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# The synthesis and reactions with neutral monodentate ligands of the seven-coordinate complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$

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## Abstract

The reaction of *fac*-$[Mo(CO)_3(NCMe)_3]$ (prepared *in situ*) with an equimolar quantity of $GeCl_4$ rapidly affords the molybdenum(II) seven-coordinate complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) in quantitative yield. Equimolar quantities of **1** and L (L = $PPh_3$, $AsPh_3$ or $SbPh_3$) react in $CH_2Cl_2$ or NCMe to give $[MoCl(GeCl_3)(CO)_3(NCMe)L]$ or $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$, respectively. The reactions of $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ and $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ with a series of neutral and anionic donor ligands are described. Complex **1** reacts with two equivalents of L (L = $PPh_3$, $AsPh_3$, $SbPh_3$ or $PPh_2Cy$) in $CH_2Cl_2$ to afford $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2]$ and $[MoCl(GeCl_3)(CO)_3L_2]$. Reactions of $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2]$ are also discussed.

*Key words:* Molybdenum; Acetonitrile; Germanium; Monodentate

## 1. Introduction

In comparison with the wide range of known seven-coordinate halocarbonyl complexes of molybdenum(II) and tungsten(II) [1–12], very few complexes of this type containing Group IVB halides have been described. The first complexes of this type to be reported were $[MoCl(SnCl_3)(CO)_3(bipy)]$, by Lewis and co-workers [13], and $[MoCl(SnCl_2R)(CO)_3(bipy)]$ (R = Me, $^nBu$, $CH{=}CH_2$, Ph), $[MoCl(SnClPh_2)(CO)_3(bipy)]$, and $[MoX(GeX_3)(CO)_3(bipy)]$ (X = Cl, I) and $[MoX(SnX_3)(CO)_3(bipy)]$ (X = Cl, Br, I), by Kummer and Graham [14]. Several other papers have appeared involving seven-coordinate complexes of molybdenum(II) and tungsten(II) containing Group IVB halides, including the complexes $[WBr(GeBr_3)(CO)_3(bipy)]$ [15] and $[MoCl(SnMeCl_2)(CO)_3(bipy)]$ [16], which were crystallographically characterised.

In 1989 [17] we described the synthesis and reactions with donor ligands of the seven-coordinate complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$, which was prepared from reaction of equimolar quantities of *fac*-$[Mo(CO)_3(NCMe)_3]$ and $SnCl_4$. In this paper we describe the preparation of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ and its reactions with neutral monodentate ligands. The reactions of $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$, $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ and $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2]$ are also discussed. A preliminary report has appeared [18].

## 2. Results and discussion

Refluxing a solution of $[Mo(CO)_6]$ in acetonitrile for 24 h under an inert atmosphere gave the bright yellow zero-valent complex *fac*-$[Mo(CO)_3(NCMe)_3]$ [19], and when this was treated *in situ* at 0°C with an equimolar quantity of $GeCl_4$ the solution immediately turned bright orange. The solution was stirred for 4 h, after which the solvent was removed *in vacuo* to afford the golden brown oxidised molybdenum(II) complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) formed by displacement of an acetonitrile ligand and cleavage of a Ge–Cl bond. Complex **1** is extremely air-sensitive in solution and also very air-sensitive in the solid state, but it can be stored under nitrogen for several days without decomposition. It is soluble in $CHCl_3$, $CH_2Cl_2$, NCMe and acetone, but only slightly soluble in hydrocarbon

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TABLE 1. Physical and analytical data for the seven-coordinate complex [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] and its derivatives

| Complexes | Colour | Yield (%) | Analytical data (Found (Calc.) (%)) |
|---|---|---|---|
| **1** [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] | golden brown | 94 | C: 17.2 (17.6)<br>H: 1.5 (1.3)<br>N: 6.1 (5.9) |
| **2** [MoCl(GeCl$_3$)(CO)$_3$(NCMe)(PPh$_3$)] | golden brown | 53 | C: 39.2 (39.6)<br>H: 2.7 (2.6)<br>N: 1.5 (2.0) |
| **3** [MoCl(GeCl$_3$)(CO)$_3$(NCMe)(AsPh$_3$)] | golden brown | 53 | C: 37.6 (37.2)<br>H: 2.5 (2.4)<br>N: 1.5 (1.9) |
| **4** [MoCl(GeCl$_3$)(CO)$_3$(NCMe)(SbPh$_3$)] | orange | 50 | C: 34.7 (35.0)<br>H: 2.4 (2.3)<br>N: 1.4 (1.8) |
| **5** [MoCl(GeCl$_3$)(CO)$_3$(NCMe)(PCyPh$_2$)] · CH$_2$Cl$_2$ | brown | 52 | C: 36.6 (36.6)<br>H: 3.5 (3.3)<br>N: 1.4 (1.8) |
| **6** [MoCl(GeCl$_3$)(CO)$_3$(NCMe){P(OPh)$_3$}] · $\frac{1}{2}$CH$_2$Cl$_2$ | golden brown | 29 | C: 35.6 (35.8)<br>H: 2.5 (2.5)<br>N: 1.9 (1.8) |
| **7** [MoCl(GeCl$_3$)(CO)$_2$(NCMe)(PPh$_3$)$_2$] | orange | 40 | C: 51.5 (51.6)<br>H: 3.5 (3.6)<br>N: 1.0 (1.5) |
| **8** [MoCl(GeCl$_3$)(CO)$_3$(AsPh$_3$)$_2$] | golden brown | 49 | C: 46.8 (46.5)<br>H: 3.0 (3.0)<br>N: – – |
| **9** [MoCl(GeCl$_3$)(CO)$_3$(SbPh$_3$)$_2$] | orange | 52 | C: 42.5 (42.6)<br>H: 2.7 (2.7)<br>N: – – |
| **10** [MoCl(GeCl$_3$)(CO)$_3$(PCyPh$_2$)$_2$] | golden brown | 61 | C: 49.8 (50.4)<br>H: 4.9 (4.6)<br>N: – – |
| **11** [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$)$_3$] · $\frac{1}{2}$CH$_2$Cl$_2$ | golden brown | 75 | C: 56.8 (56.8)<br>H: 3.9 (3.9)<br>N: – – |
| **12** [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$)$_2$(AsPh$_3$)] | brown | 52 | C: 55.9 (56.2)<br>H: 3.9 (3.8)<br>N: – – |
| **13** [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$)$_2$(SbPh$_3$)] | brown | 61 | C: 53.7 (54.1)<br>H: 3.9 (3.7)<br>N: – – |
| **14** [Mo(GeCl$_3$)(CO)$_2$(PPh$_3$)$_2${Ph$_2$P(CH$_2$)PPh$_2$}]Cl | orange | 80 | C: 58.8 (59.3)<br>H: 4.1 (4.1)<br>N: – – |
| **15** [Mo(GeCl$_3$)(CO)$_2$(PPh$_3$)$_2${Ph$_2$P(CH$_2$)$_2$PPh$_2$}]Cl | orange | 69 | C: 59.4 (59.6)<br>H: 4.3 (4.2)<br>N: – – |
| **16** [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$)(bipy)] | brown | 77 | C: 45.7 (45.9)<br>H: 3.0 (3.0)<br>N: 3.4 (3.6) |
| **17** [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$)(1,10-phen)] · CH$_2$Cl$_2$ | brown | 71 | C: 44.4 (44.3)<br>H: 2.7 (2.8)<br>N: 3.5 (3.1) |
| **18** [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$){Ph$_2$P(CH$_2$)PPh$_2$}] · $\frac{1}{2}$CH$_2$Cl$_2$ | orange | 72 | C: 51.7 (51.8)<br>H: 3.7 (3.5)<br>N: – – |
| **19** [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$){Ph$_2$P(CH$_2$)$_2$PPh$_2$}] · $\frac{1}{2}$CH$_2$Cl$_2$ | orange | 72 | C: 51.8 (52.2)<br>H: 3.5 (3.4)<br>N: – – |
| **20** [N$^n$Bu$_4$][MoCl$_2$(GeCl$_3$)(CO)$_3$(PPh$_3$)] | golden brown | 59 | C: 47.5 (47.6)<br>H: 5.7 (5.5)<br>N: 1.3 (1.5) |

TABLE 1 (continued)

| Complexes | Colour | Yield (%) | Analytical data (Found (Calc.) (%)) |
|---|---|---|---|
| **21** $[N^nBu_4][MoCl(Br_3)(GeCl_3)(CO)_3(PPh_3)]$ | golden brown | 55 | C: 39.2 (39.0)<br>H: 4.9 (4.5)<br>N: 0.8 (1.2) |
| **22** $[N^nBu_4][MoClI(GeCl_3)(CO)_3(PPh_3)]$ | golden brown | 65 | C: 43.2 (43.3)<br>H: 5.2 (5.0)<br>N: 1.3 (1.4) |
| **23** $[N^nBu_4][MoClBr(GeCl_3)(CO)_3(PPh_3)]$ | golden brown | 67 | C: 45.6 (45.4)<br>H: 5.5 (5.3)<br>N: 1.2 (1.4) |
| **24** $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ | yellow | 47 | C: 40.0 (40.6)<br>H: 2.9 (3.0)<br>N: 3.7 (3.9) |
| **25** $[MoCl(GeCl_3)(CO)_2(NCMe)_2(AsPh_3)]$ | yellow | 41 | C: 37.7 (38.2)<br>H: 2.7 (2.8)<br>N: 3.4 (3.7) |
| **26** $[MoCl(GeCl_3)(CO)_2(NCMe)_2(SbPh_3)]$ | yellow | 44 | C: 36.0 (36.0)<br>H: 2.6 (2.6)<br>N: 3.2 (3.5) |
| **27** $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)(AsPh_3)] \cdot CH_2Cl_2$ | orange | 62 | C: 46.6 (46.4)<br>H: 3.3 (3.3)<br>N: 1.0 (1.3) |
| **28** $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)(SbPh_3)]$ | orange | 57 | C: 46.5 (47.0)<br>H: 3.2 (3.3)<br>N: 1.0 (1.4) |
| **29** $[MoCl(GeCl_3)(CO)_2(NCMe)(AsPh_3)(SbPh_3)]$ | orange | 51 | C: 44.8 (45.0)<br>H: 3.1 (3.1)<br>N: 0.8 (1.3) |

solvents and diethyl ether. It was characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2) and $^1H$ NMR spectroscopy (Table 3). The magnetic susceptibility of **1** ($\chi = 0.244 \times 10^{-6}$ cgs) shows it to be diamagnetic, as expected since the complex obeys the effective atomic number rule. The low temperature $^{13}C$ NMR ($-70°C$, $CD_2Cl_2$) spectrum of **1** in the carbonyl region shows resonances at $\delta = 231.53$, 229.57, 223.75, 218.89, 216.48 and 202.92 ppm. This suggests several isomers are present in solution. The related complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ [17] shows 12 resonances in the range $\delta = 227.84$–201.97 pm, whereas the diiodo complex $[WI_2(CO)_3(NCMe)_3]$ [20] shows two resonances at $\delta$ 202.36 and 228.48 ppm, in an intensity ratio of *ca.* 2:1. In the light of the work of Colton and Kevekordes [21], the resonances for **1** at $\delta = 231.53$ and 229.57 can be assigned to a capping carbonyl in a capped octahedral structure. Since the X-ray crystal structure of $[WI_2(CO)_3(NCMe)_2]$ has a capped octahedral geometry [20], one likely structure of **1** is shown in Fig. 1, that has the two iodide groups replaced by a Cl and a $GeCl_3$ group, with the larger $GeCl_3$ group in the less crowded uncapped face. Attempts to grow suitable single crystals for X-ray crystallography were unsuccessful. Many attempts were made to prepare the tungsten analogue $[WCl(GeCl_3)(CO)_3(NCMe)_2]$ by reaction of *fac*-$[W(CO)_3(NCMe)_3]$ [19] (prepared *in situ*) with an equimolar quantity of $GeCl_4$, the green material generally isolated from these reactions showed a number of carbonyl bands in the IR spectrum and there are probably several products in the solution. One of these may be $[WCl_2(CO)_3(NCMe)_2]$, in view of Buzar's work [22] on the photochemical reactions of $[W(CO)_6]$ and $N^\frown N$ ($N^\frown N$ = 2,2′-bipy, 1,10-phen or NCMe) in $CCl_4$ to give $[W(CO)_4(N^\frown N)]$, $[WCl_2(CO)_3(N^\frown N)]$ ($N^\frown N$ = 2,2′-bipy, 1,10-phen), $[W(CO)_5(NCMe)]$ or $[W(CO)_4(NCMe)_2]$. It should be noted [17] that the analogous complex $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ could not be isolated in a pure state.

The reactions of **1** with one equivalent of L (L = $PPh_3$, $AsPh_3$, $SbPh_3$, $PCyPh_2$ or $P(OPh)_3$) or two equivalents of L (L = $PPh_3$, $AsPh_3$, $SbPh_3$ or $PCyPh_2$) in $CH_2Cl_2$ at room temperature give either products from replacement of acetonitrile, *viz.*, $[MoCl(GeCl_3)(CO)_3(NCMe)L]$ (**2–6**) or of both carbon monoxide and acetonitrile, *viz.* $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2]$ (**7**) and $[MoCl(GeCl_3)(CO)_3L_2]$ (**8–10**). The new complexes **2–10** were all characterised by elemental analysis (C, H and N) (Table 1) and IR (Table 2) and, in selected cases, $^1H$ NMR spectroscopy (Table 3). Con-

TABLE 2. Infrared data [a] for the seven-coordinate complex [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] and its derivatives

| Complex | $\nu$(C≡O) (cm$^{-1}$) | $\nu$(C≡N) (cm$^{-1}$) |
|---|---|---|
| **1** | 2040s, 1953s and 1877m | 2314w and 2286w |
| **2** | 2025m, 1940s and 1870s | 2300w and 2280w |
| **3** | 2020s, 1930s and 1875s | 2300w and 2280w |
| **4** | 2020s, 1925s and 1860s | 2300w and 2280w |
| **5** | 2040m, 1930s and 1860s | 2300w and 2280w |
| **6** | 2045m, 1960s and 1895s | 2300w and 2280w |
| **7** | 1930s and 1865s | 2300w and 2280w |
| **8** | 2030m, 1935s and 1870s | – |
| **9** | 2025m, 1935s and 1870s | – |
| **10** | 2020m, 1942s and 1866s | – |
| **11** | 1955s and 1880s | – |
| **12** | 1960s and 1880s | – |
| **13** | 1955s and 1875s | – |
| **14** | 1950s and 1875s | – |
| **15** | 1950s and 1880s | – |
| **16** | 1930s and 1855s | – |
| **17** | 1915s and 1840s | – |
| **18** | 1930s and 1865s | – |
| **19** | 1925s and 1860s | – |
| **20** | 2010m, 1940s and 1870s | – |
| **21** | 2020s, 1950s and 1880s | – |
| **22** | 2010m, 1960s and 1870s | – |
| **23** | 2020m, 1935s and 1865s | – |
| **24** | 1945s and 1870s | 2300w and 2280w |
| **25** | 1945s and 1875s | 2300w and 2285w |
| **26** | 1945s and 1880s | 2290w and 2275w |
| **27** | 1930s and 1860s | 2300w and 2280w |
| **28** | 1935s and 1870s | 2300w and 2280w |
| **29** | 1935s and 1870s | 2300w and 2280w |

[a] Spectra recorded in CHCl$_3$ as thin films between NaCl plates; s = strong, w = weak, m = medium.

firmation of the existence of complexes **5** and **6**, as CH$_2$Cl$_2$ and $\frac{1}{2}$CH$_2$Cl$_2$ solvates, respectively come from repeated elemental analyses (C, H and N) and $^1$H NMR spectroscopy. Complexes **2–10** were in general less soluble but more stable than **1**. However, they are air-sensitive in solution and as solids must be stored under nitrogen. The reaction times needed to give [MoCl(GeCl$_3$)(CO)$_3$(NCMe)L] (**2–6**) were similar to those required for the diiodo complexes [MI$_2$(CO)$_3$(NCMe)L] [23]. Several attempts were made to prepare the chloro-bridged dimers [Mo($\mu$-Cl)(GeCl$_3$)(CO)$_3$L]$_2$ by stirring solutions of [MoCl(GeCl$_3$)(CO)$_3$(NCMe)L] in CH$_2$Cl$_2$ at room temperature or in refluxing CHCl$_3$ for 24 h. In both cases the complexes did not dimerise and only the mono(acetonitrile) starting materials were isolated from these reactions. This is in marked contrast to the reactions of [MoCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$] with equimolar amounts of L (L = PPh$_3$, AsPh$_3$, SbPh$_3$, py, 3Br-py, 4Br-py, or P(OPh)$_3$) in CH$_2$Cl$_2$ solution at room temperature, which rapidly afford the chloro-bridged dimers, [Mo($\mu$-Cl)(SnCl$_3$)(CO)$_3$L]$_2$ [24]. It is likely that both steric and electronic effects play a part in this large difference in reactivity. The SnCl$_3$ group is larger, and hence would force out the acetonitrile ligand more readily from these crowded seven-coordinate complexes, and GeCl$_3$ is a more electronegative group than SnCl$_3$ and so would make the metal more positive and hence strengthen the Mo–NCMe bond in [MoCl(GeCl$_3$)(CO)$_3$(NCMe)L].

It is noteworthy that reaction of **1** with two equivalents of PPh$_3$ in CH$_2$Cl$_2$ at room temperature gave, after much evolution of carbon monoxide, the complex [MoCl(GeCl$_3$)(CO)$_2$(NCMe)(PPh$_3$)$_2$] (**7**) by displacement of an acetonitrile and a carbonyl ligand. The IR spectrum of **7**, which has two carbonyl stretching bands at 1930 and 1865 cm$^{-1}$, confirmed the loss of carbon monoxide from **1**. It might have been expected that two equivalents of L would react with **1** to give the acetonitrile-displaced products [MoCl(GeCl$_3$)(CO)$_3$L$_2$], as is found for L = AsPh$_3$, SbPh$_3$ and PCyPh$_2$. It should be noted that reactions of [MI$_2$(CO)$_3$(NCMe)$_2$] (M = Mo or W) [25] and [MoCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$] [17] with two equivalents of PPh$_3$ in CH$_2$Cl$_2$ at room temperature give the expected acetonitrile-replaced products [MI$_2$(CO)$_3$(PPh$_3$)$_2$] and [MoCl(SnCl$_3$)(CO)$_3$(PPh$_3$)$_2$], respectively. The different behaviour arising from the presence of the GeCl$_3$ group is likely to be due to the higher electronegativity of the latter which lowers the electron density at the metal thus strengthening the Mo–NCMe bond and weakening the Mo–CO bond as a result of there being less electron density on the metal to back-bond into the empty $\pi^*$-orbitals of the CO ligand. It should also be noted that Brisdon and Hodson [26] prepared the analogous dihalo complexes [MoX$_2$(CO)$_2$(NCMe)L$_2$] (X = Br, L = PEtPh$_2$, PEt$_2$Ph or PMe$_2$Ph; X = Cl, Br or I, L = PMePh$_2$) by bubbling N$_2$ through solutions of [MoX$_2$(CO)$_3$L$_2$] in acetonitrile at room temperature. They also found that the ease of decarbonylation of [MoX$_2$(CO)$_3$(PMePh$_2$)$_2$] to [MoX$_2$(CO)$_2$(PMePh$_2$)$_2$] was in the order Cl$^-$ > Br$^-$ > I$^-$, in agreement with our observations. However, it should be noted that reactions of [MoCl(GeCl$_3$)(CO)$_2$(NCMe)(PPh$_3$)$_2$] (**7**) with an equimolar quantity of L (L = PPh$_3$, AsPh$_3$ or SbPh$_3$) gives the tris-ligand complexes [MoCl(GeCl$_3$)(CO)$_2$(PPh$_3$)$_2$L] (**11–13**) by displacement of the labile acetonitrile ligand. Also reaction of **7** with an equimolar amount of the ligands Ph$_2$P(CH$_2$)$_n$PPh$_2$ ($n$ = 1 and 2) in CH$_2$Cl$_2$ at room temperature gives the seven-coordinate cationic complexes [Mo(GeCl$_3$)(CO)$_2$(PPh$_3$)$_2${Ph$_2$P(CH$_2$)$_n$PPh$_2$}]Cl (**14** and **15**) by displacement of an acetonitrile and a chloride ligand. Complexes **11–15** were characterised by elemental analysis (Table 1) and by IR (Table 2) and, for the $\frac{1}{2}$CH$_2$Cl$_2$ solvated complex **11** by $^1$H NMR spectroscopy (Table 3).

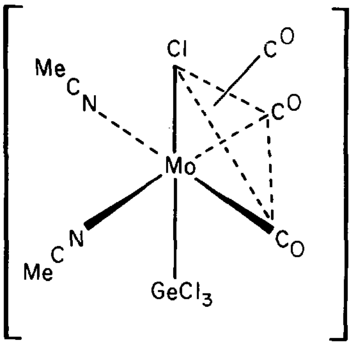


Fig. 1. One possible structure for $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (1).

The complex $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ (**2**) (prepared *in situ*) reacts with an equimolar quantity of the neutral bidentate donor ligands $L\frown L$ {$L\frown L$ = 2,2'-bipy, 1,10-phen, or $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ or 2)} in $CH_2Cl_2$ at room temperature to afford the mixed ligand complexes $[MoCl(GeCl_3)(CO)_2(PPh_3)(L\frown L)]$ (**16–19**) in high yield. Reaction of **2** with an equimolar quantity of $[N^nBu_4]X$ (X = Cl, $Br_3$, I, Br) gives the anionic seven-coordinate compounds $[N^nBu_4][MoClX(GeCl_3)(CO)_3(PPh_3)]$ (**20–23**). The new complexes **16–23** were characterised as before (Tables 1-3). The existence of **17**, **18** and **19** as $CH_2Cl_2$ (**17**) or $\frac{1}{2}CH_2Cl_2$ (**18** and **19**) solvates was confirmed by repeated elemental analyses (C, H and N) and $^1H$ NMR spectroscopy. A number of low temperature (−70°C) $^{13}C$ NMR spectra was obtained, but, they did not show satisfactory carbonyl resonances owing to the poor solubility and low stability of the complexes in solution. It is noteworthy that the reaction of the related diiodo complexes $[MI_2(CO)_3(NCMe)(PPh_3)]$ with an equimolar amount of $L\frown L$ {$L\frown L$ = 2,2-bipy or 1,10-phen} affords the cationic complexes $[MI(CO)_3(PPh_3)(L\frown L)]I$ by displacement of acetonitrile and an iodide ligand [27]. The differences in the reaction pathways can again be attributed to the large difference in electronegativity of Cl and $GeCl_3$ groups and two iodo-ligands, which would enhance the lability of the carbonyl group in the $GeCl_3$/Cl complex.

Reaction of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) with one equivalent of L (L = $PPh_3$, $AsPh_3$ or $SbPh_3$) in NCMe rather than $CH_2Cl_2$ gives with evolution of carbon monoxide, the dicarbonyl compounds $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$ (**24–26**) as yellow precipitates in good yield. This is in contrast to the reaction of **1** with L (1:1 ratio) in $CH_2Cl_2$, which give the tricarbonyl complexes **2–6**. Since Brisdon and Hodson [26] found a rapid exchange between "free" and coordinated acetonitrile, it is probable that the reaction of

TABLE 3. Proton NMR spectroscopic data [a,b] (δ) for the seven-coordinate complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ and its derivatives

| Complex | $^1H$ NMR δ(ppm) |
|---|---|
| **1** | 2.45 (s, Me) [a] |
| **2** | 7.4 (m, 15H, Ph); 2.4 (s, 3H, Me) [a] |
| **3** | 7.35 (m, 15H, Ph); 2.4 (s, 3H, Me) [a] |
| **4** | 7.6, 7.45, 7.35 (m, 15H, Ph); 2.2 (s, 3H, Me) [a] |
| **5** | 7.7, 7.6, 7.5, 7.4 (m, 10H, Ph); 5.3 (s, 2H, $CH_2Cl_2$); 2.2 (s, 3H, Me); 1.65 (m, 11H, Cy) [a] |
| **6** | 7.45 (m, 15H, Ph); 5.3 (s, 1H, $CH_2Cl_2$); 2.4 (s, 3H, Me) [a] |
| **7** | 7.35 (m, 30H, Ph); 2.2 (s, 3H, Me) [a] |
| **10** | 7.6, 7.45, 7.35 (m, 20H, Ph); 1.7, 1.3 (m, 22H, Cy) [a] |
| **11** | 7.35 (m, 45H, Ph); 5.3 (s, 1H, $CH_2$) [a] |
| **14** | 7.4, 7.2, 7.1 (m, 50H, Ph); 4.85 (m, 2H, $PCH_2$) [a] |
| **15** | 7.4 (m, 50H, Ph); 2.95 (m, 4H, $PCH_2$) [a] |
| **16** | 9.6 (d, 2H, bipy); 8.7 (m, 4H, bipy); 8.3 (m, 2H, bipy); 7.5 (m, 15H, Ph) [a] |
| **17** | 9.7 (d, 2H, phen); 9.55 (d, 2H, phen); 9.05 (d, 2H, phen); 8.8 (d, 2H, phen); 7.45 (m, 15H, Ph); 5.3 (s, 2H, $CH_2Cl_2$) [a] |
| **18** | 7.55, 7.4, 7.25 (m, 35H, Ph); 5.3 (s, 1H, $CH_2$); 4.8 (m, 2H, $PCH_2$) [a] |
| **19** | 7.5 (m, 35H, Ph); 5.3 (s, 1H, $CH_2$); 3.0 (m, 4H, $PCH_2$) [a] |
| **20** | 7.35 (m, 15H, Ph); 3.1 (m, 8H, $NCH_2$); 1.45 (m, 16H, $CH_3\mathit{CH_2CH_2}$); 1.0 (m, 12H, $CH_3$) [a] |
| **21** | 7.4 (m, 15H, Ph); 3.2 (m, 8H, $NCH_2$); 1.6 (m, 16H, $CH_3\mathit{CH_2CH_2}$); 1.05 (m, 12H, $CH_3$) [a] |
| **22** | 7.4 (m, 15H, Ph); 3.3 (m, 8H, $NCH_2$); 1.75 (m, 8H, $NCH_2\mathit{CH_2}$); 1.5 (m, 8H, $CH_3\mathit{CH_2}$); 1.1 (m, 12H, $CH_3$) [a] |
| **23** | 7.5 (m, 15H, Ph); 3.2 (m, 8H, $NCH_2$); 1.6 (m, 8H, $NCH_2\mathit{CH_2}$); 1.45 (m, 8H, $\mathit{CH_2}CH_3$); 0.95 (m, 12H, $CH_3$) [a] |
| **24** | 7.4 (m, 15H, Ph); 2.35 (s, 6H, Me) [b] |
| **25** | 7.35 (m, 15H, Ph); 2.3 (s, 6H, Me) [b] |
| **26** | 7.6, 7.45, 7.35 (m, 15H, Ph); 2.3 (s, 6H, Me) [b] |
| **27** | 7.35 (m, 30H, Ph); 5.3 (s, 2H, $CH_2$); 2.2 (s, 3H, Me) [a] |
| **28** | 7.45, 7.3 (m, 30H, Ph); 2.2 (s, 3H, Me) [a] |
| **29** | 7.4 (m, 30H, Ph); 2.3 (s, 3H, Me) [a] |

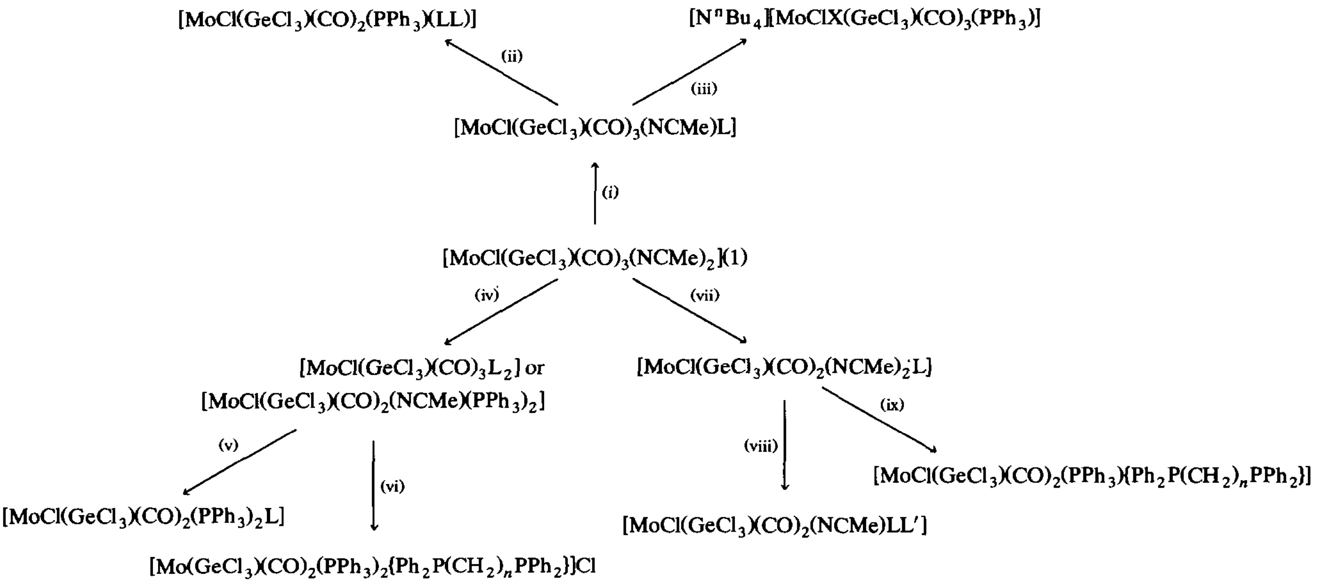
[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to $Me_4Si$. [b] Spectra recorded in $CD_3COCD_3$ (+25°C) and referenced to $Me_4Si$.

**1** with L initially gives the acetonitrile-replaced product $[MoCl(GeCl_3)(CO)_3(NCMe)L]$ (**2**). In these complexes which contain $PPh_3$, $AsPh_3$ and $SbPh_3$, which are stronger $\pi$-acceptor ligands than NCMe, carbon monoxide is more easily displaced by the acetonitrile to give $[MoCl(GeCl_3)(CO)_2(NCMe)_2L]$. Equimolar quantities of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ (**24**) and L (L = $PPh_3$, $AsPh_3$ or $SbPh_3$) react in a large volume of $CH_2Cl_2$ (necessary because of the poor solubility of **24**) to give the orange complexes $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)L]$ (**7**, **27**, **28**). Similarly, reaction of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(AsPh_3)]$ with an equimolar amount of $SbPh_3$ in $CH_2Cl_2$ gives the six-different ligand complex $[MoCl(GeCl_3)(CO)_2(NCMe)(AsPh_3)(SbPh_3)]$ (**29**) in good yield. Complex **24** also reacts with an equimolar amount of $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ or 2) to give the previously described complexes $[MoCl(GeCl_3)(CO)_2(PPh_3)\{Ph_2P(CH_2)_nPPh_2\}] \cdot \frac{1}{2}CH_2Cl_2$ (**18** and **19**) in high yield. All the complexes (**24**–**29** and **7**, **18** and **19**) were characterised by elemental analysis (C, H and N) (Table 1 for **24**–**29**; Experimental section for **7**, **18** and **19** by the alternative route), and by IR (Table 2) and $^1H$ NMR spectroscopy (Table 3). The complex $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)(AsPh_3)] \cdot CH_2Cl_2$ (**27**) was confirmed as a solvate by repeated elemental analyses and $^1H$ NMR spectroscopy. The IR and $^1H$ NMR data for **7**, **18** and **19** prepared by this alternative method are identical to those shown in Tables 2 and 3. Many unsuccessful attempts were made to grow suitable single crystals for X-ray crystallography, and because of instability in solution it is difficult to obtain data on which to base structures for any of the complexes **2**–**29**.

The various types of reactions of 1 described in this paper are summarised in Scheme 1. In conclusion it can be seen from our work that changes in both halide or Group IVB halide anion and reaction solvent can have a very large effect in the reaction pathways of $[MXY(CO)_3(NCMe)_2]$ type complexes.

## 3. Experimental details

All reactions described in this paper were carried out under dry nitrogen unless otherwise stated, by use of standard Schlenk line techniques. The complex *fac*-$[Mo(CO)_3(NCMe)_3]$ (used *in situ*) was prepared by the published method [19]. All chemicals used were purchased from commercial sources. Proton NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer with tetramethylsilane as reference. The $^{13}C$ NMR spectrum for $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ was recorded on a Bruker WH 400 NMR spectrometer and with tetramethylsilane as reference. Infrared spectra were recorded as thin films between NaCl plates in $CHCl_3$ on a Perkin-Elmer 1600 FT IR spectrometer. Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Magnetic susceptibilities were determined using a Johnson-Matthey magnetic susceptibility balance.



Scheme 1. All reactions were carried out in $CH_2Cl_2$ at room temperature except for (vii) where reactions were carried out in NCMe at room temperature. Reagents: (i) L = $PPh_3$, $AsPh_3$, $SbPh_3$, $PPh_2Cy$, $P(OPh)_3$. (ii) $L\frown L$ = 2,2-bipy, 1,10-phen, $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ and 2). (iii) $[N^nBu_4]X$ (X = Cl, $Br_3$, I, Br). (iv) 2L = $PPh_3$, $AsPh_3$, $SbPh_3$, $PPh_2Cy$. (v) L = $PPh_3$, $AsPh_3$, $SbPh_3$, $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ and 2). (vii) L = $PPh_3$, $AsPh_3$, $SbPh_3$. (viii) L′ = $PPh_3$, $AsPh_3$, $SbPh_3$. (ix) $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ and 2).

### 3.1. $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (1)

A suspension of $[Mo(CO)_6]$ (4.14 g, 15.68 mmol) was refluxed for 24 h in degassed acetonitrile under nitrogen. The solution was cooled to 0°C in an ice bath, and $GeCl_4$ (3.36 g, 15.68 mmol) was added causing a change in colour from golden yellow to red. After 4 h stirring the solvent was removed *in vacuo*, to leave the golden-brown crystalline product $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) (yield = 7.02 g, 94%).

### 3.2. $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ (2)

To a stirred solution of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (0.500 g, 1.049 mmol) in $CH_2Cl_2$ (15 ml) under a stream of dry nitrogen was added $PPh_3$ (0.275 g, 1.049 mmol). After 1 min stirring the solution was filtered and the solvent removed *in vacuo* to give the golden brown product $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ (**2**) (yield = 0.39 g, 53%), which was recrystallised from $CH_2Cl_2$.

Similar reactions of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ with one equivalent of L {L = $AsPh_3$, $SbPh_3$, $PCyPh_2$ and $P(OPh)_3$} gave the products $[MoCl(GeCl_3)(CO)_3(NCMe)L]$ (**3**–**6**).

Reaction times for

$$[MoCl(GeCl_3)(CO)_3(NCMe)_2] \xrightarrow{L} [MoCl(GeCl_3)(CO)_3(NCMe)L] + NCMe$$

were as follows: L = $AsPh_3$, 3 min; L = $SbPh_3$, 5 min; L = $PCyPh_2$, 5 min; L = $P(OPh)_3$, 5 min (see Table 1 for physical and analytical data).

### 3.3. $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2]$ (7)

To a stirred solution of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (0.500 g, 1.049 mmol) in $CH_2Cl_2$ (15 ml) under a stream of dry nitrogen was added $PPh_3$ (0.550 g, 2.098 mmol). After 15 min stirring the solution was filtered and the solvent removed *in vacuo* to give the orange product $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2]$ (**7**) (yield = 0.39 g, 40%), which was recrystallised from $CH_2Cl_2$.

Similar reactions of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ with 2L (L = $AsPh_3$, $SbPh_3$ and $PCyPh_2$) gave the complexes $[MoCl(GeCl_3)(CO)_3L_2]$ (**8**–**10**) (see Table 1 for physical and analytical data).

### 3.4. $[MoCl(GeCl_3)(CO)_2(PPh_3)_3]$. $\frac{1}{2}CH_2Cl_2$ (11)

To a stirred solution of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (0.500 g, 1.049 mmol) in $CH_2Cl_2$ (15 ml) under a stream of dry nitrogen was added $PPh_3$ (0.550 g, 2.098 mmol). After 15 min stirring additional $PPh_3$ (0.275 g, 1.049 mmol) was added, and the mixture stirred for a further 18 h. The solution was then filtered and solvent removed *in vacuo* to give the golden brown compound $[MoCl(GeCl_3)(CO)_2(PPh_3)_3] \cdot \frac{1}{2}CH_2Cl_2$ (**11**) (yield = 0.94 g, 75%), which was recrystallised from $CH_2Cl_2$.

Similar reactions *in situ* of one equivalent of $AsPh_3$ or $SbPh_3$ with $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2]$ afforded the complexes $[MoCl(GeCl_3)(CO)_2(PPh_3)_2L]$ (L = $AsPh_3$ (**12**) and L = $SbPh_3$ (**13**)) (see Table 1 for physical and analytical data).

### 3.5. $[Mo(GeCl_3)(CO)_2(PPh_3)_2\{Ph_2P(CH_2)PPh_2\}]Cl$ (14)

To a stirred solution of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (0.500 g, 1.049 mmol) in $CH_2Cl_2$ (15 ml) under a stream of dry nitrogen was added $PPh_3$ (0.55 g, 2.098 mmol). After 15 min stirring $Ph_2P(CH_2)PPh_2$ (0.403 g, 1.049 mmol) was added and the mixture stirred for a further 18 h. Filtration, followed by the removal of solvent, *in vacuo* gave the orange complex $[Mo(GeCl_3)(CO)_2(PPh_3)_2\{Ph_2P(CH_2)PPh_2\}]Cl$ (**14**) (yield = 1.07 g, 80%).

A similar reaction of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ with two equivalents of $PPh_3$ in $CH_2Cl_2$, followed by an equimolar quantity of $Ph_2P(CH_2)_2PPh_2$ gave $[Mo(GeCl_3)(CO)_2(PPh_3)_2\{Ph_2P(CH_2)_2PPh_2\}]Cl$ (**15**) (see Table 1 for physical and analytical data).

### 3.6. $[MoCl(GeCl_3)(CO)_2(PPh_3)(bipy)]$ (16)

To a stirred solution of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (0.500 g, 1.049 mmol) in $CH_2Cl_2$ (15 ml) under a stream of dry nitrogen was added $PPh_3$ (0.275 g, 1.049 mmol). After 1 min stirring 2,2′-bipyridyl (0.164 g, 1.049 mmol) was added, and the mixture stirred for 18 h. Filtration and removal of the solvent *in vacuo* then gave the brown complex $[MoCl(GeCl_3)(CO)_2(PPh_3)(bipy)]$ (**16**) (yield = 0.63 g, 77%), which was recrystallised from $CH_2Cl_2$.

Similar reactions of $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ (prepared *in situ*) with $L^\frown L$ ($L^\frown L$ = 1,10-phen, $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ and 2)) gave the products $[MoCl(GeCl_3)(CO)_2(PPh_3)(L^\frown L)]$ {$L^\frown L$ = 1,10-phen (**17**), $Ph_2P(CH_2)PPh_2$ (**18**) and $Ph_2P(CH_2)_2PPh_2$ (**19**)} (see Table 1 for physical and analytical data).

### 3.7. $[N^nBu_4][MoCl_2(GeCl_3)(CO)_3(PPh_3)]$ (20)

To a stirred solution of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (0.500 g, 1.049 mmol) in $CH_2Cl_2$ (15 ml) under a stream of dry nitrogen was added $PPh_3$ (0.275 g, 1.049 mmol). After 1 min stirring, $[N^nBu_4]Cl$ (0.292 g, 1.049 mmol) was added and the mixture stirred for a further 30 min. Filtration, followed by removal of the solvent *in vacuo*, gave the golden brown complex $[N^nBu_4][MoCl_2(GeCl_3)(CO)_3(PPh_3)]$ (**20**) (yield = 0.58 g, 59%), which was recrystallised from $CH_2Cl_2$.

Similar reactions of [$MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)$] (**7**) with [$N^nBu_4$]X (X = $Br_3$, I, Br) gave the products [$N^nBu_4$][$MoXCl(GeCl_3)(CO)_3(PPh_3)$] (X = $Br_3$ (**21**), I (**22**), Br (**23**)) (see Table 1 for physical and analytical data).

### 3.8. [$MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] (24)

To a stirred solution of [$MoCl(GeCl_3)(CO)_3(NCMe)_2$] (0.500 g, 1.049 mmol) in NCMe (15 ml) under a stream of dry nitrogen was added $PPh_3$ (0.275 g, 1.049 mmol). After 1 min a yellow precipitate started to form, and the mixture was stirred for a further 18 h after which the solvent was removed *in vacuo*, and the products were washed several times with NCMe to give the pure yellow complex [$MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] (**24**) (yield = 0.35 g, 47%).

Similar reactions of [$MoCl(GeCl_3)(CO)_3(NCMe)_2$] with one equivalent of $AsPh_3$ or $SbPh_3$ in NCMe afforded the complexes [$MoCl(GeCl_3)(CO)_2(NCMe)_2L$] (L = $AsPh_3$ (**25**) or $SbPh_3$ (**26**)) (see Table 1 for physical and analytical data).

### 3.9. Alternative preparation of [$MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2$] (7)

To a stirred solution of [$MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] (0.500 g, 0.703 mmol) in $CH_2Cl_2$ (30 ml) under a stream of dry nitrogen was added $PPh_3$ (0.184 g, 0.703 mmol). After 1 h stirring, the solution was filtered and the solvent removed *in vacuo* to give the orange complex [$MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)_2$] (**7**) (yield = 0.27 g, 41%) which was recrystallised from $CH_2Cl_2$. Found: C, 51.3; H, 3.5; N, 1.1. Calcd. for $C_{40}H_{33}NO_3P_2Cl_4GeMo$ C, 51.6; H, 3.6; N, 1.5%. The spectroscopic properties for this complex are identical to those of **7** prepared by an alternative route.

Similar reactions of [$MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] with one equivalent of $AsPh_3$ or $SbPh_3$ in $CH_2Cl_2$ gave the compounds [$MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)L$] (L = $AsPh_3$ (**27**) and $SbPh_3$ (**28**)). The reaction of [$MoCl(GeCl_3)(CO)_2(NCMe)_2(AsPh_3)$] with an equimolar quantity of $SbPh_3$ in $CH_2Cl_2$ gave [$MoCl(GeCl_3)(CO)_2(NCMe)(AsPh_3)(SbPh_3)$] (**29**) in a similar manner (see Table 1 for physical and analytical data).

### 3.10. Alternative preparation of [$MoCl(GeCl_3)(CO)_2(PPh_3)\{Ph_2P(CH_2)PPh_2\}$]$\frac{1}{2}CH_2Cl_2$ (18)

To a stirred solution of [$MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] (0.500 g, 0.703 mmol) in $CH_2Cl_2$ (30 ml) under a stream of dry nitrogen was added $Ph_2P(CH_2)PPh_2$ (0.270 g, 0.703 mmol). After 18 h stirring, the solution was filtered and the solvent removed *in vacuo* to give the orange complex [$MoCl(GeCl_3)(CO)_2(PPh_3)\{Ph_2P(CH_2)_2PPh_2\}$] $\cdot \frac{1}{2}CH_2Cl_2$ (**18**) (yield = 0.48 g, 65%) which was recrystallised from $CH_2Cl_2$.

A similar reaction of [$MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] with an equimolar quantity of $Ph_2P(CH_2)_2PPh_2$ in $CH_2Cl_2$ gave [$MoCl(GeCl_3)(CO)_2(PPh_3)\{Ph_2P(CH_2)_2PPh_2\}$]. The complexes [$MoCl(GeCl_3)(CO)_2(PPh_3)\{Ph_2P(CH_2)_nPPh_2\}$] $\cdot \frac{1}{2}CH_2Cl_2$ ($n = 1$ and 2) were identical to complexes **18** and **19** prepared by an alternative route.

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