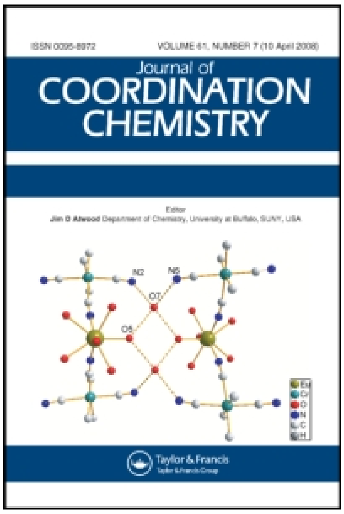

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Paul K. Baker[a]; Stuart G. Fraser[a]
[a] Department of Chemistry, University College of North Wales, Bangor, Gwynedd, UK

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COMMUNICATION

THE FIRST EXAMPLES OF TRIPHENYLBISMUTH SEVEN-COORDINATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

PAUL K. BAKER* and STUART G. FRASER
Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW, UK

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INTRODUCTION

It is well known that triphenylbismuth is a very poor "soft" donor ligand and although several complexes such as $[Mn(CO)_2(BiPh_3)(\eta^5\text{-}C_5H_5)]$[1] and $[Fe(CO)_3(BiPh_3)_2]$[2,3] have been prepared they are much less common than their PPh_3, $AsPh_3$ and $SbPh_3$ analogues.

Although the bistriphenylphosphine, triphenylarsine and triphenylantimony 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 several different methods[4–9], it is surprising that no seven-coordinate complexes of molybdenum(II) and tungsten(II) with triphenylbismuth as an attached ligand have hitherto been reported. The complexes $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl and Br; L = PPh_3 and $AsPh_3$) are catalysts for the ring opening polymerisation of norbornene and norbornadiene.[10,11] In this communication we wish to report the synthesis of the new triphenylbismuth compounds $[MI_2(CO)_3(BiPh_3)_2]$ (M = Mo and W), $[MI_2(CO)_3(NCMe)(BiPh_3)]$, $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$, $[MI_2(CO)_3\{P(OPh)_3\}(BiPh_3)]$, $[MoI_2(CO)_3(AsPh_3)(BiPh_3)]$ and $[WI_2(CO)_3(PPh_3)(BiPh_3)]$ NCMe.

EXPERIMENTAL

$[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) were prepared according to literature methods[12] and $BiPh_3$, $P(OPh)_3$, PPh_3 and $AsPh_3$ were purchased from commercial sources. Dichloromethane was distilled before use. ^1H n.m.r. spectra were recorded on a Jeol FX60 MHz n.m.r. spectrometer (all spectra were calibrated against tetramethylsilane). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were obtained using a Carlo Erba Elemental Analyser MOD 1106 (using helium carrier gas). The molecular weight of the complex $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ was determined using Rast's method.[13]

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

To $MoI_2(CO)_3(NCMe)_2$ (0.212g, 0.411 mmol) dissolved in CH_2Cl_2 (15 cm^3) with

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*Author for correspondence

continuous stirring under a stream of dry nitrogen was added BiPh$_3$ (0.362g, 0.822 mmol). After stirring for 25 hours and filtration, removal of the solvent *in vacuo* gave brown crystals of [MoI$_2$(CO)$_3$(BiPh$_3$)$_2$] (yield = 0.29g, 54%), which were recrystallised from CH$_2$Cl$_2$.

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$_3$)$_2$].

[MoI$_2$(CO)$_3$(NCMe)(BiPh$_3$)]

To MoI$_2$(CO)$_3$(NCMe)$_2$ (0.212g, 0.411 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3) with continuous stirring under a stream of dry nitrogen was added BiPh$_3$ (0.181g, 0.411 mmol). After stirring for 5 minutes and filtration, removal of the solvent *in vacuo* gave black crystals of [MoI$_2$(CO)$_3$(NCMe)(BiPh$_3$)] (yield = 0.16g, 43%), which were rapidly recrystallised from CH$_2$Cl$_2$. At room temperature the ^{1}H n.m.r. spectrum in CDCl$_3$ showed resonances at $\delta = 2.45$ (s, 3H, Me) and 7.35 (m, 15H, Ph).

In a similar reaction of [WI$_2$(CO)$_3$(NCMe)$_2$] with one equivalent of BiPh$_3$ the new complex [WI$_2$(CO)$_3$(NCMe)(BiPh$_3$)] was obtained. At room temperature the ^{1}H n.m.r. spectrum in CDCl$_3$ showed resonances at $\delta = 2.41$ (s, 3H, Me) and 7.35 (m, 15H, Ph).

[Mo(μ-I)I(CO)$_3$(BiPh$_3$)]$_2$

The complex [MoI$_2$(CO)$_3$(NCMe)(BiPh$_3$)] (0.100g, 0.109 mmol) was dissolved in CH$_2$Cl$_2$ (15 cm^3) and stirred under a stream of dry nitrogen for 5 hours. Filtration and removal of solvent *in vacuo* gave black crystals of [Mo(μ-I)I(CO)$_3$(BiPh$_3$)]$_2$ (yield = 0.045g, 47%), which were recrystallized from CH$_2$Cl$_2$. Molecular weight for C$_{42}$H$_{30}$Mo$_2$O$_6$Bi$_2$I$_4$: Calc. 1748; found, 1379.

Attempts to prepare the analogous tungsten complex [W(μ-I)I(CO)$_3$(BiPh$_3$)]$_2$ failed, even after several days the monomer had still not dimerised and there was extensive decomposition.

[MoI$_2$(CO)$_3${P(OPh)$_3$}(BiPh$_3$)]

To MoI$_2$(CO)$_3$(NCMe)$_2$ (0.186g, 0.361 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3) with continuous stirring under a stream of dry nitrogen was added BiPh$_3$ (0.159g, 0.361 mmol). After stirring for 5 minutes, P(OPh)$_3$ (0.111g, 0.361 mmol) was added and the mixture was stirred for a further 24 minutes. After filtration, removal of the solvent *in vacuo* gave

TABLE I
Physical and analytical data for the new seven-coordinate triphenylbismuth complexes

Complex	*Colour*	*Yield (%)*	*Found (Calcd.) %*		
			C	H	N
(1) [MoI$_2$(CO)$_3$(BiPh$_3$)$_2$]	Brown	54	36.0(35.6)	2.5(2.3)	
(2) [WI$_2$(CO)$_3$(BiPh$_3$)$_2$]	Brown	53	33.5(33.4)	2.3(2.4)	
(3) [MoI$_2$(CO)$_3$(NCMe)(BiPh$_3$)]	Black	43	28.5(30.2)	2.0(2.0)	1.8(1.5)
(4) [WI$_2$(CO)$_3$(NCMe)(BiPh$_3$)]	Black	31	28.2(27.5)	1.9(1.8)	1.7(1.4)
(5) [Mo(μ-I)I(CO)$_3$(BiPh$_3$)]$_2$	Black	47	28.2(28.9)	1.7(1.7)	
(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)$_3$(AsPh$_3$)(BiPh$_3$)]	Orange	63	39.1(39.7)	2.6(2.6)	
(9) [WI$_2$(CO)$_3$(PPh$_3$)(BiPh$_3$)]NCMe	Yellow	57	38.9(38.9)	2.5(2.6)	1.2(1.1)

orange crystals of [$MoI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$] (yield = 0.290g, 68%), which were recrystallised from CH_2Cl_2.

In a similar reaction of [$WI_2(CO)_3(NCMe)_2$] with $BiPh_3$ followed by $P(OPh)_3$ gave the new compound [$WI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$].

[$MoI_2(CO)_3(AsPh_3)(BiPh_3)$]

To $MoI_2(CO)_3(NCMe)_2$ (0.212g, 0.411 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $AsPh_3$ (0.126g, 0.411 mmol). After stirring for 3 minutes, $BiPh_3$ (0.181g, 0.411 mmol) was added and the mixture was stirred for a further 110 minutes. After filtration, removal of the solvent *in vacuo* gave orange crystals of [$MoI_2(CO)_3(AsPh_3)(BiPh_3)$] (yield = 0.307g, 63%), which were recrystallised from CH_2Cl_2.

In a similar reaction of [$WI_2(CO)_3(NCMe)_2$] with PPh_3 followed by $BiPh_3$ the new compound [$WI_2(CO)_3(PPh_3)(BiPh_3)$]NCMe was obtained. At room temperature the ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at δ = 1.96 (s, 3H, Me) and 7.43 (m, 30H, Ph).

RESULTS AND DISCUSSION

Elemental analysis (C, H and N) (Table I) and infrared spectroscopy (Table II) and in the case of the complexes [$MI_2(CO)_3(NCMe)(BiPh_3)$] ^1H n.m.r. spectroscopy (see experimental) support the formulation of the new compounds [$MI_2(CO)_3(BiPh_3)_2$], [$MI_2(CO)_3(NCMe)(BiPh_3)$], [$Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$, [$MI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$], [$MoI_2(CO)_3(AsPh_3)(BiPh_3)$] and [$WI_2(CO)_3(PPh_3)(BiPh_3)$]NCMe. Repeated micro-analyses and ^1H n.m.r. spectroscopy support the formulation of [$WI_2(CO)_3(PPh_3)(BiPh_3)$]NCMe as an acetonitrile solvate.

Reaction of [$MI_2(CO)_3(NCMe)_2$] (M = Mo and W) with two equivalents of $BiPh_3$ in CH_2Cl_2 smoothly affords good yields of the new [$MI_2(CO)_3(BiPh_3)_2$] complexes *via*

TABLE II
Infrared data[a] for the seven-coordinate triphenylbismuth complexes

Complex	ν(CO) cm^{-1}	ν(CN) cm^{-1}
(1)	2020(m), 1950(s) and 1930(s)	
(2)	2035(s), 1945(s) and 1916(s)	
(3)	2045(s), 2015(s) and 1936(s)	2310(w)
(4)	2040(s), 2000(s) and 1939(s)	2310(w)
(5)	2020(s), 1984(s) and 1950(s)	
(6)	2045(m), 1995(s) and 1935(s)	
(7)	2045(s), 1988(s) and 1921(s)	
(8)	2045(s), 1977(s) and 1923(s)	
(9)	2045(s), 1964(s) and 1914(s)	2290(w)

[a]Spectra recorded in $CHCl_3$ unless stated; w, weak; m, medium; s, strong.

displacements of two acetonitrile ligands. Several X-ray crystal structures of known seven-coordinate complexes have been carried out,[14–22] all showing capped octahedral geometry. Since the i.r. spectral properties of $[MI_2(CO)_3(BiPh_3)_2]$ closely resemble the analogous seven-coordinate compounds it is likely they will have a similar geometry.

Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) with one equivalent of $BiPh_3$ initially gives the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)(BiPh_3)]$ similar to $[MI_2(CO)_3(NCMe)L]$ (L = PPh_3, $AsPh_3$ and $SbPh_3$) which have been previously reported,[23] and as expected the larger bismuth atom forces the molybdenum complex $[MoI_2(CO)_3(NCMe)(BiPh_3)]$ to dimerise more readily than do the smaller donor atoms. The order of increasing ease of dimerisation is $PPh_3 < AsPh_3 < SbPh_3 < BiPh_3$ and in fact the complex $[MoI_2(CO)_3(NCMe)(BiPh_3)]$ was very difficult to isolate in a pure state as it dimerises very rapidly compared with the analogous tungsten compound. The dimeric nature of the complex $[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$ was confirmed by molecular weight studies (see experimental); the low value found is probably due to thermal instability of the complex. The tungsten complex $[WI_2(CO)_3(NCMe)(BiPh_3)]$, however, does not appear to dimerise even after several days in CH_2Cl_2 giving only decomposition products and unchanged monomer. The use of the complexes $[MI_2(CO)_3(NCMe)L]$ (L = PPh_3, $AsPh_3$ and $SbPh_3$) to form a variety of mixed complexes has been previously observed[24,25] and similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with $BiPh_3$ followed by $P(OPh)_3$ *in situ* gave the new mixed complexes $[MI_2(CO)_3\{P(OPh)_3\}(BiPh_3)]$. The new mixed complexes $[MoI_2(CO)_3(AsPh_3)(BiPh_3)]$ and $[WI_2(CO)_3(PPh_3)(BiPh_3)]NCMe$ were also made in a similar manner. We are currently investigating the chemistry of these $[MI_2(CO)_3(NCMe)(BiPh_3)]$ compounds, in particular their catalytic activity, in view of Bencze's recent work.[10,11]

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