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LETTER

The preparation of the novel seven-coordinate compound $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ and its reactions with one equivalent of L ($L=PPh_3$, $AsPh_3$ or $SbPh_3$) to give $[MoCl(GeCl_3)(CO)_3(NCMe)L]$ or $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$ depending upon the solvent

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Many seven-coordinate dihalocarbonyl complexes of the type $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl, Br or I; L = Group 5 donor ligand) have been prepared [1]. The importance of these compounds has been 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 [2]. However, analogous halogermanium compounds are scarce; some early examples of this type which have been reported are $[MoX(GeX_3)(CO)_3(bipy)]$ (X = Cl or I) [3]. In this communication we describe the synthesis of the novel highly reactive seven-coordinate compound $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**), and report its reactions with 1 equiv. of L ($L=PPh_3$, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 and NCMe.

Results and discussion

Equimolar quantities of $[Mo(CO)_3(NCMe)_3]$ (prepared *in situ* by reacting $[Mo(CO)_6]$ in refluxing acetonitrile for 24 h [4]) and $GeCl_4$ react *in situ* to afford an orange solution which after removal of the solvent *in vacuo* gives the golden yellow solid $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) in high yield. This reaction presumably occurs by oxidative-addition of the zero-valent complex $[Mo(CO)_3(NCMe)_3]$ with $GeCl_4$ to give via cleavage of a Ge–Cl bond and elimination of an acetonitrile molecule the oxidized product **1**. Compound **1** is very air-sensitive in the solid state and extremely air-sensitive in solution, however it can be stored under nitrogen for prolonged periods of time. Compound **1** is soluble in polar solvents such as $CHCl_3$, CH_2Cl_2, NCMe or $OC(Me)_2$, however it is only very slightly soluble in hydrocarbon solvents and Et_2O. Complex **1** has been characterised by IR (Table 1), ^1H NMR spectroscopy (Table 2) and elemental analysis (C, H and N) (Table 3). The structure of **1** is likely to be capped octahedral since most seven-coordinate $[MX_2(CO)_3L_2]$ complexes have this geometry [5]. The related diiodo compound $[WI_2(CO)_3(NCMe)_2]$ has been shown by X-ray crystallography [6] to have the structure shown in Fig. 1, where the two iodide ligands have been replaced by a chloride ligand on the capping face and the considerably larger $GeCl_3$ group on the uncapped face, which may be the structure of **1**.

The reactions of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) with an equimolar amount of L ($L=PPh_3$, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 at room temperature gave the acetonitrile displaced products $[MoCl(GeCl_3)$-

TABLE 1. IR data[a] for the complexes $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$, $[MoCl(GeCl_3)(CO)_3(NCMe)L]$ and $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$

Complex	$\nu(C\equiv O)$ (cm^{-1})	$\nu(N\equiv C)$ (cm^{-1})
1	2040(s), 1953(s), 1877(m)	2314(m), 2286(m)
2	2025(m), 1940(s), 1870(s)	2300(w), 2280(w)
3	2020(m), 1930(s), 1875(s)	2300(w), 2280(w)
4	2020(s), 1925(s), 1860(s)	2300(w), 2280(w)
5	1945(s), 1870(s)	2300(w), 2280(w)
6	1945(s), 1875(s)	2300(w), 2285(w)
7	1945(s), 1880(s)	2300(w), 2285(w)

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

TABLE 2. ^1H NMR data for the complexes $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$[a], $[MoCl(GeCl_3)(CO)_3(NCMe)L]$[a] and $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$[b]

Complex	^1H NMR (δ) (ppm)
1	2.45 (s, Me)
2	7.4 (m, 15H, Ph); 2.4 (s, 3H, Me)
3	7.35 (m, 15H, Ph); 2.4 (s, 3H, Me)
4	7.6, 7.45, 7.35 (m, 15H, Ph); 2.2 (s, 3H, Me)
5	7.40 (m, 15H, Ph); 2.35 (s, 6H, Me)
6	7.35 (m, 15H, Ph); 2.3 (s, 6H, Me)
7	7.6, 7.45, 7.35 (m, 15H, Ph); 2.3 (s, 6H, Me)

[a]Spectra recorded in $CDCl_3$ (25 °C) and referenced to Me_4Si. [b]Spectra recorded in CD_3COCD_3 (25 °C).

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TABLE 3. Physical and analytical data for the complexes $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$, $[MoCl(GeCl_3)(CO)_3(NCMe)L]$ and $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$

Compound	Colour	Yield (%)	Analysis (%)[a] C	H	N	Reaction times
$[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**)	golden brown	94	17.2 (17.6)	1.5 (1.3)	6.1 (5.9)	
$[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ (**2**)	golden brown	53	39.2 (39.6)	2.7 (2.6)	1.5 (2.0)	1 min
$[MoCl(GeCl_3)(CO)_3(NCMe)(AsPh_3)]$ (**3**)	golden brown	53	37.6 (37.2)	2.5 (2.4)	1.5 (1.9)	3 min
$[MoCl(GeCl_3)(CO)_3(NCMe)(SbPh_3)]$ (**4**)	orange	50	34.7 (35.0)	2.4 (2.3)	1.4 (1.8)	5 min
$[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ (**5**)	yellow	47	40.1 (40.6)	2.4 (3.0)	3.7 (3.9)	18 h[b]
$[MoCl(GeCl_3)(CO)_2(NCMe)_2(AsPh_3)]$ (**6**)	yellow	41	37.7 (38.2)	2.7 (2.8)	3.4 (3.7)	18 h[b]
$[MoCl(GeCl_3)(CO)_2(NCMe)_2(SbPh_3)]$ (**7**)	yellow	44	36.0 (36.0)	2.6 (2.6)	3.2 (3.5)	18 h[b]

[a]Calculated values in parentheses.[b]A precipitate of the products started to form after 1, 3 and 5 min for **5** and **6** and **7**, respectively; however, these reactions were left overnight to obtain a higher yield.

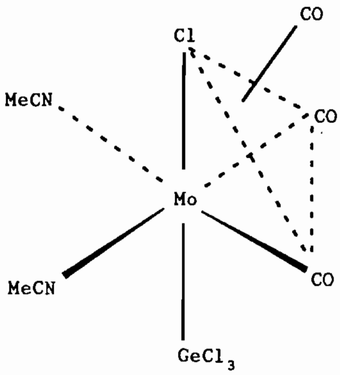

Fig. 1. Proposed structure of the seven-coordinate complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**).

$(CO)_3(NCMe)L]$ (**2**–**4**) in good yield. Compounds **2**–**4** have been characterised by elemental analysis, IR and ^1H NMR spectroscopy (Tables 1–3). However, equimolar quantities of **1** and L ($L = PPh_3$, $AsPh_3$ or $SbPh_3$) react in NCMe to give, after initial effervescence of CO, the bis-acetonitrile complexes $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$ (**5**–**7**). Complexes **5**–**7** have also been characterised by elemental analysis (Table 3), IR (Table 1) and ^1H NMR spectroscopy (Table 2). Compounds **2**–**7** are all considerably more stable than **1**. The mono-acetonitrile compounds **2**–**4** are more soluble in polar solvents than the bis-acetonitrile complexes **5**–**7**.

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