2(CO)_3(PPh_3)_2]$ which rearrange to give the phosphonium salts $[PPh_3H][MI_3(CO)_3(PPh_3)]$ [42]. The mechanism for this unusual rearrangement is at present unknown.

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