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Seven-coordinate complexes of molybdenum(II) containing a trichlorogermyl ligand: X-ray crystal structure of a novel $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$

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Abstract

The oxidative–addition of $GeCl_4$ to $[Mo(CO)_4(NCMe)_2]$ in CH_2Cl_2 provides a high-yield and fast route to the trichlorogermyl complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**). Beside **1**, other compounds containing a Mo–Ge bond are formed, as was shown by IR and NMR investigation of the reaction mixture. These compounds react further with an excess of propionitrile giving among others, a novel, crystallographically characterized $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (**3**). Compound **3** is the first structurally characterized molybdenum(II) carbonyl complex, containing two trichlorogermyl ligands. Reaction of **1** or **3** with an alkyne (PhC≡CPh, PhC≡CMe, PhC≡CH) affords compounds in which CO and/or nitrile ligands were replaced by alkyne ligands. The alkyne molybdenum(II) complexes formed were characterized structurally by IR and NMR spectroscopy. However, the reaction of **1** with phenylacetylene (PA) leads to the catalytic coupling of alkyne molecules and the formation of cyclotrimers and polymers. The possible mechanisms for the formation of molybdenum(II) complexes and their role in the catalytic process are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum(II); Germanium; Crystal structure; Seven-coordinate; Heterobimetallic complexes; Nitrile complexes; Alkyne complexes; Cyclotrimerization

1. Introduction

The synthesis and reactivity of Group 6 metal, seven-coordinate complexes is an area of considerable interest at present [1]. Recent reports include the use of such complexes for alkene metathesis and ring-opening metathesis polymerization applications [2–4], and for alkyne polymerization [2,5]. In recent years we have been investigating the chemistry of the seven-coordinate compounds of tungsten(II) and molybdenum(II) [2,5–9]. Such compounds can be formed easily in an oxidative–addition reaction of d^6 Group 6 metal complexes and Group 14 element tetrahalides. In this way we have synthesized and structurally characterized by X-ray, several seven-coordinate chlorocarbonyl complexes of tungsten(II) and molybdenum(II) with a W–Sn [5–7], W–Ge [8] and Mo–Sn bond [9]. However, the chemistry of analogous heterobimetallic Mo–Ge complexes has been developed very weakly. Baker and Kendrick briefly mentioned the formation of $[MCl(GeCl_3)(CO)_3(NCMe)_2]$, M = W, Mo, by the reaction of $[M(CO)_3(NCMe)_3]$ with $GeCl_4$ in acetonitrile, but they could not obtain those compounds in a pure state [10]. Therefore, we decided to repeat the synthesis and to verify the nature of the Mo–Ge compound formed in the oxidative–addition reaction of molybdenum(0) compound and germanium tetrachloride. However, we found that the compound with Mo–Ge bond is more conveniently obtained in high yield by using CH_2Cl_2 instead of acetonitrile, as the solvent for the reaction of $[Mo(CO)_4(NCMe)_2]$ with $GeCl_4$. Here, we describe the improved synthesis of $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) and the first characterization of the bis(trichlorogermyl) complex $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (**3**). A novel compound **3** was isolated in crystalline form and its structure established by X-ray crystallography. The intent of

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this work was to obtain molybdenum(II) complexes with loosely bound, labile nitrile ligands in the hope that this will lead to active homogeneous catalysts. To determine whether **1** is a convenient precursor for the alkyne polymerization catalyst, we studied the substitution of the labile acetonitrile and CO ligands by alkynes.

2. Experimental

2.1. General data

All operations were carried out in an inert atmosphere using standard Schlenk techniques. All solvents and liquid reagents were dried and distilled over CaH_2. Solution IR spectra were obtained using KBr or NaCl plates while solid samples were recorded using KBr pellets on an FT-IR model-400 Nicolet instrument. Far-IR spectra were recorded (500–50 cm^{-1}) with a Brücker IFSv instrument in Nujol mull on a polyethylene film. NMR spectra were obtained using a Bruker AMX-300 spectrometer. The analysis of the catalytic reaction products was performed on a Hewlett–Packard 5890 GC–MS system and by ^1H-NMR and IR spectroscopy.

2.2. Synthesis

*2.2.1. [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] (**1**)*

Dissolution of $[Mo(CO)_4(NCMe)_2]$ [11] (2.2 g, 7.7 mmol) in CH_2Cl_2 (30 cm^3) was followed by addition of an equimolar quantity of $GeCl_4$ (0.9 cm^3, 7.7 mmol) by means of a syringe. The mixture was stirred for 30 min, during which time the yellow solution gradually changed to a golden brown color, while the ν(CO) frequency of $[Mo(CO)_4(NCMe)_2]$ disappeared. After this reaction time IR spectroscopy confirmed the reaction to be complete. Evaporation of the solvent led to the isolation of a mixture of molybdenum(II) complexes as a golden brown powder. The crude product was washed with heptane (3 × 10 cm^3) to remove $Mo(CO)_6$ and a compound with two ν(CO) bands at 2078 vw and 1949 vs cm^{-1}, characteristic of a $[Mo(CO)_5]$ unit. The residue was redissolved in CH_2Cl_2 (50 cm^3), heptane (10 cm^3) was layered on top and it was stored in the freezer for several days affording a precipitate identified by analysis and by IR and NMR spectra as $[MoCl(GeCl_3)(CO)_3(NCMe)]_2$. Anal. Calc. for $C_{10}H_6Cl_8Ge_2Mo_2N_2O_6$: C, 13.79; H, 0.69; N, 3.22. Found: C, 14.21; H, 0.89; N, 3.08%. Recrystallization of this compound from acetonitrile gives the chlorine bridge cleaved mononuclear compound **1**, contaminated with a small amount of dicarbonyl compound as was shown by the IR spectra (Table 1). Anal. Calc. for $C_7H_6Cl_4GeMoN_2O_3$: C, 17.65; H, 1.27; N, 5.88. Found: C, 16.95; H, 1.47; N, 5.95%. The remaining compounds (Scheme 1) were not separated and were detected only by IR and NMR spectroscopy in the reaction mixture (Table 1).

*2.2.2. [MoCl(GeCl$_3$)(CO)$_3$(NCEt)$_2$] (**2**)*

Compound **1** was dissolved in propionitrile and the solution was stirred for 60 min. Filtration followed by removal of the solvent in vacuo, gave a residue which was recrystallized from CH_2Cl_2–heptane giving a bis(nitrile) complex **2** contaminated with a small amount of dicarbonyl compound as was shown by IR spectra (Table 1).

*2.2.3. [Mo(GeCl$_3$)$_2$(CO)$_2$(NCEt)$_3$] (**3**)*

The mixture of Mo–Ge compounds obtained in the reaction of $[Mo(CO)_4(NCMe)_2]$ and $GeCl_4$ was dissolved in propionitrile. The removal of the solvent in vacuo, gave a residue which was recrystallized from CH_2Cl_2–heptane giving the large golden yellow crystals in a reddish brown oily precipitate which was extracted to toluene. Insoluble in toluene, the crystalline compound was identified as clear compound **3**. Anal. Calc. for $C_{11}H_{15}Cl_6GeMoN_3O_2$: C, 19.57; H, 2.24; N, 6.22. Found: C, 19.48; H, 2.30; N, 6.12%.

*2.3. Crystal and refinement data for compound **3***

Crystal data and relevant refinement details are collected in Table 2. A golden yellow crystal approximately 0.15 × 0.15 × 0.20 mm was removed from the flask and rapidly coated with a light hydrocarbon oil to protect it from the atmosphere. Data collection was performed on a KM4 κ-axis computer controlled [12] four-circle diffractometer operating in the ω–2θ scan mode with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) at 293 K. The accurate cell dimensions and the crystal orientation matrix were determined by a least-squares refinement of the setting angles of 90 carefully centered reflections in the range $20.6 < 2\theta < 40.2°$. A total of 5163 unique reflections were measured, of which 4539 (230 variables) with $[I \geq 2\sigma(I)]$ in the range 6–57° were used to solve and refine the structure in the monoclinic space group $P\bar{1}$.

The hydrogen atoms were placed in the geometrically calculated positions with the isotropic temperature factors taken as 1.2 and 1.5 U_{eq} of the neighboring heavier atoms for CH_2 and CH_3, respectively. Several cycles of refinement of the coordinates and anisotropic thermal parameters for non-hydrogen atoms (parameters of the H atoms were fixed) reduced the R_1 to 0.0615 and wR_2 to 0.1703. The maximum and minimum residual densities in the difference map were 1.93 and −1.262 e Å^{-3}, respectively. Goodness-of-fit was 1.118.

The structure was solved by heavy-atom methods with the SHELXS-86 program [13] and refined by a full-matrix least-squares method, using the SHELXL pro-

Table 1
Selected IR and NMR spectral data for the seven-coordinate nitrile complexes with Mo–Ge bond

Complex	IR(ν, cm^{-1})		^{1}H-NMR (δ, ppm) [b]	^{13}C-NMR (δ, ppm) [b]
	ν(CO) [a]	ν(CN) [a]		
[$MoCl(GeCl_3)(CO)_3(NCMe)_2$] (**1**)	2041 s, 1988 s, 1949 vs	2316 w, 2289 w	2.45 (s, 2 $\mathrm{C}H_3\mathrm{CN}$)	219.34 (s, 3 CO), 125.56 (s, 2 $\mathrm{CH_3}C\mathrm{N}$), 4.60 (s, 2 $C\mathrm{H_3CN}$)
[$MoCl(GeCl_3)(CO)_3(NCMe)$]$_2$	2041 s, 1963 s	2316 w, 2289 w	2.24 (s, 1 $\mathrm{C}H_3\mathrm{CN}$)	224.21 (s, 6 CO), 128.98 (s, 2 $\mathrm{CH_3}C\mathrm{N}$), 4.14 (s, 2 $C\mathrm{H_3CN}$)
[$MoCl(GeCl_3)(CO)_2(NCMe)_3$]	1949 vs, 1879 s	2320 m, 2290 w	2.41 (s, 3 $\mathrm{C}H_3\mathrm{CN}$)	218.98 (s, 2 CO), 128.17 (s, 3 $\mathrm{CH_3}C\mathrm{N}$), 4.20 (s, 3 $C\mathrm{H_3CN}$)
[$Mo(GeCl_3)_2(CO)_3(NCMe)_2$]	2047 s, 1956 vs	2326 w, 2298 w	2.66 (s, 2 $\mathrm{C}H_3\mathrm{CN}$)	229.99 (s, 3 CO), 129.97, (s, 2 $\mathrm{CH_3}C\mathrm{N}$), 4.60 (s, 2 $C\mathrm{H_3CN}$)
[$Mo(GeCl_3)_2(CO)_2(NCMe)_3$]	1963 vs, 1890 s	2326 m, 2298 w	2.52 (s, 3 $\mathrm{C}H_3\mathrm{CN}$)	231.67 (s, 2 CO), 130.36, (s, 3 $\mathrm{CH_3}C\mathrm{N}$), 5.16 (s, 3 $C\mathrm{H_3CN}$)
[$MoCl(GeCl_3)(CO)_3(NCEt)_2$] (**2**)	2039 s, 1952 vs	2283 m	2.83 (q, 2 $\mathrm{CH_3C}H_2\mathrm{CN}$), 1.50 (t, 2 $\mathrm{C}H_3\mathrm{CH_2CN}$)	219.27 (s, 3 CO), 128.98 (s, 2 $\mathrm{CH_3CH_2}C\mathrm{N}$),12.81 (s, 2 $\mathrm{CH_3}C\mathrm{H_2CN}$), 8.90 (s, 2 $C\mathrm{H_3CH_2CN}$)
[$MoCl(GeCl_3)(CO)_3(NCEt)$]$_2$	2038 s, 1955 vs	2285 m	2.83 (q, 2 $\mathrm{CH_3C}H_2\mathrm{CN}$), 1.50 (t, 2 $\mathrm{C}H_3\mathrm{CH_2CN}$)	223.87 (s, 6 CO), 128.98 (s, 2 $\mathrm{CH_3CH_2}C\mathrm{N}$), 12.81 (s, 2 $\mathrm{CH_3}C\mathrm{H_2CN}$), 8.90 (s, 2 $C\mathrm{H_3CH_2CN}$)
[$MoCl(GeCl_3)(CO)_2(NCEt)_3$]	1950 s, 1870 vs	2285 m	2.84 (q, 3 $\mathrm{CH_3C}H_2\mathrm{CN}$), 1.50 (t, 3 $\mathrm{C}H_3\mathrm{CH_2CN}$)	218.36 (s, 2 CO), 127.43 (s, 3 $\mathrm{CH_3CH_2}C\mathrm{N}$), 12.81 (s, 3 $\mathrm{CH_3}C\mathrm{H_2CN}$), 8.90 (s, 3 $C\mathrm{H_3CH_2CN}$)
[$Mo(GeCl_3)_2(CO)_3(NCEt)_2$]	2043 s, 1960 s, 1940 s	2285 m	2.95 (q, 2 $\mathrm{CH_3C}H_2\mathrm{CN}$), 1.50 (t, $\mathrm{C}H_3\mathrm{CH_2CN}$)	230.16, (s, 3 CO), 128.22 (s, 2 $\mathrm{CH_3CH_2}C\mathrm{N}$), 13.22 (s, 2 $\mathrm{CH_3}C\mathrm{H_2CN}$), 9.17 (s, 2 $C\mathrm{H_3CH_2CN}$)
[$Mo(GeCl_3)_2(CO)_2(NCEt)_3$] (**3**)	1961 s, 1897 vs	2286 m	2.78 (q, 3 $\mathrm{CH_3C}H_2\mathrm{CN}$), 1.43 (t, 3 $\mathrm{C}H_3\mathrm{CH_2CN}$)	231.49, (s, 2 CO), 133.31 (s, 3 $\mathrm{CH_3CH_2}C\mathrm{N}$), 12.40 (s, 3 $\mathrm{CH_3}C\mathrm{H_2CN}$), 8.73 (s, 3 $C\mathrm{H_3CH_2CN}$)

[a] Spectra recorded in KBr disc.

[b] Spectra recorded in $CDCl_3$ at 293 K.

gram [14]. Neutral atomic scattering factors were taken from the SHELXL-93 program [14].

2.4. *Reactions with alkynes*

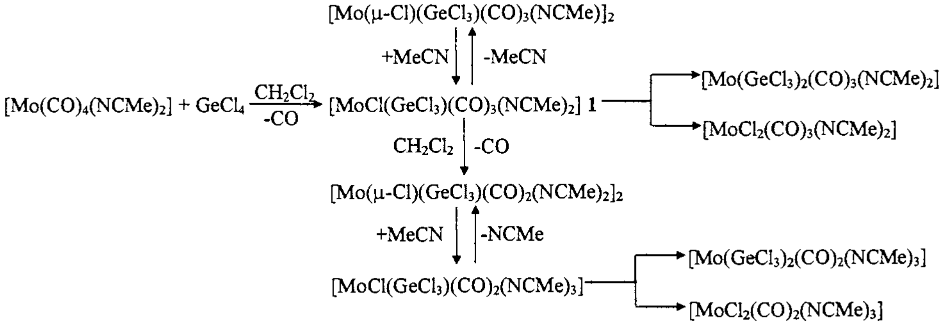
2.4.1. *Reaction of **1** with diphenylacetylene (DPA)*

To a solution of **1** (0.5 g, 1.1 mmol) in 20 cm^3 of CH_2Cl_2 was added PhC≡CPh (0.4 g, 2.2 mmol) in CH_2Cl_2 (5 cm^3). The mixture was stirred and the progress of the reaction was monitored by the disappearance of ν(CO) bands due to **1**. At the beginning of the reaction (2–4 h) several new ν(CO) bands appear and increase (2100, 2073, 1984 and 1951 cm^{-1}). The band at 2100 cm^{-1} next decays after a prolonged reaction time. At least one week was allowed for the reaction to go to completion. The solution was filtered off and the solvent removed in vacuo. The residue was washed several times with heptane and toluene to remove a compound with two ν(CO) bands at 2073 vw and 1951 vs cm^{-1} characteristic of a [$Mo(CO)_5$] unit. The product was identified by IR and NMR studies (Table 3) as a mixture of DPA compounds. The major product [$MoCl_2(NCMe)_2$(PhC≡CPh)$_2$] was detected due to two signals of acetylenic carbons in ^{13}C-NMR spectra at δ 191.34 and 186.77. In CH_2Cl_2 solution this compound dimerizes with a loss of acetonitrile molecule to yield the less soluble [Mo(μ-Cl)Cl(NCMe)(PhC≡CPh)$_2$]$_2$. This process is reversible in the presence of an excess of acetonitrile. The alkyne compound with ν(CO) band at 1984 cm^{-1} can be formulated as [$MoCl_2(CO)(GeCl_2)(NCMe)$(PhC≡CPh)] (Scheme 2). The resulting compounds were not separated but characterized by IR and NMR spectroscopy (see Table 3) in the reaction mixture.

Recrystallization of the mixture of the above DPA compounds from propionitrile leads to the formation of a better soluble [$MoCl_2(NCEt)_2$(PhC≡CPh)$_2$] and less soluble [$MoCl_2(CO)(GeCl_2)(NCEt)$(PhC≡CPh)] (Table 3).

2.4.2. *Reaction of **3** with DPA*

The alkyne (0.07 g, 0.4 mmol) was added to a solution of complex **3** (0.14 g, 0.2 mmol) in CH_2Cl_2 (20 cm^3) at room temperature (r.t.). The mixture was stirred and the progress of the reaction was monitored by the disappearance of ν(CO) bands due to **3**. From the beginning of the reaction the new ν(CO) band at 2013 cm^{-1} appears and increases. At least 1 week was allowed for reaction to go to completion. The solution was filtered and reduced to a greenish yellow residue. Washing with heptane removed an yellow oil and unreacted DPA from the desired product remained as a light green solid. The IR spectrum of reaction product was characterized by a strong ν(CO) band at 2003, a weak one at 1908 and a very weak one at 2092 cm^{-1}.



Scheme 1.

The product was identified by IR and NMR (Table 3) as a mixture of compounds with two and one alkyne ligand in the coordination sphere of molybdenum(II): $[MoCl_2(NCEt)_2(PhC{\equiv}CPh)_2]$ and $[MoCl_2(CO)(GeCl_2)_2(PhC{\equiv}CPh)]$.

2.4.3. Reaction of **1** with 1-phenylprop-1-yne (PhC≡CMe)

The alkyne (0.5 cm^3, 4 mmol) was added to a solution of complex **1** (0.53 g, 1.1 mmol) in a CH_2Cl_2/CH_3CN mixture (15/1 cm^3) at r.t. The progress of the reaction was monitored by the disappearance of ν(CO) bands of **1**. At the beginning of the reaction several new ν(CO) bands appear and increase. The band at 2087 cm^{-1} next decays after a prolonged reaction time. Stirring for four days followed by the filtration and evaporation of the solvent under low pressure gave a green solid. The crude product was washed out with heptane and toluene to remove a compound with two ν(CO) bands at 2072 vw and 1949 vs cm^{-1}, characteristic of a $[Mo(CO)_5]$ unit and organic compounds. The product was identified by IR and NMR studies (Table 3) as a mixture of compounds. The major product with a ν(CO) band at 1977 cm^{-1} and two signals of acetylenic carbons in ^{13}C-NMR spectra at δ 224.28 and 222.91 can be formulated as $[MoCl_2(CO)(GeCl_2)(NCMe)(PhC{\equiv}CMe)]$. The second alkyne compound $[MoCl_2(NCMe)_2(PhC{\equiv}CMe)_2]$ was identified due to two signals of acetylenic carbons in ^{13}C-NMR spectra at δ 194.98 and 178.51. In CH_2Cl_2 solution the last compound dimerizes with the loss of an acetonitrile molecule to yield the less soluble $[Mo(\mu\text{-}Cl)Cl(NCMe)(PhC{\equiv}CMe)_2]_2$. The organic products based on GC–MS characterization were mainly cyclotrimers 1,2,4-trimethyltriphenylbenzene and 1,3,5-trimethyltriphenylbenzene in the ratio 4:1.

2.4.4. Reaction of **1** with phenylacetylene (PA)

The addition of four equivalents of PA (0.22 cm^3, 2.1 mmol) to a stirred CH_2Cl_2 solution (10 cm^3) of **1** (0.25 g, 0.5 mmol) at r.t. resulted in a color change from light orange to dark orange. The progress of the reaction was monitored by the disappearance of ν(CO) bands of **1**. At the beginning of the reaction a new ν(CO) band appears and increases at 2098 cm^{-1} which next decays after a prolonged reaction time. Stirring for 21 h, followed by the filtration and evaporation of the solvent under low pressure gave an orange solid. The crude product was washed out with heptane to remove a compound with two ν(CO) bands at 2072 vw and 1949 vs cm^{-1}, characteristic of

Table 2
Crystal data and details of refinement for $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (**3**)

Chemical formula	$C_{11}H_{15}Cl_6Ge_2MoN_3O_2$
Molecular weight	675.08
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.568(2)
b (Å)	11.591(2)
c (Å)	12.498(2
α (°)	98.27(3)
β (°)	93.28(3)
γ (°)	101.02(3)
V ($Å^3$)	1201.0(4)
Z	2
Reflections determining lattice	90
T (K)	293(2)
Crystal size (mm)	0.15 × 0.15 × 0.20
D_{calc} (g cm^{-3})	1.867
λ (Mo–K_α) (Å)	71073
μ (Mo–K_α) (cm^{-1})	36.78
F(000)	652
Method of collection	$\omega/2\theta$ scan
2θ Range (°)	$6<2\theta<57$
Index ranges	$-11\leq h\leq 11$, $15\leq k\leq 15$, $0\leq l\leq 16$
No. of unique data	5163
No. of data with $[I\leq 2\sigma(I)]$	4539/230
Residuals R_1, wR_2	0.0615, 0.1703
Goodness-of-fit	1.118
Extinction coefficient	0.0070(18)
Final ($\Delta\rho$)(e $Å^{-3}$)	1.930/−1.262

Table 3
Selected IR and NMR data for molybdenum(II) alkyne complexes

Complex	IR (ν, cm^{-1})		^{1}H-NMR (δ, ppm) [b]	^{13}C-NMR (δ, ppm) [b]
	ν(CO)	ν(CN) [a]		
$[MoCl_2(CO)(NCMe)(PhC{\equiv}CPh)_2]$	2100 [c]	– [d]	–	–
$[MoCl_2(CO)(GeCl_2)(NCMe)(PhC{\equiv}CPh)]$	1981 [a]	2325 w, 2297 vw	2.06 (s, 1 $C\mathit{H}_3CN$)	227.33 (s, 1 CO), 224.36 (s, 1 $Ph\mathit{C}{\equiv}CPh$), 222.83, (s, 1 $PhC{\equiv}\mathit{C}Ph$), 137.42 (s, 1 C_i–Ph), 137.17, (C_i–Ph),126.63 (s, 1 $CH_3\mathit{C}N$), 4.04 (s, 1 $C\mathit{H}_3CN$)
$[MoCl_2(NCMe)_2(PhC{\equiv}CPh)_2]$	–	2319 w, 2289 vw	2.35 (s, 2 $C\mathit{H}_3CN$)	191.34 (s, 2 $Ph\mathit{C}{\equiv}CPh$), 186.77 (s, 2 $PhC{\equiv}\mathit{C}Ph$), 136.22 (s, 2 C_i–Ph), 135.17, (s, 2 C_i–Ph), 126.64 (s, 2 $CH_3\mathit{C}N$), 4.75 (s, 2 $C\mathit{H}_3CN$)
$[MoCl_2(CO)(GeCl_2)(NCEt)(PhC{\equiv}CPh)]$	1977 [a]	–	–	–
$[MoCl_2(NCEt)_2(PhC{\equiv}CPh)_2]$		2293 w	2.47 (q, 2 $CH_3C\mathit{H}_2CN$), 1.26 (t, 2 $C\mathit{H}_3CH_2CN$) [e]	193.24 (s, 2 $Ph\mathit{C}{\equiv}CPh$), 188.47 (s, 2 $PhC{\equiv}\mathit{C}Ph$), 138.11 (s, 2 C_i–Ph), 136.71, (s, 2 C_i–Ph), 132.85 (s, 2 $CH_3CH_2\mathit{C}N$), 14.32 (s, 2 $CH_3C\mathit{H}_2CN$), 10.13 (s, 2 $C\mathit{H}_3CH_2CN$) [e]
$[MoCl_2(CO)(GeCl_2)_2(PhC{\equiv}CPh)]$	2003 [a]		–	231.94 (s, 1 CO), 226.13 (s, 1 $Ph\mathit{C}{\equiv}CPh$), 224.51 (s, 1 $PhC{\equiv}\mathit{C}Ph$), 136.31 (s, 1 C_i–Ph), 136.02, (s, 1 C_i–Ph) [e]
$[MoCl_2(CO)(NCMe)(PhC{\equiv}CMe)_2]$	2087 [c]	–	–	–
$[MoCl_2(CO)(GeCl_2)(NCMe)(PhC{\equiv}CMe)]$	1972 [a]		3.27 (s, 1 $PhC{\equiv}C\mathit{Me}$), 2.31 (s, $C\mathit{H}_3CN$)	226.69 (s, 1 CO), 224.28 (s, 1 $Ph\mathit{C}{\equiv}Cme$), 222.91 (s, 1 $PhC{\equiv}\mathit{CMe}$), 137.20 (s, 1 C_i–Ph),127.73, (s, 1 $CH_3\mathit{C}N$), 18.77 (s, 2 $PhC{\equiv}C\mathit{Me}$), 4.05 (s, 1 $C\mathit{H}_3CN$)
$[MoCl_2(NCMe)_2(PhC{\equiv}CMe)_2]$	–	2325 w, 2397 vw	3.27 (s, 2 $PhC{\equiv}C\mathit{Me}$), 2.31 (s, 2 $C\mathit{H}_3CN$)	194.98 (s, 2 $Ph\mathit{C}{\equiv}CMe$), 178.51 (s, 2 $PhC{\equiv}\mathit{C}M\mathit{e}$), 135.98 (s, 2 C_i–Ph),126.41 (s, 2 $CH_3\mathit{C}N$), 18.40 (s, 2 $PhC{\equiv}C\mathit{Me}$), 4.75 (s, 2 $C\mathit{H}_3CN$)
$[MoCl_2(CO)(NCMe)(PhC{\equiv}CH)_2]$	2096 [c]	–	–	–
$[MoCl_2(NCMe)_2(PhC{\equiv}CH)_2]$ and other	–	2325 w, 2397 vw	11.24, 11.09, 10.85, 10.68 ($PhC{\equiv}C\mathit{H}$), 2.53 ($C\mathit{H}_3CN$)	–

[a] Spectra recorded in KBr disc.
[b] Spectra recorded in $CDCl_3$.
[c] Spectra recorded in CH_2Cl_2.
[d] Not observable.
[e] Spectra recorded in CD_2Cl_2.

a $[Mo(CO)_5]$ unit and of PA oligomerization products. The heptane extract contained organic products identified by GC–MS as 1,2,4-triphenylbenzene (68.8%), 1,3,5-triphenylbenzene (29.9%), diphenylbutadiene (0.8%) and 1*H*-indene-1-(phenylmethylene) (0.5%). The residue was dried in vacuo to give a brownish yellow mixture of compounds with four signals in the ^{1}H-NMR spectrum characteristic for PA coordinated to molybdenum in the region of δ 11–10. As was shown by elemental analysis there are compounds with two alkynes in the coordination sphere of molybdenum, probably $[MoCl_2(NCMe)_2(PhC{\equiv}CH)_2]$, $[Mo(\mu\text{-}Cl)Cl)(NCMe)(PhC{\equiv}CH)_2]_2$ and $[Mo_2(\mu\text{-}Cl)_3Cl(NCMe)(PhC{\equiv}CH)_4]$.

Anal. Calc. for $C_{34}H_{27}Cl_4Mo_2N$: C, 52.14; H, 3.47; N, 1.79. Found: C, 51.17; H, 3.67; N, 1.48%.

2.5. Catalytic conversion of PA

In a typical experiment, the mixture was composed of CH_2Cl_2 (5 cm^3), *ortho*-xylene (the internal chromatographic standard), PA (1 mol dm^{-3}), and a molybdenum complex **1** (PA/Mo 100 or PA/Mo 50) was stirred at r.t. under nitrogen for 24 h. The slow disappearance of PA was confirmed by GC (45% after 24 h). The polyphenylacetylene (PPA) was precipitated in methanol (20 cm^3) as a dark orange powder. The polymerization yield (%), defined by comparing the polymer weight to the weight of the PA used, was no greater than 17%. The polymer was analyzed by ^{1}H-NMR, IR spectroscopy and gel-permeation chromatography. Molecular weights of the PPA were measured using $CHCl_3$ solutions, a refractive index monitor and a Plgel 10 m MIXED-B column. The values recorded are the weight of polystyrene that would exhibit the chromatograms observed. Molecular weights of the PPA achieved the value, 1×10^4. ^{1}H-NMR spectra of the polymers were recorded in a $CDCl_3$ solution at 300 MHz. The stereostructure of the polymer was elucidated to be 58% *cis-transoidal*, using the ^{1}H-NMR data by the following equation according to Ref. [15],% $cis = A_{5.85} \times 10^4/A_t \times 16.66$, where A denotes the integrated absorption area of the signal at $\delta = 5.85$ ppm and A_t = the total integral of the NMR spectrum.

The filtrate obtained after the precipitation of the polymers was evaporated to dryness and the CH_2Cl_2 solution of the residue was investigated by GC–MS. Analysis showed mainly 1,2,4-triphenylbenzene and 1,3,5-triphenylbenzene in an average ratio of 3:1. The PA dimers, 1*H*-indene-1-(phenylmethylene), different isomers of diphenylbutadiene were formed in low yield (below 2%). The yield of oligomerization, calculated as the difference between the conversion and yield of polymerization reaction, was about 28% after 24 h reaction time.

3. Results and discussion

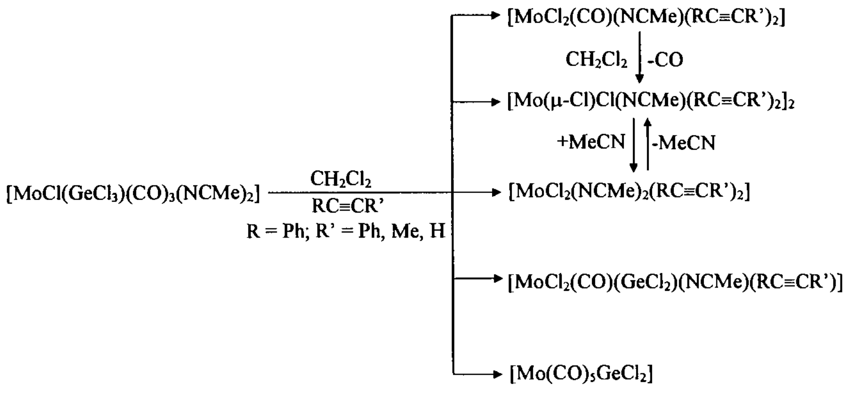
3.1. Synthesis of Mo–Ge compounds

Following our report [8] of the synthesis, molecular structure and reactivity of the unusual bimetallic tungsten–germanium compounds $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ and $[WCl(GeCl_3)(CO)_3(NCR)_2]$, R = Me, Et, Bu, Ph, it has recently been found that the oxidative–addition reaction of $[Mo(CO)_4(NCMe)_2]$ with $GeCl_4$ leads to an analogous $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**). The first time compound **1** was obtained in the reaction of $[Mo(CO)_3(NCMe)_3]$ and $GeCl_4$ in acetonitrile [10]. However, we found that compound **1** is more conveniently obtained in high yield by using CH_2Cl_2 instead of acetonitrile as solvent for the reaction of $[Mo(CO)_4(NCMe)_2]$ with $GeCl_4$. Besides **1**, other compounds containing Mo–Ge bonds are formed (Scheme 1). They include seven-coordinate mononuclear and dinuclear compounds with varying numbers (1–3) of CO and nitrile ligands (Scheme 1). They are less soluble in CH_2Cl_2 or $CHCl_3$, but the dimers can be restored to readily soluble monomers by recrystallization from nitrile (Scheme 1). The formation of compounds with two $GeCl_3$ groups coordinated to the molybdenum center was also observed (Scheme 1). These compounds can be formed in a disproportionation reaction giving $[MoCl_2(CO)_{5-n}(NCR)_n]$, where $n = 2$ or 3. Such a course of the reaction may well be a consequence of lower thermal stability of the $[MoCl_2(CO)_{5-n}(NCR)_n]$ by-product in comparison to $[Mo(GeCl_3)_2(CO)_{5-n}(NCR)_n]$ as a result of the π-acceptor character of the $GeCl_3$ ligand [16] in relation to the π-donor character of the chloride ligand. Subsequently, as earlier studies of molybdenum(II) nitrile compounds suggest [17,18], compounds of the type $[MoCl_2(CO)_{5-n}(NCR)_n]$ upon further reaction with the nitrile undergo disproportionation to compounds of molybdenum(0) and $MoCl_3$ solvated by nitrile. In this case $Mo(CO)_6$ and $[Mo(CO)_5(NCMe)]$ were identified as side products.

3.2. Spectral studies of Mo–Ge compounds

The IR spectra of $[MoCl(GeCl_3)(CO)_3(NCR)_2]$ (R = Me and Et) compounds in KBr show a common profile which includes three bands in the CO region, with only small changes in frequencies within the nitrile series (Table 1). They are similar to that for the analogous molybdenum–tin complex obtained for the first time by Baker and Bury [9,19] and are in excellent agreement with the data reported for tungsten compounds of the type $[WCl(MCl_3)(CO)_3(NCMe)_2]$, M = Sn [7], Ge [8]. The germyl ligand can be identified by far-IR spectra due to the ν(GeCl) band at ca. 380 cm^{-1}.

The ^{13}C-NMR spectrum of compound **1** in $CDCl_3$ at 293 K consists of one sharp resonance at δ 219.34 ppm. Very similar single resonances were observed for three equivalent carbonyl groups of other compounds of the type $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ (δ 211.9 for W–Sn [7], 214.8 for W–Ge [8] and 219.39 for the Mo–Sn [9] compound). The single resonance in the ^1H-NMR spectrum clearly indicates that all bis(nitrile) compounds contain two equivalent nitrile ligands (Table 1).



Scheme 2.

The complex $[MoCl(GeCl_3)(CO)_3(NCMe)_2]$ (**1**) synthesized by Baker and Kendrick showed three carbonyl bands at ν(CO) 2040 (s), 1953 (s), 1877 (m) cm^{-1} but six resonances in the carbonyl region (δ 231.53–202.92) of the ^{13}C-NMR spectrum [10]. This is in contrast to the results for $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ [7], $[WCl(GeCl_3)(CO)_3(NCMe)_2]$ [8] and $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ [9] which showed analogous distorted capped octahedron geometry and similar IR spectrum containing three carbonyl bands, but only one carbonyl resonance of three equivalent CO groups. Besides the ν(CO) frequency at 1877 cm^{-1}, it is characteristic for dicarbonyl rather than tricarbonyl species (Table 1).

However, compound **3** and other compounds containing two $GeCl_3$ groups coordinated to molybdenum, have different spectral data (Table 1). First of all there is a downfield shift of the carbon resonance of CO groups to δ ca. 230 in ^{13}C-NMR spectra. This shift is consistent with the lowering of electron density on molybdenum due to the higher electron-withdrawing character of two trichlorogermyl ligands. Thus the molybdenum atom in **3** is effectively more oxidized than in **1**. The IR spectrum of **3** shows two ν(CO) bands at 1961 s and 1897 vs cm^{-1}, which is in the region, and intensely characteristic of other seven-coordinate bis(carbonyl) nitrile compounds [1,9]. The spectroscopic data obtained for **3** are analogous to those presented by $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ [9].

3.3. Structure of $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (3)

Although the structures of numerous complexes containing a molybdenum–germanium bond have been determined crystallographically [20–22], no bis(trichlorogermyl) complexes have thus far been studied.

The structure of compound **3**, is shown in Fig. 1 with the atom-numbering scheme. Table 2 gives a summary of the crystal data and refinement obtained for **3**. The principal interatomic bond distances and angles are presented in Table 4.

The geometry of the coordination sphere of molybdenum atom in **3** approximates that of the 4:3 'piano stool' structure identified in several molybdenum(II) complexes ($[Mo(CNPh)_7]^{2+}$ [23], $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^+$ [24] and $[Mo\text{-}Br(CO)_3(1,4,7\text{-triazacyclononane})]^+$ [25]). In the description of **3** the tetragonal base is defined by two carbon atoms, Mo–C = 1.968 Å (average) and two germanium atoms, Mo–Ge = 2.534 Å (average). In the trigonal base there are three nitrogen atoms with a mean Mo–N bond length of 2.186(5), 2.193(5) and 2.212(5) Å and *cis* N–Mo–N bond angles 79.8(2), 79.9(2) and 79.3(2)°. The angle between tetragonal and trigonal base is 2.6 (1)° confirming the 4:3 geometry [26]. One nitrogen atom (N(21)) of the trigonal base and one carbon atom (C(1)) of the tetragonal base almost overlap (Fig. 2).

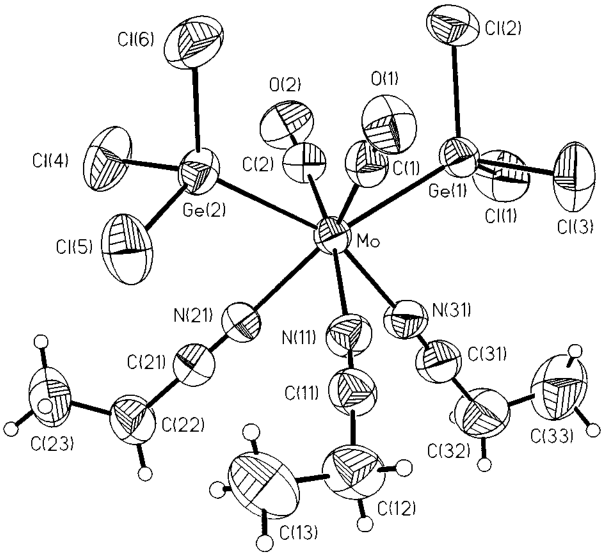


Fig. 1. Molecular structure of $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (**3**).

The molybdenum–germanium bond is short, at 2.534 Å (average), compared to the sum of the relevant covalent radii of 2.83 Å [27,28]. In view of the established π-acceptor properties of the $GeCl_3$ group [16] it clearly indicates that the Mo–Ge bond does possess some double-bond character. Similar Mo–Ge distances had been observed for $[CpMo(CO)_2(PMe_3)(GeCl_2H]$ (2.531(2) [20]) and $[CpMo(CO)_2(PMe_3)(GeCl_3]$ (2.505(7) [20]) but longer for the triphenylgermyl complexes (2.658(2) [21] and 2.604(2) Å [22]).

The germanium atom is four-coordinate with a geometry that is best described as a distorted tetrahedral with Cl–Ge–Cl angles in the range 99.7(1)–101.2(1) and Cl–Ge–Mo angles in the range 113.7(8)–121.9(8)°, so the tetrahedral geometry is distorted by the greater repulsions associated with the molybdenum atom.

An X-ray study of complex **3** showed that the $GeCl_3$ ligands occupy a position mutually *trans* with the Ge–Mo–Ge angle of 124.6(3)°. The 4:3 'piano stool' geometry similar to that for **3**, with two mutually *trans* trichlorostannyl ligands, and three mutually *cis* nitrile ligands, was observed previously for analogous $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ [9]. However, the Mo–N distances are longer (av. 2.197 vs. 2.179) and Mo–C distances are shorter (av. 1.968 vs. 1.984) in **3** than in the bis(trichlorostannyl) compound [9].

3.4. Reactions of molybdenum(II) compounds with alkynes

The complexes obtained in the reaction of **1** and alkynes (Scheme 2) are listed in Table 3 along with their IR and NMR spectroscopic data.

When the reaction of **1** with two molecular equivalents of DPA at r.t. in CH_2Cl_2 was monitored by IR, at the beginning, decay of ν(CO) bands due to **1** was accompanied by appearance and growth of several ν(CO) bands at 2100, 2073, 1984 and 1950 cm^{-1}. But after a prolonged reaction time (24 h), a new ν(CO) band at 2100 cm^{-1} of the alkyne complex decays. Based on the IR data the initial complex can be described as $[MoCl_2(CO)(NCMe)(PhC{\equiv}CPh)_2]$ with the structure close to the one obtained and characterized crystallographically by Baker et al. in the reaction of $[WI_2(CO)_3(NCMe)_2]$ and RC≡CR (R = Me, Ph) [29,30]. The loss of the CO group leads to formation of chloride-bridged dimer $[Mo(\mu\text{-}Cl)Cl(NCMe)(PhC{\equiv}CPh)_2]_2$ (Scheme 2). The IR and NMR spectral data for the reaction product indicate that it is a mixture of compounds with and without CO in the coordination sphere of the molybdenum. The mononuclear compound $[MoCl_2(NCMe)_2(PhC{\equiv}CPh)_2]$, with two mutually *cis* alkyne ligands, which are magnetically equivalent and give two signals of acetylenic carbons in ^{13}C-NMR spectra at δ 191.34 and 186.77, was identified as the main product. In CH_2Cl_2 solution this compound dimerizes with a loss of acetonitrile molecule to yield less soluble chloride-bridged complexes. This process is reversible in the presence of an excess of acetonitrile (Scheme 2). Thus, nitrile effects the nucleophilic cleavage of an $Mo(\mu\text{-}Cl)_2Mo$ bridge. The alkyne compound with a ν(CO) band at 1984 cm^{-1} was characterized only in the reaction mixture by IR and NMR spectroscopy and can be formulated as $[MoCl_2(CO)(GeCl_2)(NCMe)(PhC{\equiv}CPh)]$. The spectral characteristic of the latter compound is very similar to the $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(PhC{\equiv}CPh)]$ observed by Baker et al. in the reaction of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ with DPA [31] and to the other monoalkyne compounds of molybdenum of the type $[MoBr_2(CO)(PR_3)_2(RC{\equiv}CR')]$ observed by Templeton et al. [32–34]. The acetylenic ^{1}H- and ^{13}C-NMR chemical shift values observed here (Table 2) are comparable to literature values for other four-electron donor alkyne ligands in mono(alkyne) compounds [32–34]. The reaction of **1** with alkynes in dichloromethane solution containing acetonitrile leads to the formation of higher yield of mono(alkyne) than bis(alkyne) compound.

Table 4
Selected bond lengths (Å) and bond angles (°) for $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (**3**)

Mo(1)–Ge(1)	2.529(1)	Ge(1)–Cl(3)	2.179(2)
Mo(1)–Ge(2)	2.539(1)	Ge(1)–Cl(2)	2.180(2)
Mo(1)–C(1)	1.962(7)	Ge(2)–Cl(4)	2.175(2)
Mo(1)–C(2)	1.974(6)	Ge(2)–Cl(6)	2.179(2)
Mo(1)–N(3)	2.186(5)	Ge(2)–Cl(5)	2.181(2)
Mo(1)–N(2)	2.193(5)	N(1)–C(11)	1.126(8)
Mo(1)–N(1)	2.212(5)	N(2)–C(21)	1.121(8)
Ge(1)–Cl(1)	2.172(2)	N(3)–C(31)	1.118(9)
C(1)–Mo(1)–C(2)	106.0(2)	N(1)–Mo(1)–Ge(2)	97.6(1)
C(1)–Mo(1)–N(3)	127.2(2)	Ge(1)–Mo(1)–Ge(2)	124.6(3)
C(2)–Mo(1)–N(3)	100.5(2)	Cl(1)–Ge(1)–Cl(3)	99.7(1)
C(1)–Mo(1)–N(2)	141.9(2)	Cl(1)–Ge(1)–Cl(2)	99.8(1)
C(2)–Mo(1)–N(2)	92.2(2)	Cl(3)–Ge(1)–Cl(2)	101.2(1)
N(3)–Mo(1)–N(2)	79.8(2)	Cl(1)–Ge(1)–Mo(1)	117.4(8)
C(1)–Mo(1)–N(1)	80.2(2)	Cl(3)–Ge(1)–Mo(1)	118.1(7)
C(2)–Mo(1)–N(1)	171.3(2)	Cl(2)–Ge(1)–Mo(1)	117.3(7)
N(3)–Mo(1)–N(1)	79.9(2)	Cl(4)–Ge(2)–Cl(6)	100.5(1)
N(2)–Mo(1)–N(1)	79.3(2)	Cl(4)–Ge(2)–Cl(5)	100.5(1)
C(1)–Mo(1)–Ge(1)	68.7(2)	Cl(6)–Ge(2)–Cl(5)	101.2(1)
C(2)–Mo(1)–Ge(1)	74.4(2)	Cl(4)–Ge(2)–Mo(1)	116.0(7)
N(3)–Mo(1)–Ge(1)	75.9(1)	Cl(6)–Ge(2)–Mo(1)	121.9(8)
N(2)–Mo(1)–Ge(1)	149.4(1)	Cl(5)–Ge(2)–Mo(1)	113.7(8)
N(1)–Mo(1)–Ge(1)	114.0(1)	C(11)–N(1)–Mo(1)	175.6(5)
C(1)–Mo(1)–Ge(2)	73.8(2)	C(21)–N(2)–Mo(1)	176.7(5)
C(2)–Mo(1)–Ge(2)	78.6(2)	C(31)–N(3)–Mo(1)	177.0(6)
N(3)–Mo(1)–Ge(2)	157.3(2)	O(1)–C(1)–Mo(1)	174.4(6)
N(2)–Mo(1)–Ge(2)	77.5(1)	O(2)–C(2)–Mo(1)	177.4(6)

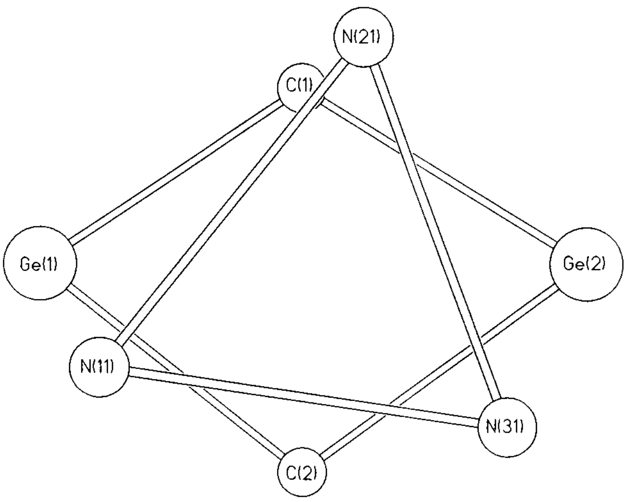


Fig. 2. Projection of the coordination sphere of Mo on the trigonal base illustrating the 4:3 geometry of **3**. Lines joining the atoms to define the planes. The angle between tetragonal and trigonal base is 2.6(1)°.

Spectral studies revealed that in the reaction of **1** with PhC≡CH (PA) the precursor complex **1** is liable to lose CO and acetonitrile, but at the beginning, one CO and acetonitrile ligand still remains in the coordination sphere of the molybdenum. The IR spectrum of this product showed one ν(CO) band at 2095 cm^{-1}. However, the isolated compound does not contain carbonyl ligand and after recrystallization from acetonitrile, was identified as $[MoCl_2(NCMe)_2(PhC{\equiv}CH)_2]$ contaminated with dinuclear species. The hydrogen resonance due to phenylacetylene coordinated to molybdenum was observed at δ 11.09, 11.24, 10.85 and 10.68.

As was mentioned above we were unable to prepare the alkyne complexes containing trichlorogermyl ligand, because the hydrolysis of $GeCl_3$ occurred and $GeCl_2$ coordinated to molybdenum(II), $[MoCl_2(CO)(GeCl_2)(NCMe)(PhC{\equiv}CPh)]$ or molybdenum(0),

$[Mo(CO)_5GeCl_2]$, identified by IR and NMR spectroscopy, resulted. The latter compound which is extremely air-sensitive, readily soluble even in cyclohexane and other hydrocarbons, gives characteristic (for the pentacarbonyl unit) ν(CO) bands at 2072 w and 1950 vs cm^{-1} in the IR spectrum and two carbon resonances at δ 213.26 (1 CO) and 205.94 (4 CO) in the intensity ratio 1:4, in the ^{13}C-NMR spectrum. These data are in a good agreement with the spectral data for compounds of the type, $[Mo(CO)_5(GeX_2)]$ [16,35].

3.5. Catalytic reactions

Conversion of PA occurs very smoothly at r.t. in CH_2Cl_2 containing compound **1** (45% after 24 h). Treatment of the reaction mixture with a large amount of methanol produced quantitatively PPA as a fine dark orange powder which has a number-average molecular weight (M_w) from 4 to 10×10^3, determined by GPC. The resulting PPA was completely soluble, enabling us to investigate its molecular structure by spectroscopy. We used ^1H-NMR spectroscopy to determine the stereostructure of the PPA according to Simionescu and Percec's method [12]. The ^1H-NMR spectra of PPA in $CDCl_3$ displayed a sharp singlet due to the vinylic protons at δ 5.85 ppm in addition to a set of multiplets at 6.60–7.00 ppm which has been correlated to the *cis-transoidal* (58%) structure of PPA [15]. The IR spectrum of PPA is characterized by a low intensity band at 740 cm^{-1}.

However, the catalytic coupling of alkynes in the presence of **1** yields at least two types of products in the approximate ratio 2:1, namely polymers with conjugated polyenic structures and cyclic oligomers, especially the aromatic cyclotrimers 1,2,4- and 1,3,5-triphenylbenzene (TPB). Minor amounts of other oligomers arise, mainly linear diphenylbutadienes (DPBD), which contain, for example, hydrogen derived from the solvent and also a dimer of PA detected by MS as 1*H*-indene-1-(phenylmethylene).

A plausible mechanism for the formation of cyclotrimers from PA shown in Scheme 3 involves the initial coordination of two alkynes to the metal, rearrangement to a metallacyclopentadiene, insertion of a coordinated alkyne into a Mo–C σ-bond leading to metalacycloheptatriene and reductive elimination of cyclotrimers with release of the coordinatively unsaturated metal fragment. The formation of linear conjugated polyenic polymers involves oxidative coupling and formation of a series of metallacyclic species. The metallacycle formed with four molecules of alkyne can then rearrange to an alkylidene ligand initiating the increase of the polymer chain, as was observed by Yeh et al. [36,37] (Scheme 3).

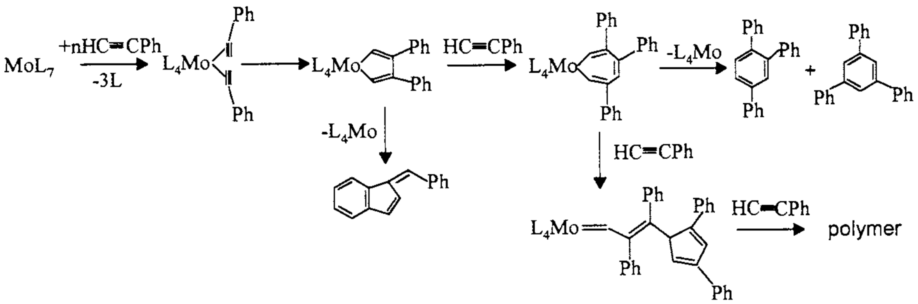
Our experimental results suggest that the catalytic cycle (Scheme 3) which has long been suggested ([36,37] and Refs. cited therein) is operating in our system. The following points have been proven: (i) in the reactions of **1** with alkyne a *cis*-bis(alkyne) complex is a detectable species, (ii) decomposition of the catalytic system with methanol gives phenylacetylene dimers (1*H*-indene-1-(phenylmethylene) and DPBD), (iii) the departure of the cyclotrimer from the coordination sphere of molybdenum recovers alkyne complex and (iv) PPA has a regular *cis-transoidal* (58%) structure.

The reactivity of **1** towards acetylenes is compared with that of the related $[WCl(GeCl_3)(CO)_3(NCMe)_2]$ [8]. In contrast with its tungsten analogue, reaction of the molybdenum complex **1** with terminal acetylenes yielded the cyclotrimers in greater yield. The tungsten complex is more selective towards polymer formation.

4. Conclusions

The generation of the Mo–Ge species was achieved in a straightforward manner that demonstrates that oxidative–addition is a viable reaction to generate metal–metal bonds in organometallic compounds.

A compound with two trichlorogermyl ligands is unusual, and $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (**3**) is the first structurally characterized example of such a compound.



Scheme 3.

Alkyne complexes can indeed be readily formed in the reaction of the seven-coordinate molybdenum(II) complexes. The resulting air-unstable compounds are all characterized mainly by IR, ^{1}H- and ^{13}C-NMR spectroscopy in the reaction mixture.

The Mo–Ge compound appears as a very good catalyst in polymerization and cyclooligomerization of alkynes. The catalytic coupling of alkynes in the presence of Mo–Ge compounds yields at least two types of product, namely polymers with conjugated polyenic structures and cyclic oligomers, especially the aromatic cyclotrimers.

5. Supplementary material

Atomic coordinates, thermal parameters, and bond lengths and angles of compound **3** have been deposited at the Cambridge Crystallographic Data Center (CCDC 129669) and are available on request.

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