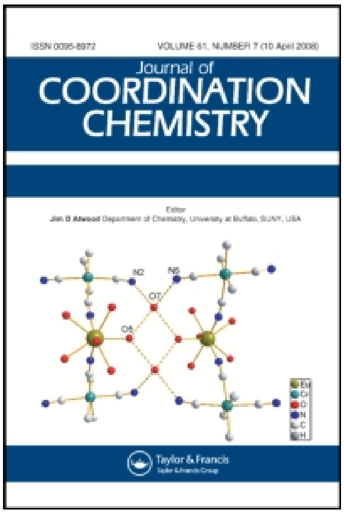

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THE REACTIONS OF $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ WITH NEUTRAL BI- AND TERDENTATE DONOR LIGANDS

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The reaction of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ with an equimolar quantity of L^L {L^L = 2,2′-bipy, 1,10-phen, $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2)} in CH_2Cl_2 at room temperature gave either $[MoCl(GeCl_3)(CO)_3(L$^$L)]$ (L^L = 2,2′-bipy or 1,10-phen) (**1** and **2**) or $[MoCl(GeCl_3)(CO)_2(NCMe)(L$^$L)]$ {L^L = $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) (**3** or **4**), respectively. Equimolar quantities of $[MoCl(GeCl_3)(CO)_2(NCMe)\{Ph_2P(CH_2)PPh_2\}]$ (**3**) and L^L {L^L = 2,2′-bipy or $Ph_2P(CH)_2PPh_2$} react in CH_2Cl_2 at room temperature to afford the cationic complexes $[Mo(GeCl_3)(CO)_2\{Ph_2P(CH_2)PPh_2\}(L$^$L)]Cl$ (**5** and **6**) in good yield. The cationic nature of **6** was established by chloride exchange by reacting $Na[BPh_4]$ with **6** in acetonitrile to give the tetraphenylborate complex $[Mo(GeCl_3)(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BPh_4]$ (**7**). Reaction of equimolar quantities of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ and $PhP(CH_2CH_2PPh_2)_2$ in CH_2Cl_2 at room temperature afforded the dicarbonyl complex $[MoCl(GeCl_3)(CO)_2\{PhP(CH_2CH_2PPh_2)_2\}]$ (**8**) in good yield.

KEYWORDS: Molybdenum, germanium chloride, carbonyl, seven-coordination, reactions, synthesis

INTRODUCTION

Many examples of seven coordinate dihalocarbonyl complexes of molybdenum(II) and tungsten(II) of the type $[MX_2(CO)_3L_2]$ have been reported.[1–8] However, far fewer complexes containing group IVb halides have been reported. The first examples of such complexes were reported in 1968, when Lewis and co-workers[9] and Kummer and Graham[10] reported the preparation of a series of complexes of the types $[MX(YX_3)(CO)_3(L$^$L)]$ {M = Mo, W; $YX_3 = GeCl_3$, $GeBr_3$, $SnCl_3$, $SnBr_3$, *etc*; L^L = 2,2′-bipy, *o*-phen, $Ph_2P(CH_2)_2PPh_2$}. They obtained $[MX(YX_3)(CO)_3(L$^$L)]$ type complexes from reaction of the zero-valent complexes $[M(CO)_4(L$^$L)]$ with YX_4. More recently Riera and co-workers[11] have described the reactions of $[Mo(CO)_3(NCR)_3]$ (M = Mo, R = Me; M = W, R = Et) with $SnBuCl_3$ to give $[MCl(SnBuCl_3)(CO)_3(NCR)_2]$, which react with three equivalents of $P(OR^1)_3$ (R^1 = Me, Et) to afford the dicarbonyl compounds $[MCl(SnBuCl_2)(CO)_2\{P(OR^1)_3\}_3]$.

Previously[12] we have described the preparation of the bis(acetonitrile) complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ from reaction of equimolar quantities of the zero-

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valent complex *fac*-[Mo(CO)$_3$(NCMe)$_3$] (prepared *in situ*) and GeCl$_4$. In this paper we describe the reactions of [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] with bi- and terdentate donor ligands.

EXPERIMENTAL

All reactions described in this paper were carried out under dry nitrogen, using standard Schlenk techniques. The complex [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] was prepared by the published method.[12] The solvent CH$_2$Cl$_2$ was distilled over P$_4$O$_{10}$ before use. 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 carrier gas). Infrared spectra were recorded on a Perkin-Elmer 197 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC 250 CP/MAS spectrometer. All spectra were calibrated against tetramethylsilane. Magnetic susceptibilities were measured using a Johnson-Matthey magnetic susceptibility balance.

[MoCl(GeCl$_3$)(CO)$_3$(2,2'-bipy)] (1)

To [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] (0.500 g, 1.049 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3) with continuous stirring under a stream of dry nitrogen was added 2,2'-bipyridyl (0.164 g, 1.049 mmol), and the mixture stirred for two hours. Filtration, followed by removal of the solvent *in vacuo* afforded the brown complex [MoCl(GeCl$_3$)(CO)$_3$(2,2'-bipy)] (**1**) (yield = 0.32 g, 56%) which was recrystallised from CH$_2$Cl$_2$.

The complexes [MoCl(GeCl$_3$)(CO)$_3$(1,10-phen)] (**2**), [MoCl(GeCl$_3$)(CO)$_2$-(NCMe)(L^L)] {L^L = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1 and 2)} (**3** and **4**) and [MoCl(GeCl$_3$)(CO)$_2${PhP(CH$_2$CH$_2$PPh$_2$)$_2$}] (**8**) were prepared by an analogous method. See Table 1 for physical and analytical data.

[Mo(GeCl$_3$)(CO)$_2$(2,2'-bipy){Ph$_2$P(CH$_2$)PPh$_2$}]Cl (5)

To [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] (0.500 g, 1.049 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3) with continuous stirring under a stream of dry nitrogen was added Ph$_2$P(CH$_2$)PPh$_2$ (0.403, 1.049 mmol). Stirring was continued for two hours, after which 2,2'-bipyridyl (0.164 g, 1.049 mmol) was added *in situ*, and the mixture stirred for a further 18 hours. The mixture was filtered and the solvent removed *in vacuo* to give the brown complex [Mo(GeCl$_3$)(CO)$_2$(2,2'-bipy){Ph$_2$P(CH$_2$)PPh$_2$}]Cl (**5**) (yield = 0.72 g, 76%), which was recrystallised from CH$_2$Cl$_2$.

The complex [Mo(GeCl$_3$)(CO)$_2${Ph$_2$P(CH$_2$)PPh$_2$}$_2$]Cl (**6**) was prepared in a similar manner. See Table 1 for physical and analytical data.

[Mo(GeCl$_3$)(CO)$_2${Ph$_2$P(CH$_2$)PPh$_2$}$_2$][BPh$_4$] (7)

To [Mo(GeCl$_3$)(CO)$_2${Ph$_2$P(CH$_2$)PPh$_2$}$_2$]Cl (0.5 g, 0.430 mmol) dissolved in NCMe (15 cm^3) was added Na[BPh$_4$] (0.147 g, 0.430 mmol), with continous stirring, under a stream of dry nitrogen for 18 hrs. Removal of the solvent *in vacuo*, followed by resolvation in CH$_2$Cl$_2$ (15 cm^3), and filtration to remove NaCl, gave the mustard

Table 1 Physical and Analytical Data[a] for the Reaction Products of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ with Bi- and Terdentate Ligands.

Complex	Colour	Yield (%)	Found (calcd.)%		
			C	H	N
(**1**) $[MoCl(GeCl_3)(CO)_3(2,2'\text{-bipy})]$	Brown	56	28.5	1.4	4.7
			(28.4)	(1.5)	(5.1)
(**2**) $[MoCl(GeCl_3)(CO)_3(1,10\text{-phen})]CH_2Cl_2$	Brown	81	28.8	1.6	4.9
			(29.1)	(1.5)	(4.3)
(**3**) $[MoCl(GeCl_3)(CO)_2(NCMe)\{Ph_2P(CH_2)PPh_2\}]$	Golden Brown	49	43.6	3.4	1.5
			(44.0)	(3.2)	(1.8)
(**4**) $[MoCl(GeCl_3)(CO)_2(NCMe)\{Ph_2P(CH_2)_2PPh_2\}]$	Golden Brown	50	45.2	3.4	1.2
			(44.7)	(3.4)	(1.7)
(**5**) $[Mo(GeCl_3)(CO)_2(2,2'\text{-bipy})\{Ph_2P(CH_2)PPh_2\}]Cl$	Brown	76	49.1	3.6	3.0
			(49.0)	(3.3)	(3.1)
(**6**) $[Mo(GeCl_3)(CO)_2\{Ph_2P(CH_2)PPh_2\}_2]Cl$	Mustard	77	55.0	4.1	
			(54.2)	(3.9)	
(**7**) $[Mo(GeCl_3)(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BPh_4]$	Mustard	55	64.5	4.8	
			(64.3)	(4.5)	
(**8**) $[MoCl(GeCl_3)(CO)_2\{PhP(CH_2CH_2PPh_2)_2\}]$	Orange	87	48.1	3.9	
			(48.0)	(3.7)	

[a] Calculated values are in parentheses.

coloured complex $[Mo(GeCl_3)(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BPh_4]$ (**7**) (yield = 0.34 g, 55%), which was recrystallised from CH_2Cl_2. See Table 1 for physical and analytical data.

RESULTS AND DISCUSSION

Equimolar quantities of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ and $L^\frown L$ $\{L^\frown L = 2,2'$-bipy, 1,10-phen, $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2)$\}$ react in CH_2Cl_2 at room temperature to afford the previously reported[10] complex $[MoCl(GeCl_3)(CO)_3(2;2'\text{-bipy})]$ (**1**) and the new complexes $[MoCl(GeCl_3)(CO)_3(1,10\text{-phen})]$ (**2**) and $[MoCl(GeCl_3)(CO)_2(NCMe)\{Ph_2P(CH_2)_nPPh_2\}]$ (**3**,**4**) in good yield. Treatment of $[MoCl(GeCl_3)(CO)_2(NCMe)\{Ph_2P(CH_2)PPh_2\}]$ (**3**) with one equivalent of $L^\frown L$ $\{L^\frown L = 2,2'$-bipy, $Ph_2P(CH_2)PPh_2\}$ in CH_2Cl_2 at room temperature gave the cationic complexes $[Mo(GeCl_3)(CO)_2(L^\frown L)\{Ph_2P(CH_2)PPh_2\}]Cl$ (**5** and **6**) in high yield. The cationic nature of the complexes **5** and **6** was confirmed by reaction of **6** with an equimolar quantity of $Na[BPh_4]$ in acetonitrile at room temperature to give the chloro-exchanged product $[Mo(GeCl_3)(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BPh_4]$ (**7**). The reaction of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ with an equimolar amount of $PhP(CH_2CH_2PPh_2)_2$ in CH_2Cl_2 at room temperature gave the terdentate $PhP(CH_2CH_2PPh_2)_2$ complex $[MoCl(GeCl_3)(CO)_2\{PhP(CH_2CH_2)PPh_2)_2\}]$ (**8**) in excellent yield. Complexes **1** to **8** were characterised by elemental analysis (C, H and N) (Table 1), infrared (Table 2) and ^1H NMR spectroscopy (Table 3). Confirmation of $[MoCl(GeCl_3)(CO)_3$ (1,10-phen)$]\cdot CH_2Cl_2$ (**2**) as a CH_2Cl_2 solvate was shown by repeated elemental analyses and ^1H NMR spectroscopy. All the complexes **1** to **8** were shown by magnetic susceptibility measurements to be diamagnetic, which would be expected since they obey the effective atomic number rule. The complexes **1** to **8** are all soluble in chlorinated solvents such as

Table 2 Infrared Data[a] for the Reaction Products of [MoCl($GeCl_3$)$(CO)_3$$(NCMe)_2$] with Bi- and Terdentate Ligands.

Complex	ν(CO) cm^{-1}	ν(CN) cm^{-1}
(**1**)	2020 (s), 1920 (s) and 1875 (m)	
(**2**)	2015 (s), 1930 (s) and 1870 (s)	
(**3**)	1950 (s) and 1885 (s)	2300 (w) and 2285 (w)
(**4**)	1920 (s) and 1865 (s)	2300 (w) and 2285 (w)
(**5**)	1948 (s) and 1876 (s)	
(**6**)	1950 (s) and 1885 (s)	
(**7**)	1950 (s) and 1886 (s)	
(**8**)	1947 (s) and 1901 (s)	

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

CH_2Cl_2 and $CHCl_3$; however, the 2,2′-bipy and 1,10-phen complexes **1**, **2** and **5** are much less soluble than the bidentate phosphine ligand complexes **3**, **4**, **6–8**. All complexes are insoluble in diethyl ether and hydrocarbon solvents.

It is interesting to note that reaction of [MoCl($GeCl_3$)$(CO)_3$$(NCMe)_2$] with an equimolar amount of the electron-rich bidentate nitrogen donor ligands 2,2′-bipy and 1,10-phen gave the acetonitrile replaced complexes [MoCl($GeCl_3$)$(CO)_3$($L^{\frown}L$)], whereas with the less electron-rich donor ligands $Ph_2P(CH_2)_nPPh_2$ one acetonitrile and one carbon monoxide ligand are replaced. This difference in behaviour is likely to be due to the different electronic properties of the bidentate nitrogen and phosphorus donor ligands. Reaction of [MoCl($GeCl_3$)$(CO)_3$$(NCMe)_2$] with an equimolar quantity of $Ph_2P(CH_2)_nPPh_2$ must initially give the mono(acetonitrile) complex [MoCl($GeCl_3$)$(CO)_3$(NCMe){η^1-$Ph_2P(CH_2)_nPPh_2$}] whereby the metal is less electron rich following displacement of acetonitrile. This would result in less back-bonding from the metal to the empty π^*-orbitals on the carbonyl ligands, and hence displacement of the carbonyl ligand occurs in perference to an acetonitrile ligand. The X-ray crystal structure of the tungsten complex [WBr($GeBr_3$)$(CO)_3$(2,2′-bipy)] has been determined[13] and the metal has a capped trigonal prismatic structure with the bromide ligand in the capping position. It may be that the molybdenum analogue (**1**) and the 1,10-phen complex (**2**) have a similar geometry. It should also be noted that the spectroscopic properties of **1**

Table 3 ^{1}H-NMR Data[a] for the Reaction Products of [MoCl($GeCl_3$)$(CO)_3$$(NCMe)_2$] with Bi- and Terdentate Ligands.

Complex	^{1}H (δ) ppm
(1)	9.65 (d, 2H, 2,2′-bipy); 9.35 (m, 4H, 2,2′-bipy); 8.82 (d, 2H, 2,2′-bipy)
(2)	9.75 (d, 2H, 1,10-phen); 9.6 (d, 2H, 1,10-phen); 9.1 (d, 2H, 1,10-phen); 8.85 (d, 2H, 1,10-phen); 5.3 (s, 2H, CH_2Cl_2)
(3)	7.35 (m, 20H, Ph); 4.5 (m, 2H, PCH_2); 2.2 (s, 3H, Me)
(4)	7.4 (m, 20H, Ph); 3.0 (m, 4H, PCH_2); 2.3 (s, 3H, Me)
(5)	9.3 (d, 2H, 2,2′-bipy); 8.9 (m, 4H, 2,2′-bipy); 8.3 (d, 2H, 2,2′-bipy); 7.25, 7.05 (m, 20H, Ph); 4.4 (m, 2H, PCH_2)
(6)	7.25 (m, 40H, Ph); 4.15 (m, 4H, PCH_2)
(7)	7.6–7.2 (m, 60H, Ph); 4.2 (m, 4H, PCH_2)
(8)	7.25 (m, 25H, Ph); 3.4 (m, 8H, PCH_2)

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

and **2** closely resemble those of [WBr(GeBr$_3$)(CO)$_3$(2,2′-bipy)], a fact which would support a capped trigonal prismatic structure. However, the molecular structure[14] of the related molybdenum-tin complex [MoCl(SnMeCl$_2$)(CO)$_3$(2,2′-bipy)] has a capped octahedral structure, with the tin atom occupying the capping position. Also, the X-ray crystal structure[11] of the *tris*-trimethylphosphite complex [MoCl(SnBuCl$_2$)(CO)$_2${P(OMe)$_3$}$_3$] shows the geometry to be intermediate between a distorted capped trigonal prism and a distorted capped octahedral geometry. The molecular structure of the majority of [MX$_2$(CO)$_3$L$_2$] complexes have a capped octahedral structure[15] and thus this geometry cannot be ruled out (in particular for complexes **3** to **8**). Many attempts were made to grow suitable crystals for X-ray crystallography without success.

As expected, reactions of [MoCl(GeCl$_3$)(CO)$_2$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}] (**3**) with L^L{L^L = 2,2′-bipy and Ph$_2$P(CH$_2$)PPh$_2$} gave the acetonitrile and chloride replaced products [Mo(GeCl$_3$)(CO)$_2$(L^L){Ph$_2$P(CH$_2$)PPh$_2$}]Cl (**5** and **6**), which have two carbonyl bands in their infrared spectra at ν(CO) = 1948 and 1876 cm^{-1} (**5**) and 1950 and 1885 cm^{-1} (**6**), respectively. The terdentate ligand PhP(CH$_2$CH$_2$PPh$_2$)$_2$ reacts with [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] to give the product [MoCl(GeCl$_3$)(CO)$_2${PhP(CH$_2$CH$_2$PPh$_2$)$_2$}] *via* displacement of two acetonitrile molecules and a carbonyl ligand.

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