Triphenylbismuth Seven-coordinate Complexes of Molybdenum(II) and Tungsten(II)

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Abstract

The seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) react with one equivalent of $BiPh_3$ in CH_2Cl_2 at room temperature to give the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)(BiPh_3)]$. The molybdenum complex $[MoI_2(CO)_3(NCMe)(BiPh_3)]$ after stirring in CH_2Cl_2 at room temperature for 5 h affords the iodide-bridged dimer $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$, whereas the tungsten complex $[WI_2(CO)_3(NCMe)(BiPh_3)]$ does not appear to dimerise even after stirring for 48 h in CH_2Cl_2 at room temperature. Reaction of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of $BiPh_3$ gives the bistriphenylbismuth compounds $[MI_2(CO)_3(BiPh_3)_2]$ in good yield. The new mixed ligand complexes $[MI_2(CO)_3L(BiPh_3)]$ were prepared either by reaction of $[MI_2(CO)_3(NCMe)(BiPh_3)]$ *in situ* with one equivalent of L (L = $P(OPh)_3$), or an *in situ* reaction of $[MI_2(CO)_3(NCMe)L]$ (L = PPh_3 and $SbPh_3$; and L = $AsPh_3$ and PPh_2Cy (for M = Mo only)) with an equimolar quantity of $BiPh_3$. Reaction of $[MoI_2(CO)_3(NCMe)(BiPh_3)]$ with one equivalent of 2,2′-bipyridyl (bipy) in CH_2Cl_2 at room temperature afforded the cationic complex $[MoI(CO)_3(bipy)(BiPh_3)]I$ in good yield. The complex $[WI_2(CO)_3(NCMe)(BiPh_3)]$ (prepared *in situ*) reacts with two equivalents of $NaS_2CNMe_2 \cdot 2H_2O$ to eventually give the non-triphenylbismuth containing product $[W(CO)_3(S_2CNMe_2)_2]$ in high yield.

Introduction

Over the years triphenylphosphine, triphenylarsine and triphenylantimony have proved to be important ligands when coordinated to transition metals. For example, the seven-coordinate complexes $[MX_2(CO)_3L_2]$ (M = Mo and W, X = Cl, Br and I; L = PPh_3, $AsPh_3$ and $SbPh_3$) have been synthesised by a wide variety of methods [1–7], and the compounds $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl and Br; L = PPh_3 and $AsPh_3$) have been shown to be catalysts for the ring-opening polymerisation of norbornene and norbornadiene [8, 9]. However, far fewer triphenylbismuth compounds have been prepared which is probably due to the very poor donor ability of $BiPh_3$ as a ligand. Some examples of $BiPh_3$ complexes include $[Fe(CO)_3(BiPh_3)_2]$ [10, 11], $[Mn(CO)_2(BiPh_3)(\eta^5\text{-}C_5H_5)]$ [12] and more recently $[Fe(CO)_2(BiPh_3)(\eta^5\text{-}C_5H_5)][BF_4]$ [13].

In recent years we have been investigating the chemistry of the highly versatile seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) [14] which are prepared by reacting the trisacetonitrile complexes $[M(CO)_3(NCMe)_3]$ [15] *in situ* with an equimolar quantity of I_2 at 0 °C. In this paper we wish to describe in full the reactions of $[MI_2(CO)_3(NCMe)_2]$ and their derivatives with triphenylbismuth. Preliminary results of this work have been reported in an earlier communication [16].

Experimental

All reactions described in this paper were carried out using standard Schlenk line techniques. The seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) were prepared by the published method [14]. All chemicals were purchased from commercial sources. CH_2Cl_2 was dried over P_2O_5 and distilled before use.

Elemental analyses (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. ^1H NMR spectra were recorded on a Jeol FX60 NMR spectrometer. The low temperature (−70 °C) ^{13}C NMR spectrum of $[WI_2(CO)_3(BiPh_3)_2]$ was recorded on a Bruker WH-400 NMR spectrometer at the University of Warwick. (All spectra were calibrated against tetramethylsilane.) The molecular weight of the complex $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ was determined by Rast's method [17].

$[MoI_2(CO)_3(NCMe)(BiPh_3)]$ (1)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.212 g, 0.411 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $BiPh_3$

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(0.181 g, 0.411 mmol). After stirring the solution for 5 min and filtration, removal of the solvent *in vacuo* gave black crystals of [$MoI_2(CO)_3(NCMe)(BiPh_3)$] (**1**) (yield = 0.16 g, 43%), which were rapidly recrystallised from CH_2Cl_2.

A similar reaction of [$WI_2(CO)_3(NCMe)_2$] with one equivalent of $BiPh_3$ gave the compound [$WI_2(CO)_3(NCMe)(BiPh_3)$] (**2**) (see Table I for physical and analytical data).

[$Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ (3)

The compound [$MoI_2(CO)_3(NCMe)(BiPh_3)$] (0.100 g, 0.109 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and stirred under a stream of dry nitrogen for 5 h. Filtration and removal of the solvent *in vacuo* gave black crystals of [$Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ (**3**) (yield = 0.045 g, 47%), which were recrystallised from CH_2Cl_2. Molecular weight for $C_{42}H_{30}Mo_2O_6Bi_2I_4$: calc. 1748; found, 1379.

Attempts made to prepare the analogous tungsten complex [$W(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ were unsuccessful. After several days the monomer had still not dimerised and there was extensive decomposition.

[$MoI_2(CO)_3(BiPh_3)_2$] (4)

To [$MoI_2(CO)_3(NCMe)_2$] (0.212 g, 0.411 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $BiPh_3$ (0.362 g, 0.822 mmol). After stirring the solution for 25 h and filtration, removal of the solvent *in vacuo* gave brown crystals of [$MoI_2(CO)_3(BiPh_3)_2$] (**4**) (yield = 0.29 g, 54%), which were recrystallised from CH_2Cl_2.

A similar reaction of [$WI_2(CO)_3(NCMe)_2$] with two molar equivalents of $BiPh_3$ gave the new complex [$WI_2(CO)_3(BiPh_3)_2$] (**5**) (see Table I for physical and analytical data).

[$MoI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$] (6)

To [$MoI_2(CO)_3(NCMe)_2$] (0.186 g, 0.361 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $BiPh_3$ (0.159 g, 0.361 mmol). After stirring the solution for 5 min, $P(OPh)_3$ (0.112 g, 0.361 mmol) was added and the mixture was stirred for a further 24 min. After filtration, removal of the solvent *in vacuo* gave orange crystals of [$MoI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$] (**6**) (yield = 0.290 g, 68%), which were recrystallised from CH_2Cl_2.

A similar reaction of [$WI_2(CO)_3(NCMe)_2$] with one equivalent of $BiPh_3$ followed by an *in situ* reaction with one equivalent of $P(OPh)_3$ gave the new compound [$WI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$] (**7**) (see Table I for physical and analytical data).

[$MoI_2(CO)_3(PPh_3)(BiPh_3)$] (8)

To [$MoI_2(CO)_3(NCMe)_2$] (0.5 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.254 g, 0.969 mmol). After stirring the solution for 1 min, $BiPh_3$ (0.427 g, 0.969 mmol) was added and the mixture was stirred for a further 3 h. After filtration, removal of the solvent *in vacuo* gave brown crystals of [$MoI_2(CO)_3(PPh_3)(BiPh_3)$] (**8**) (yield = 0.264 g, 24%).

Similar reactions of [$MI_2(CO)_3(NCMe)_2$] with one equivalent of L (L = PPh_3 and $SbPh_3$; PPh_2Cy and $AsPh_3$ (for M = Mo only)); followed by an *in situ* reaction with one equivalent of $BiPh_3$ gave the compounds [$MI_2(CO)_3L(BiPh_3)$] (**9**–**13**) (see Table I for physical and analytical data).

[$MoI(CO)_3(bipy)(BiPh_3)$]I (14)

To [$MoI_2(CO)_3(NCMe)_2$] (0.5 g, 0.969 mmol) dissolved in degassed CH_2Cl_2 (15 cm^3) was added

TABLE I. Physical and Analytical Data[a] for the Triphenylbismuth Complexes

Complex	Colour	Yield (%)	Analysis (%)[a]		
			C	H	N
1 [$MoI_2(CO)_3(NCMe)(BiPh_3)$]	black	43	28.5(30.2)	2.0(2.0)	1.8(1.5)
2 [$WI_2(CO)_3(NCMe)(BiPh_3)$]	black	31	28.2(27.5)	1.9(1.8)	1.7(1.4)
3 [$Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$	black	47	28.2(28.9)	1.7(1.7)	
4 [$MoI_2(CO)_3(BiPh_3)_2$]	brown	54	36.0(35.6)	2.5(2.3)	
5 [$WI_2(CO)_3(BiPh_3)_2$]	brown	53	33.5(33.4)	2.3(2.4)	
6 [$MoI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$]	orange	68	39.5(39.6)	2.7(2.6)	
7 [$WI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$]	orange	62	37.2(36.8)	2.6(2.4)	
8 [$MoI_2(CO)_3(PPh_3)(BiPh_3)$]	brown	24	40.4(41.2)	2.9(2.7)	
9 [$WI_2(CO)_3(PPh_3)(BiPh_3)$]·NCMe	yellow	57	38.9(38.9)	2.5(2.6)	1.2(1.1)
10 [$MoI_2(CO)_3(PPh_2Cy)(BiPh_3)$]·$CH_2Cl_2$	brown	43	39.5(39.1)	3.6(3.1)	
11 [$MoI_2(CO)_3(AsPh_3)(BiPh_3)$]	orange	63	39.1(39.7)	2.6(2.6)	
12 [$MoI_2(CO)_3(SbPh_3)(BiPh_3)$]	brown	33	37.7(38.2)	2.6(2.4)	
13 [$WI_2(CO)_3(SbPh_3)(BiPh_3)$]·$CH_2Cl_2$	red–brown	32	33.3(34.3)	2.5(2.7)	
14 [$MoI(CO)_3(bipy)(BiPh_3)$]I	brown	67	39.3(38.5)	2.3(2.3)	2.5(2.7)

[a]Calculated values in parentheses.

$BiPh_3$ (0.427 g, 0.969 mmol). After stirring the solution for 7 min bipy (0.151 g, 0.969 mmol) was added and the mixture was stirred for a further 2 h. After filtration, removal of the solvent *in vacuo* gave brown crystals of $[MoI(CO)_3(bipy)(BiPh_3)]I$ (**14**) (yield = 0.67 g, 67%), which were recrystallised from CH_2Cl_2 (see Table I for physical and analytical data).

Reaction of [$WI_2(CO)_3(NCMe)(BiPh_3)$] with Two Equivalents of $NaS_2CNMe_2 \cdot 2H_2O$

To $[WI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.828 mmol) dissolved in degassed CH_2Cl_2 (15 cm^3) was added $BiPh_3$ (0.365 g, 0.829 mmol). After stirring the solution for 7 min $NaS_2CNMe_2 \cdot 2H_2O$ (0.297 g, 1.657 mmol) in MeOH (5 cm^3) was added and the mixture was stirred for a further 30 min. After removal of the solvent *in vacuo* and redissolving in degassed CH_2Cl_2, filtration to remove NaI, removal of the solvent *in vacuo* gave orange crystals of $[W(CO)_3(S_2CNMe_2)_2]$ (yield = 0.36 g, 86%), which were recrystallised from CH_2Cl_2. *Anal.* Calc. for $C_9H_{12}N_2O_3S_4W$: C, 21.2; H, 2.4; N, 5.5. Found: C, 21.8; H, 2.6; N, 5.4%. IR, ν(CO) ($CHCl_3$) = 2010(s), 1925(s) and 1910(sh). ^1H NMR ($CDCl_3$, +25 °C) δ = 3.25(s, Me).

Results and Discussion

The new triphenylbismuth complexes of the types $[MI_2(CO)_3(NCMe)(BiPh_3)]$ (M = Mo and W) (**1** and **2**), $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ (**3**), $[MI_2(CO)_3(BiPh_3)_2]$ (**4** and **5**), $[MI_2(CO)_3L(BiPh_3)]$ (for M = Mo and W, L = $P(OPh)_3$ (**6** and **7**), PPh_3 (**8** and **9**), $SbPh_3$ (**12** and **13**); for M = Mo only, L = PPh_2Cy and $AsPh_3$ (**10** and **11**)) and $[MoI(CO)_3(bipy)(BiPh_3)]I$ (**14**) described in this paper have been characterised by elemental analysis (C, H and N) (Table I), IR (Table II) and in selected cases ^1H NMR spectroscopy (Table III). The complexes **9**, **10** and **13** are confirmed as either NCMe (**9**) or CH_2Cl_2 (**10** and **13**) solvates by repeated elemental analyses and ^1H NMR spectroscopy. The triphenylbismuth compounds (**1**–**14**) are all soluble in $CHCl_3$ or CH_2Cl_2. $[MoI(CO)_3(bipy)(BiPh_3)]I$ is as expected insoluble in Et_2O and hydrocarbon solvents as it is ionic. The mixed triphenylphosphite compounds $[MI_2(CO)_3\{P(OPh)_3\}(BiPh_3)]$ (**7** and **8**) are the most soluble complexes and are soluble in diethylether. All the complexes are moderately air-sensitive (particularly in solution) and thermally unstable (much less stable than their PPh_3, $AsPh_3$ and $SbPh_3$ counterparts) [7, 18], however, they can be stored under nitrogen for several days at 0 °C.

Equimolar quantities of the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) and $BiPh_3$ react in CH_2Cl_2 at room temperature to give the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)(BiPh_3)]$ (**1** and **2**) in good yield. These complexes are analogous to the $[MI_2(CO)_3(NCMe)L]$ (M = Mo and W; L = PPh_3 $AsPh_3$ and $SbPh_3$) compounds previously reported [18]. It is interesting to note that as expected the $BiPh_3$ ligand (with the largest donor atom) allows the molybdenum complex $[MoI_2(CO)_3(NCMe)(BiPh_3)]$ to dimerise to $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ with loss of acetonitrile more readily than its PPh_3, $AsPh_3$ and $SbPh_3$ counterparts. The order for the ease of dimerisation of $[MoI_2(CO)_3(NCMe)L]$ is $BiPh_3 > SbPh_3 > AsPh_3 > PPh_3$. The dimeric nature of the molybdenum complex $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ was confirmed by molecular weight measurements by Rast's method [17] (see 'Experimental'). It is surprising that the tungsten complex $[WI_2(CO)_3(NCMe)(BiPh_3)]$ does not dimerise even after stirring in CH_2Cl_2 for 48 h in CH_2Cl_2, only decomposition products and the unreacted monoacetonitrile complex $[WI_2(CO)_3(NCMe)(BiPh_3)]$ were isolated.

Two equivalents of $BiPh_3$ react with $[MI_2(CO)_3(NCMe)_2]$ at room temperature in CH_2Cl_2 to give the expected substituted products $[MI_2(CO)_3(BiPh_3)_2]$. It is highly likely that these reactions

TABLE II. Infrared Data[a] for the Triphenylbismuth Complexes

Complex	ν(CO) (cm^{-1})	ν(CN) (cm^{-1})
1	2045(s), 2015(s), 1936(s)	2310(w)
2	2040(s), 2000(s), 1939(s)	2310(w)
3	2020(s), 1984(s), 1950(s)	
4	2020(m), 1950(s), 1930(s)	
5	2035(s), 1945(s), 1916(s)	
6	2045(m), 1995(s), 1935(s)	
7	2045(m), 1988(s), 1921(s)	
8	2040(m), 1960(m), 1920(m)	
9	2045(s), 1964(s), 1914(s)	2290(w)
10	2020(w), 1990(w), 1920(s)	
11	2045(s), 1977(s), 1923(s)	
12	2030(m), 1960(m), 1920(m)	
13	2040(m), 1940(m), 1915(m)	
14	2040(s), 1970(s), 1930(m)	

[a]Spectra recorded in $CHCl_3$ as thin films between NaCl plates; (w) weak; (m) medium; (s) strong.

TABLE III. ^1H NMR Data[a] for Selected Triphenylbismuth Complexes

Complex	^1H NMR (δ) (ppm)
1	2.45(s, 3H, Me), 7.35(m, 15H, Ph)
2	2.41(s, 3H, Me), 7.35(m, 15H, Ph)
9	1.96(s, 3H, Me), 7.43(m, 30H, Ph)
10	1.28(bm, 11H, Cy), 5.31(s, 2H, CH_2), 7.38(m, 25H, Ph)
13	5.32(s, 2H, CH_2), 7.35(m, 30H, Ph)

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

occur via successive dissociative displacements of acetonitrile ligands since the complexes $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)(BiPh_3)]$ (see previous section) are coordinatively saturated and are unlikely to gain a $BiPh_3$ ligand to give the 20 electron complexes $[MI_2(CO)_3(NCMe)_2(BiPh_3)]$. The proposed mechanism for these reactions is given in Scheme 1. Evidence to support these dissociative mechanism comes from some work by Tripathi and co-workers [19]. They described the reaction of $[Mo(CO)_5L]$ ($L = PPh_3$, $AsPh_3$ and $SbPh_3$) with X_2 (X = Cl, Br and I) in hexane to give the coordinatively unsaturated compounds $[MoX_2(CO)_3L]$ which were isolated and characterised. These $[MoX_2(CO)_3L]$ compounds are analogous to the acetonitrile dissociated intermediates $[MI_2(CO)_3(NCMe)]$ and $[MI_2(CO)_3(BiPh_3)]$ resulting from loss of acetonitrile from either $[MI_2(CO)_3(NCMe)_2]$ or $[MI_2(CO)_3(NCMe)(BiPh_3)]$ (see Scheme 1).

$$[MI_2(CO)_3(NCMe)_2] \longrightarrow [MI_2(CO)_3(NCMe)] + NCMe \qquad (a)$$

$$[MI_2(CO)_3(NCMe)] + BiPh_3 \longrightarrow [MI_2(CO)_3(NCMe)(BiPh_3)] \qquad (b)$$

$$[MI_2(CO)_3(NCMe)(BiPh_3)] \longrightarrow [MI_2(CO)_3(BiPh_3)] + NCMe \qquad (c)$$

$$[MI_2(CO)_3(BiPh_3)] + BiPh_3 \longrightarrow [MI_2(CO)_3(BiPh_3)_2] \qquad (d)$$

Scheme 1. Proposed dissociative mechanisms for the reactions of $[MI_2(CO)_3(NCMe)_2]$ with $BiPh_3$.

Reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent $BiPh_3$ in CH_2Cl_2 at room temperature gives $[MI_2(CO)_3(NCMe)(BiPh_3)]$ which when reacted *in situ* with $P(OPh)_3$ gives the novel mixed ligand compounds $[MI_2(CO)_3\{P(OPh)_3\}(BiPh_3)]$ (**6** and **7**). However, attempts to prepare other mixed ligand compounds of the type $[MI_2(CO)_3L(BiPh_3)]$ ($L = PPh_3$, $AsPh_3$ and $SbPh_3$) were less successful by initial reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of $BiPh_3$, since the $[MI_2(CO)_3(NCMe)(BiPh_3)]$ complexes are less stable than their PPh_3, $AsPh_3$ and $SbPh_3$ counterparts. Reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L ($L = PPh_3$ and $SbPh_3$; $L = PPh_2Cy$ and $AsPh_3$ (for M = Mo only)) gives $[MI_2(CO)_3(NCMe)L]$ which react *in situ* with an equimolar quantity of $BiPh_3$ to give the expected mixed ligand compounds $[MI_2(CO)_3L(BiPh_3)]$ (**8**–**13**) in good yield.

The structures of the mononuclear seven-coordinate complexes (**1**, **2** and **4**–**14**) are highly likely to have capped octahedral geometry since most of the seven-coordinate complexes of the type $[MX_2(CO)_3L_2]$ have been shown by X-ray analysis to have capped octahedral geometry [20–28]. Also the infrared spectral properties ($\nu(CO)$) (see Table II) of **1**, **2** and **4**–**14** are similar to the complexes $[MX_2(CO)_3L_2]$ which have capped octahedral geometry. Colton and Kevekordes [29] have recently shown how ^{13}C NMR spectroscopy can be used to suggest the geometry of capped octahedral complexes from the carbonyl chemical shifts. For example, carbonyl resonances in the unique capping position in capped octahedral complexes appear at lower field than octahedral carbonyl resonances. The low temperature (−70 °C, CD_2Cl_2) ^{13}C NMR spectrum of $[WI_2(CO)_3(BiPh_3)_2]$ (**5**) shows a single resonance at $\delta = 208.31$ ppm which suggests a structure with the $BiPh_3$ ligand in the unique capping position (*i.e.* no capping carbonyl ligand). Although it is possible that the complex is fluxional even at −70 °C. The structure of the dimeric complex $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ (**3**) is likely to be based on two capped octahedra since Cotton and co-workers [30] determined the X-ray crystal structure of the related bromide-bridged carbonyl compound $[W(\mu\text{-}Br)Br(CO)_4]_2$, which has a structure based on two capped octahedra with bridging bromide ligands.

Equimolar quantities of $[MoI_2(CO)_3(NCMe)_2]$ and $BiPh_3$ react in CH_2Cl_2 to give $[MoI_2(CO)_3(NCMe)(BiPh_3)]$ which upon reaction *in situ* with 2,2′-bipyridyl (bipy) afforded the cationic compound $[MoI(CO)_3(bipy)(BiPh_3)]I$ (**14**), which is analogous to the cationic complexes $[MI(CO)_3(\overset{\frown}{NN})L]I$ (M = Mo and W; $\overset{\frown}{NN}$ = 2,2′-bipyridyl and 1,10-phenanthroline; $L = PPh_3$, $AsPh_3$ and $SbPh_3$) very recently described [31]. It is likely this reaction goes via successive displacement of acetonitrile and a weakly bonded iodide ligand.

Several attempts were made to prepare the monodithiocarbamate complexes $[MI(CO)_3(BiPh_3)(S_2CNR_2)]$ (M = Mo and W; R = Me and Et) by reaction of $[MI_2(CO)_3(NCMe)(BiPh_3)]$ (prepared *in situ*) with one equivalent of $NaS_2CNR_2{\cdot}nH_2O$ (for R = Me, $n = 2$; R = Et, $n = 3$). These were unsuccessful mainly due to the instability of these $[MI(CO)_3(BiPh_3)(S_2CNR_2)]$ complexes compared to the previously reported compounds $[MI(CO)_3L(S_2CNEt_2)]$ (M = Mo and W; $L = PPh_3$, $AsPh_3$ and $SbPh_3$) [32]. However, reaction of $[WI_2(CO)_3(NCMe)(BiPh_3)]$ (prepared *in situ*) with two equivalents of $NaS_2CNMe_2{\cdot}2H_2O$ eventually gave the non-triphenylbismuth containing product $[W(CO)_3(S_2CNMe_2)_2]$ previously reported, for example, by Broomhead and Young [33].

In summary although the synthesis of several new seven-coordinate complexes containing triphenylbismuth as attached ligands have been described herein, they are considerably less stable than their triphenylphosphine, triphenylarsine and triphenylantimony analogues.

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