

Insertion of GeCl_2 into molybdenum–hydrogen bonds: a convenient route to dichlorogermeryl complexes

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Abstract

Insertion of GeCl_2 into the molybdenum–hydrogen bond of $\text{CpMo}(\text{CO})_3\text{H}$ (**1**) affords the dichlorogermeryl complex $\text{CpMo}(\text{CO})_3\text{GeCl}_2\text{H}$ (**2**). Complex **2** reacts with PMe_3 to give *trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_2\text{H}$ (**5**). The mechanism of this ligand exchange reaction involving GeCl_2 extrusion and insertion steps is described. Insertion of GeCl_2 into the molybdenum–hydrogen bond of *cis/trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ (**4**) offers an alternative route to complex **5**. The dichlorogermeryl complexes **2** and **5** are slowly chlorinated by CH_2Cl_2 to give the trichlorogermeryl complexes $\text{CpMo}(\text{CO})_3\text{GeCl}_3$ (**3**) and *trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_3$ (**6**), respectively. Chlorination of the dichlorogermeryl complexes occurs also with $\text{GeCl}_2(\text{dioxane})$ in toluene. The crystal structure of **5** is described. © 1997 Elsevier Science S.A.

Keywords: Germanium; Germylene; Molybdenum; Insertion

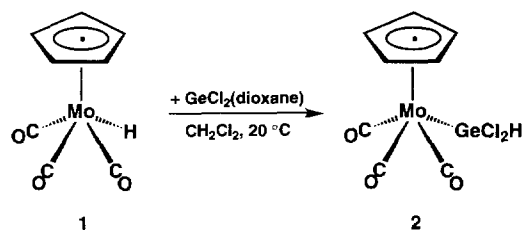
1. Introduction

Divalent germanium compounds have been the subject of considerable interest in recent years [1]. Among the oldest known stable Ge^{II} derivatives are the dihalides GeX_2 ($\text{X} = \text{F}–\text{I}$). These compounds have been shown to insert into various σ bonds between main-group elements providing an easy access to dihalogermenes [2]. In comparison, studies on insertion reactions of germanium dihalides into σ bonds of transition metals are rather limited and those into transition-metal hydrogen bonds to our knowledge are not known [2,3]. This has prompted us to carry out the following work dealing with the insertion reactions of $\text{GeCl}_2(\text{dioxane})$ into the Mo–H bond of $\text{CpMo}(\text{CO})_3\text{H}$ (**1**) and *cis/trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ (**4**).

2. Results and discussion

When the hydrido complex $\text{CpMo}(\text{CO})_3\text{H}$ (**1**) [4] was treated with one equivalent of $\text{GeCl}_2(\text{dioxane})$ in CH_2Cl_2 at ambient temperature, a fast insertion of GeCl_2 into the molybdenum–hydrogen bond of **1** was

observed affording the dichlorogermeryl complex $\text{CpMo}(\text{CO})_3\text{GeCl}_2\text{H}$ (**2**) (Eq. (1)). Evidence for the fast and selective transformation of **1** to **2** was given by the IR spectra of the reaction solutions, which revealed that the two $\nu(\text{CO})$ absorptions of the starting material at 2024 and 1932 cm^{-1} had been replaced within two hours by those of the product at 2042, 1975 and 1946 cm^{-1} . Complex **2** was isolated as a yellow, air-sensitive, microcrystalline solid in quantitative yield. It is soluble in CH_2Cl_2 and toluene, sparingly soluble in Et_2O and insoluble in pentane and decomposes at 87°C, when heated in a sealed capillary under argon.

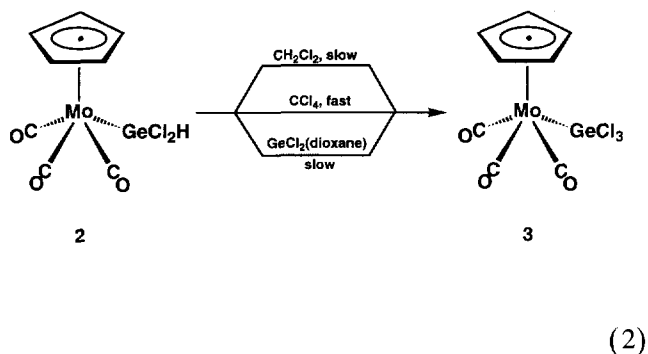


(1)

When a solution of complex **2** in CH_2Cl_2 was exposed to daylight at ambient temperature, a very slow (ca. 20 days) chlorination of **2** by the solvent occurred

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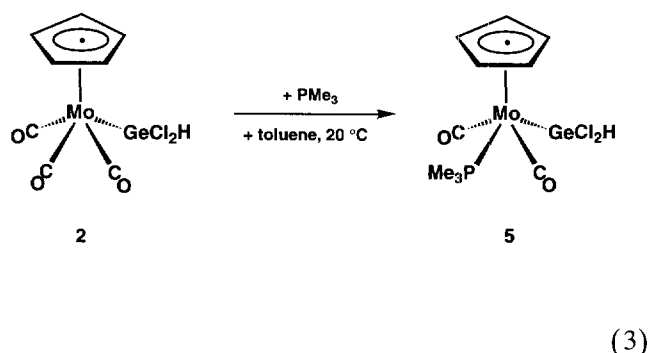
to give the trichlorogermyl complex $\text{CpMo}(\text{CO})_3\text{GeCl}_3$ (**3**) (Eq. (2)). Chlorination of **2** to afford **3** is fast (ca. 0.5 days), if CCl_4 is used as the chlorinating agent. This offers an alternative route to complex **3**, which has been previously prepared from $\text{CpMo}(\text{CO})_3\text{Cl}$ and GeCl_2 (dioxane) and characterized by a single-crystal X-ray diffraction study [3]. Complex **2** is also chlorinated by GeCl_2 (dioxane) in toluene at ambient temperature to give **3** (Eq. (2)). However, this reaction is slow and therefore not significant in the synthesis of **2** from **1**.



The IR spectrum of **2** in CH_2Cl_2 exhibits in the region $2200\text{--}1500\text{ cm}^{-1}$ three $\nu(\text{CO})$ absorptions at 2042 , 1975 and 1946 cm^{-1} as expected on the basis of group theory for a $\text{M}(\text{CO})_3$ fragment of local C_s symmetry in a 'four-legged piano-stool' complex of the type $\text{CpM}(\text{CO})_3\text{X}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{neutral, one-electron donor ligand}$) [5]. The $\nu(\text{CO})$ absorptions of **2** appear at higher wavenumbers than those of **1** ($\nu(\text{CO})$ in CH_2Cl_2 : 2024 and 1932 cm^{-1}), indicating that insertion of GeCl_2 into the $\text{Mo}\text{--}\text{H}$ bond of **1** reduces the electron density at the metal center and weakens thereby the $\text{metal}(\text{d}\pi)\text{--}\text{CO}(\pi^*)$ back bonding in **2**. In comparison, the $\nu(\text{CO})$ absorptions of **2** appear at lower wavenumbers than those of the trichlorogermyl complex **3** ($\nu(\text{CO})$ in CH_2Cl_2 : 2051 , 1988 and 1965 cm^{-1}) indicating a stronger $\text{metal}(\text{d}\pi)\text{--}\text{CO}(\pi^*)$ back bonding in **2** than in **3**. This suggests that the dichlorogermyl group is a stronger σ -donor ligand than the trichlorogermyl group. Further support for the structure assigned to **2** is given by the ^1H -NMR spectrum, which shows one singlet resonance for the protons of the Cp ligand at δ 4.43 and a singlet resonance for the germanium-bonded proton at δ 7.96. The ^1H chemical shift of the $\text{Ge}\text{--}\text{H}$ group is similar to that of HGeCl_3 ($\delta_{\text{H}} = 7.6$) [6]. Finally, the ^{13}C -NMR spectrum of **2** in C_6D_6 at 20°C , displays two carbonyl-carbon resonances in an approximate ratio of 2:1 at δ 222.9 and 228.2.

Treatment of **2** with slightly more than one equivalent of PMe_3 in toluene at ambient temperature afforded the CO substitution product *trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_2\text{H}$ (**5**) (Eq. (3)). This was isolated in 79% yield as a yellow, microcrystalline solid that is soluble in CH_2Cl_2 and toluene, but sparingly

soluble in Et_2O . Complex **5** is sensitive towards moisture and air and decomposes at 146°C , when heated in a sealed capillary under argon.



The IR and NMR spectroscopic data of **5** resemble those of the analogous dichlorosilyl complex *trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{SiCl}_2\text{H}$, which has been previously obtained from $\text{Li}[\text{CpMo}(\text{CO})_2(\text{PMe}_3)]$ and HSiCl_3 [7], and indicate unequivocally the *trans*-geometry of the dicarbonyl complex. Thus, two $\nu(\text{CO})$ absorptions are observed in the IR spectrum of **5** in CH_2Cl_2 at 1946 and 1873 cm^{-1} , the higher frequency (symmetric) CO stretching vibration being less intense than the lower frequency (antisymmetric) CO stretching vibration [8]. The angle 2θ between the two CO ligands has been calculated to be 107.5° using the relationship $I_a/I_s = \tan^2\theta$, where I_a and I_s are the intensities of the absorptions due to the antisymmetric and symmetric C–O stretching modes [8]. The calculated value for the $\text{OC}\text{--}\text{Mo}\text{--}\text{CO}$ angle of **5** in solution is close to that found in the solid-state ($\text{OC}\text{--}\text{Mo}\text{--}\text{CO} = 104.6(5)^\circ$) (see crystal structure of **5** below). The $\nu(\text{CO})$ absorptions of **5** appear at lower wavenumbers than those of *trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_3$ ($\nu(\text{CO})$ in CH_2Cl_2 : 1965 , 1891 cm^{-1}) [3], indicating that the dichlorogermyl group is a better σ donor ligand than the trichlorogermyl group (compare also the $\nu(\text{CO})$ absorptions of **2** and **3**). Additional support for the *trans*-disposition of the carbonyl ligands in **5** is given by the ^{13}C -NMR spectrum in C_6D_6 at 20°C , which displays only one resonance for the equivalent carbonyl-carbon nuclei at δ 230.7. This resonance appears as a doublet due to $^{13}\text{C}\text{--}^{31}\text{P}$ coupling, the size of the coupling constant ($^2J(\text{PC}) = 26.5\text{ Hz}$) being indicative of a *cis*-disposition of the carbonyl ligands relative to the PMe_3 ligand [3]. Finally, the ^1H -NMR spectrum of **5** in C_6D_6 at 20°C shows besides the expected doublet resonances of the PMe_3 and the Cp ligand protons at δ 0.81 and 4.65, respectively, a singlet resonance for the germanium-bonded hydrogen atom at δ 8.61.

The solid-state structure of **5** was determined by a single-crystal X-ray diffraction study. Suitable crystals were obtained after slow evaporation of a benzene solution of **5** at room temperature. A ZORTEP plot of **5**

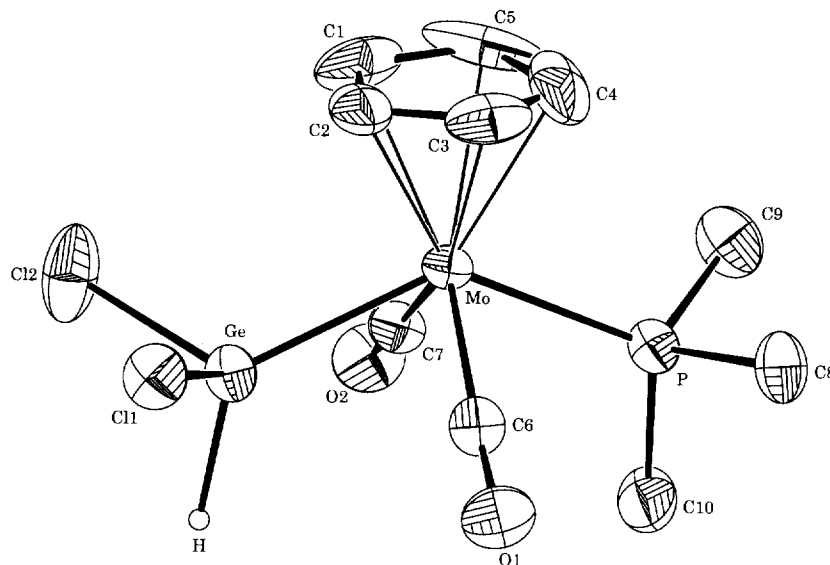


Fig. 1. ZORTEP plot of the structure of **5** with thermal ellipsoids drawn at the 50% probability level.

with the atom-labeling scheme adopted is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1.

Complex **5** shows the expected square-pyramidal coordination geometry of a 'four-legged piano-stool' complex. The dichlorogermeryl and trimethylphosphane ligands are *trans* positioned as deduced from the IR and NMR spectroscopic data of this compound. All the angles about the molybdenum center are similar to those of *trans*-CpMo(CO)₂(PMe₃)GeCl₃ (**6**) [3]. Also the Mo–C(ring), Mo–P and Mo–CO bonds have average lengths of 231.7, 246.4 and 196.9 pm respectively, which are similar to those of **6** ((Mo–C(ring))_{av.} = 231.8 pm; (Mo–P)_{av.} = 247.01 pm; (Mo–CO)_{av.} = 197.6 pm). Of specific interest are the structural features of the dichlorogermeryl ligand. The Mo–Ge bond of **5** is with 253.1(2) pm shorter than the Mo–Ge single bond of the triphenylgermyl complexes Cp(CO)₂Mo(GePh₃)[C(OEt)Ph] (Mo–Ge = 265.8(2) pm) [9] and Cp(η³-C₆H₁₁)(NO)MoGePh₃ (Mo–Ge = 260.4(2) pm) [10] or the Mo–Ge single bond of the germylydyne cluster ^tBuGeMoFeCp(CO)₈H (Mo–Ge =

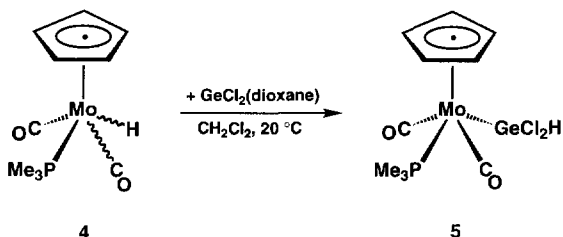
255.6(3) pm) [11]. A comparison of the structural parameters of the trichlorogermeryl ligand in *trans*-CpMo(CO)₂(PMe₃)GeCl₃ (**6**) [3] with those of the dichlorogermeryl ligand in **5** reveals that substitution of a chloro substituent by a hydrogen atom causes an elongation of the Mo–Ge bond (**6**: (Mo–Ge)_{av.} = 250.57 pm; **5**: Mo–Ge = 253.1(2) pm), an elongation of the Ge–Cl bonds (**6**: (Ge–Cl)_{av.} = 219.3 pm; **5**: (Ge–Cl)_{av.} = 221.8 pm) and a reduction of the Mo–Ge–Cl bond angles (**6**: (Mo–Ge–Cl)_{av.} = 118.41°; **5**: (Mo–Ge–Cl)_{av.} = 114.8°). The same trends have been observed, when in GeX₄ (X = F, Cl) the halogen atoms were successively substituted by more electropositive substituents such as hydrogen or methyl groups and have been explained with the changes in bond polarities using either the hybrid atomic orbital model or the valence-shell electron pair repulsion model [12].

IR monitoring of the reaction of **2** with PMe₃ in toluene to give **5** revealed the formation of two intermediates, which on the basis of their ν(CO) absorptions were identified to be **1** (ν(CO) in toluene: 2023 and 1933 cm⁻¹) and *cis/trans*-CpMo(CO)₂(PMe₃)H (**4**) (ν(CO) in toluene: 1934 and 1853 cm⁻¹). This indicates a more complicated mechanism than one might anticipate for a CO/PMe₃ substitution reaction involving GeCl₂ extrusion and insertion steps. We suggest that in the first step PMe₃ adds to the electrophilic germanium center of **2**. This is followed by the extrusion of GeCl₂ probably as PMe₃GeCl₂ to give CpMo(CO)₃H (**1**). In fact, phosphane adducts of GeCl₂ such as PPh₃GeCl₂ and P(^tBu)₃GeCl₂ have been described in the literature [13]. Complex **1** then reacts with PMe₃ to afford *cis/trans*-CpMo(CO)₂(PMe₃)H (**4**) [14], which finally inserts GeCl₂ into the Mo–H bond to give complex **5**. In a control experiment *cis/trans*-

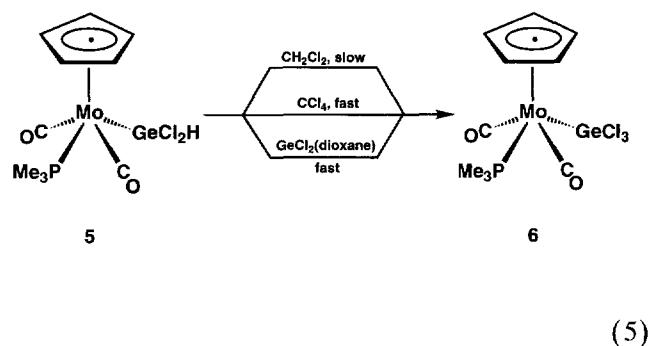
Table 1
Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **5**

Mo–C(1)	230(2)	Ge–Cl(2)	220.8(4)
Mo–C(2)	231(2)	C(6)–Mo–P	77.1(4)
Mo–C(3)	233.4(13)	C(6)–Mo–C(7)	104.6(5)
Mo–C(4)	229(2)	C(6)–Mo–Ge	73.5(4)
Mo–C(5)	235(2)	P–Mo–C(7)	78.4(4)
Mo–C(6)	197.1(14)	P–Mo–Ge	131.98(8)
Mo–C(7)	196.6(13)	C(7)–Mo–Ge	73.5(4)
Mo–P	246.4(3)	Mo–Ge–Cl(1)	114.84(13)
Mo–Ge	253.1(2)	Mo–Ge–Cl(2)	114.8(2)
Ge–Cl(1)	222.8(4)	Cl(1)–Ge–Cl(2)	99.85(14)

$\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ (**4**) was demonstrated to insert rapidly GeCl_2 into the Mo–H bond to afford selectively **5** (Eq. (4)). This gives additional support for the suggested pathway for the reaction of **2** with PMe_3 .



Like **2**, complex **5** is slowly (ca. 20 days) chlorinated by CH_2Cl_2 , when exposed to daylight, to give the trichlorogermyl complex *trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_3$ (**6**). This conversion becomes considerably faster (ca. 6 h), if CCl_4 is used as chlorinating agent (Eq. (5)) and offers an alternative route to complex **6**, which has been previously obtained by the isomerization of *cis*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_3$, the latter complex resulting from the insertion reaction of GeCl_2 into the Mo–Cl bond of *cis*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{Cl}$ [3]. However, complex **5** differs from **2** that it reacts rapidly with $\text{GeCl}_2(\text{dioxane})$ in toluene at ambient temperature to afford **6** (Eq. (5)). This was demonstrated by a control experiment, showing that addition of 1.5 equivalents of $\text{GeCl}_2(\text{dioxane})$ to a toluene solution of **5** resulted in the complete conversion to **6** within 1.5 h. Therefore a stoichiometric amount of $\text{GeCl}_2(\text{dioxane})$ should be used in the synthesis of **5** from **4** (Eq. (4)). Otherwise the product is contaminated to a variable extent with **6**.



3. Conclusion

Insertion of GeCl_2 into the Mo–H bond of $\text{CpMo}(\text{CO})_2(\text{L})\text{H}$ ($\text{L} = \text{CO}, \text{PMe}_3$) provides a high-yield and fast route to dichlorogermyl complexes (metallo-

dichlorogermenes). These compounds are of particular interest, because these might be useful starting materials for the synthesis of metallated germynes after dehydrohalogenation, and could be also employed in organic synthesis as GeCl_2 transfer reagents.

4. Experimental

Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane over CaH_2 , Et_2O and toluene over $\text{Na}/\text{benzophenone}$, CH_2Cl_2 over P_2O_5 and Na/Pb alloy), distilled under argon and stored over 4-Å molecular sieves prior to use.

Elemental analyses were obtained from the Zentrale Analytische Gruppe des Instituts für Chemie der Humboldt-Universität zu Berlin. IR spectra were recorded on a Bruker IFS-55 spectrometer in CH_2Cl_2 or toluene using a CaF_2 cell. ^1H -, $^{13}\text{C}\{^1\text{H}\}$ - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on a Bruker AM-300 spectrometer in dry deoxygenated methylene- d_2 -chloride or benzene- d_6 at 20°C. The ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were calibrated against the solvent signals (methylene- d_2 -chloride, δ_{H} 5.32 and δ_{C} 53.8 ppm; benzene- d_6 , δ_{H} 7.15 and δ_{C} 128.0 ppm) and the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra against an external 85% H_3PO_4 aqueous solution. Mass spectra were obtained with a Hewlett Packard 5995A spectrometer; m/z values are given relative to the ^{98}Mo , ^{74}Ge and ^{35}Cl isotopes. Melting points were determined using a Büchi 530 melting point apparatus and are not corrected. The samples were sealed in capillary tubes under argon and heated with a rate of 1 K/min.

The complexes $\text{CpMo}(\text{CO})_3\text{H}$ (**1**) and *cis/trans*- $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ (**4**) were obtained according to published procedures [4,14]. $\text{GeCl}_2(\text{dioxane})$ and PMe_3 were prepared following the procedures reported by O.M. Nefedov and H. Schmidbaur, respectively [15,16].

4.1. $\text{CpMo}(\text{CO})_3\text{GeCl}_2\text{H}$ (**2**)

A mixture of 1.11 g (4.51 mmol) of **1** and 1.05 g (4.53 mmol) of $\text{GeCl}_2(\text{dioxane})$ was suspended in 50 ml of CH_2Cl_2 at ambient temperature and stirred for 2 h. During this time the colour of the solution changed from orange to bright yellow. Completion of the reaction was revealed by IR spectroscopy. The solution was then filtered from some insoluble brown material through a filter canula and the filtrate was evaporated to dryness. The residue was washed twice with 10 ml of pentane to afford **2** as a yellow, microcrystalline solid. Yield: 1.74 g (99% referring to **1**). M.p.: 87°C (dec.). Anal. Found: C, 24.39; H, 1.59; Cl, 18.82%. Calcd. for $\text{C}_8\text{H}_6\text{Cl}_2\text{GeMoO}_3$ (389.59): C, 24.66; H, 1.55; Cl,

18.20%. IR (toluene, cm^{-1}): 2038 s, 2030 m, 1969 s, 1946 vs $[\nu(\text{CO})]$; IR (CH_2Cl_2 , cm^{-1}): 2042 s, 1975 s, 1946 vs $[\nu(\text{CO})]$. $^1\text{H-NMR}$ (300 MHz, C_6D_6): δ (ppm) = 4.43 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 7.96 (s, 1H, GeCl_2H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75.5 MHz, C_6D_6): δ (ppm) = 92.6 ($\eta^5\text{-C}_5\text{H}_5$), 222.9 ($2 \times \text{CO}$), 228.2 ($1 \times \text{CO}$). EI-MS (70 eV): m/z 392 ($[\text{M}]^+$), 364 ($[\text{M}-\text{CO}]^+$), 336 ($[\text{M}-2\text{CO}]^+$), 328 ($[\text{M}-\text{HCl}-\text{CO}]^+$), 308 ($[\text{M}-3\text{CO}]^+$), 272 ($[\text{M}-\text{HCl}-3\text{CO}]^+$), 198 ($[\text{M}-\text{HCl}-3\text{CO}-\text{Ge}]^+$), 163 ($[\text{M}-\text{HCl}-3\text{CO}-\text{Ge}-\text{Cl}]^+$).

4.2. $\text{CpMo}(\text{CO})_3\text{GeCl}_3$ (**3**) upon chlorination of CH_2Cl_2

80 mg (0.21 mmol) of complex **2** were dissolved in 5 ml of CH_2Cl_2 and the solution was exposed to daylight for several days. The reaction was monitored by IR spectroscopy. Completion of the reaction after ca. 20 days was indicated by the replacement of the $\nu(\text{CO})$ absorptions of **2** at 2042, 1975 and 1946 cm^{-1} by those of complex **3** at 2051, 1988 and 1965 cm^{-1} . The slight cloudy solution was then filtered through a filter canula and the filtrate was evaporated to dryness. The residue was washed twice with 10 ml of pentane to afford **3** as a yellow solid. IR (CH_2Cl_2 , cm^{-1}): 2051 s, 1988 m, 1965 vs $[\nu(\text{CO})]$. $^1\text{H-NMR}$ (300 MHz, C_6D_6): δ (ppm) = 4.34 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75.5 MHz, C_6D_6): δ (ppm) = 92.7 ($\eta^5\text{-C}_5\text{H}_5$), 222.6 ($2 \times \text{CO}$), 227.1 ($1 \times \text{CO}$). Furthermore the ^1H spectrum of the product was measured in CD_2Cl_2 at 20°C and was found to be identical with those of an analytically pure sample of **3** prepared from $\text{CpMo}(\text{CO})_3\text{Cl}$ and $\text{GeCl}_2(\text{dioxane})$ [3].

4.3. $\text{trans-CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_2\text{H}$ (**5**) from **2** and PMe_3

A yellow solution of 192 mg (0.49 mmol) of **2** in 30 ml of toluene was treated at room temperature with 61 μl (0.59 mmol) of PMe_3 and stirred for 12 h. During this time the solution slightly brightened and evolution of gas (CO) was observed. Completion of the reaction was confirmed by IR spectroscopy. The solution was then filtered through a filter cannula and the filtrate was evaporated to dryness. The residue was washed twice with 10 ml of pentane to afford complex **5** as a bright yellow, microcrystalline solid. Yield: 170 mg (79% referring to **2**). M.p.: 146°C (dec.). Anal. Found: C, 27.83; H, 3.54; Cl, 17.26%. Calcd. for $\text{C}_{10}\text{H}_{15}\text{Cl}_2\text{GeMoO}_2\text{P}$ (437.66): C, 27.44; H, 3.45; Cl, 16.20%. IR (CH_2Cl_2 , cm^{-1}) = 1946 m, 1873 s $[\nu(\text{CO})]$. IR (toluene, cm^{-1}): 1944 m, 1873 s $[\nu(\text{CO})]$. $^1\text{H-NMR}$ (300 MHz, C_6D_6): δ (ppm) = 0.81 (d, $^2J(\text{PH}) = 9.6$ Hz, 9H, $(\text{P}(\text{CH}_3)_3)$), 4.65 (d, $^3J(\text{PH}) = 1.0$ Hz, 5H, $\eta^5\text{-C}_5\text{H}_5$), 8.61 (s, 1H, GeCl_2H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75.5 MHz, C_6D_6): δ (ppm) = 20.1 (d, $^1J(\text{PC}) = 32.5$ Hz, $(\text{P}(\text{CH}_3)_3)$), 91.3 ($\eta^5\text{-C}_5\text{H}_5$), 230.7 (d, $^2J(\text{PC}) = 26.5$

Hz, $2 \times \text{CO}$). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (121.5 MHz, C_6D_6): δ (ppm) = 18.96. EI-MS (70 eV): m/z 440 ($[\text{M}]^+$), 412 ($[\text{M}-\text{CO}]^+$), 404 ($[\text{M}-\text{HCl}]^+$), 384 ($[\text{M}-2\text{CO}]^+$).

4.4. $\text{trans-CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_2\text{H}$ (**5**) from $\text{cis-} \text{trans-CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ (**4**) and $\text{GeCl}_2(\text{dioxane})$

Following the procedure described above for the synthesis of **2**, complex **5** was obtained as a yellow, microcrystalline solid after treatment of 250 mg (0.85 mmol) of **4** with 195 mg (0.84 mmol) of $\text{GeCl}_2(\text{dioxane})$ in CH_2Cl_2 . Yield: 282 mg (76% referring to **4**). The IR, ^1H - and ^{31}P -NMR spectra of the product were identical with those of an analytically pure sample of **5** obtained from **2** and PMe_3 as described above.

4.5. $\text{trans-CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_3$ (**6**) upon chlorination of **5** with CH_2Cl_2

280 mg (0.64 mmol) of **5** were dissolved in 30 ml of CH_2Cl_2 and the solution was exposed to daylight for ca. 20 days. The reaction was monitored by IR spectroscopy. Completion of the reaction was indicated by the replacement of the $\nu(\text{CO})$ absorptions of **5** at 1946 and 1873 cm^{-1} by those of the product **6** at 1965 and 1891 cm^{-1} . The solution then was filtered through a filter canula and the filtrate was evaporated to dryness. The residue was washed three times with 10 ml of pentane to give complex **6** as a yellow solid. Yield: 280 mg (93% referring to **4**). IR (CH_2Cl_2 , cm^{-1}): 1965 m, 1891 s $[\nu(\text{CO})]$. $^1\text{H-NMR}$ (300 MHz, C_6D_6): δ (ppm) = 0.69 (d, $^2J(\text{PH}) = 9.6$ Hz, 9H, $(\text{P}(\text{CH}_3)_3)$), 4.52 (d, $^3J(\text{PH}) = 0.9$ Hz, 5H, $\eta^5\text{-C}_5\text{H}_5$). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75.5 MHz, C_6D_6): δ (ppm) = 19.7 (d, $^1J(\text{PC}) = 33.1$ Hz, $(\text{P}(\text{CH}_3)_3)$), 91.3 ($\eta^5\text{-C}_5\text{H}_5$), 231.2 (d, $^2J(\text{PC}) = 27.5$ Hz, $2 \times \text{CO}$). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (121.5 MHz, C_6D_6): δ (ppm) = 16.96. Furthermore the ^1H - and ^{31}P -NMR spectra of the product were measured in CD_2Cl_2 at 20°C and were found to be identical with those of an analytically pure sample of **6** prepared by isomerization of $\text{cis-CpMo}(\text{CO})_2(\text{PMe}_3)\text{GeCl}_3$ [3].

4.6. Crystal structure determination of **5**

A summary of the crystal data, data collection and refinement for **5** is given in Table 2.

Data collection was performed on a STOE STADI4 four circle diffractometer at ambient temperature and with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Lattice parameters were determined from the setting angles of 28 reflections in the range of $25.4^\circ \leq 2\theta \leq 36.4^\circ$. Data were collected in the $\bar{\omega} - 2\theta$ scan mode. After every 2 h three standard reflections were monitored and the crystal reoriented in case of deviation between 0.1° and 0.15° . Intensity data were corrected for Lorentz and polarization effects and ab-

Table 2
Summary of crystallographic data for complex **5**

5	
Empirical formula	C ₁₀ H ₁₅ Cl ₂ GeMoO ₂ P
Molecular weight	437.64
Crystal color	orange-yellow
Crystal size (mm)	0.42 × 0.26 × 0.08
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)
a (Å)	9.7386(11)
b (Å)	12.6633(11)
c (Å)	12.935(2)
V (Å ³)	1595.2(3)
Z	4
ρ _{calcd.} (g/cm ³)	1.822
μ _{MoKα} (mm ⁻¹)	2.959
F(000)	856
2θ min./max. (°)	3, 48
hkl range	–10, 11/0, 14/0, 14
Total data	2921
Data unique (I > 2 σ(I))	2487
Min./max. density (eÅ ⁻³)	0.588/–0.389
No. of parameters refined	158
Absorption corr.	ψ-scan
Min./max.	0.380/0.556
R ₁ ^a [I > 2 σ(I)]	0.0523
wR ₂ ^b	0.1251
GOF ^c	1.032

$$^a R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$$

$$^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$$

$$^c \text{GOF} = S = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right]^{1/2}$$

sorption. The input file for the SHELX programs was prepared with the program UTILITY [17]. Structure solution was performed with the Patterson method (SHELXS-86) [18] and subsequent difference-fourier

Table 3
Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (pm² × 10⁷) for **5**

Atom	x	y	z	U _{eq} ^a
Mo	8803(1)	1556(2)	7671(1)	41(1)
C(1)	10351(28)	916(16)	8857(16)	109(8)
C(2)	10669(17)	1964(15)	8704(12)	77(5)
C(3)	9569(22)	2520(12)	9096(12)	80(5)
C(4)	8619(20)	1848(24)	9411(13)	112(8)
C(5)	9076(36)	853(20)	9340(15)	136(12)
C(6)	8376(13)	2750(10)	6748(11)	55(3)
O(1)	8131(10)	3498(8)	6252(8)	80(3)
C(7)	8396(13)	291(10)	6843(10)	55(3)
O(2)	8152(11)	–471(7)	6392(9)	79(3)
P	6273(3)	1570(3)	7649(2)	53(1)
C(8)	5462(17)	2785(12)	8062(12)	81(5)
C(9)	5450(16)	593(13)	8493(14)	84(5)
C(10)	5503(14)	1309(14)	6417(12)	81(5)
Ge	10563(1)	1508(1)	6232(1)	54(1)
Cl(1)	12042(4)	2851(3)	6231(3)	72(1)
Cl(2)	12015(4)	171(3)	6308(5)	106(2)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

synthesis (SHELXL-93) [19]. Refinement on F² was carried out by full-matrix least-squares techniques (SHELXL-93). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U_{iso} = 0.08 Å². Neutral atom scattering factors were taken from Cromer and Mann [20]. Geometrical illustrations were performed with ZORTEP [21]. Complex **5** crystallizes in the non-centrosymmetric space group P2₁2₁2₁ and could be favourably refined as racemic twin with both individuals in the ratio of 0.47/0.53. The H-atom connected to the Ge-atom was found in the difference-fourier map and was isotropically refined with U_{iso} = 0.08 Å².

Final positional and equivalent isotropic thermal parameters for **5** are given in Table 3.

Crystallographic data (excluding structure factors) for **5** have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 1223 336033; e-mail: teched@Chemcrs.cam.ac.uk).

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