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Dimetallagermanes of molybdenum and tungsten: synthesis, structure and reactions†

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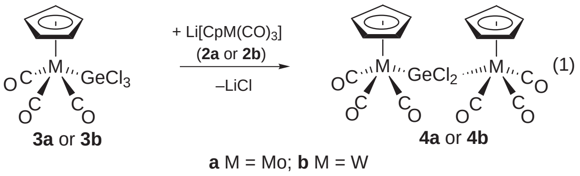
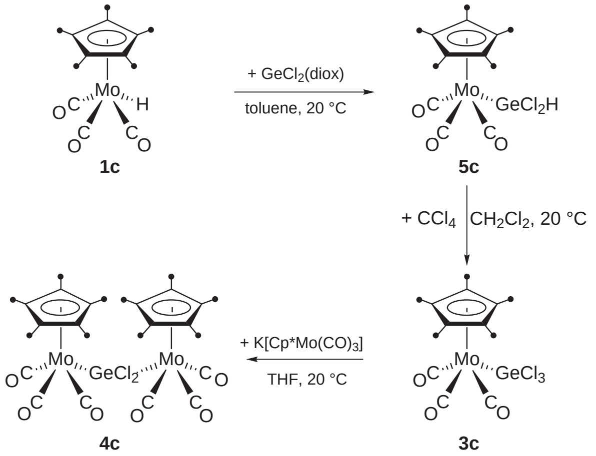
Reaction of the trichlorogermyl complexes $CpM(CO)_3GeCl_3$ **3a** or **3b** with $Li[CpM(CO)_3]$ **2a** or **2b**, which were obtained from $CpM(CO)_3H$ **1a** or **1b** and $LiBu^n$, afforded the dimetalladichlorogermanes $[CpM(CO)_3]_2GeCl_2$ **4a** or **4b** ($Cp = C_5H_5$; **a** M = Mo; **b** M = W). Similarly, treatment of $Cp^*Mo(CO)_3GeCl_3$ **3c** with $K[Cp^*Mo(CO)_3]$ **2c** yielded selectively $[Cp^*Mo(CO)_3]_2GeCl_2$ **4c** ($Cp^* = C_5Me_5$). Complex **3c** was obtained from $Cp^*Mo(CO)_3H$ **1c** in two steps. The first step involved an insertion of $GeCl_2$ into the molybdenum–hydrogen bond of **1c** to give the dichlorogermyl complex $Cp^*Mo(CO)_3GeCl_2H$ **5c** followed by chlorination of **5c** with CCl_4. The dimetalladichlorogermanes **4a**–**4c** contain two reactive sites for further functionalization, the transition-metal centers and the germanium atom. This has been demonstrated by the CO/PMe_3 ligand exchange reaction of **4a** to give $[Cp(CO)_3Mo(\mu\text{-}GeCl_2)\{trans\text{-}Mo(CO)_2(PMe_3)Cp\}]$ **6a** and the substitution reaction of **4a** with $LiAlH_4$ to afford the dimetallagermane $[CpMo(CO)_3]_2GeH_2$ **7a**. The crystal structures of **4a**, **4b** and **6a** have been reported.

Germylenes, the heavier Group 14 homologues of carbenes, have been shown to insert readily into various σ bonds between main-group elements providing an easy access to tetravalent germanium compounds.[1] In comparison, insertion reactions of germylenes into σ bonds of transition metals have been studied less extensively.[2] Recently we have shown that the insertion reactions of $GeCl_2$ into Mo–Cl, W–Cl and Mo–H bonds provide a convenient route to trichlorogermyl and dichlorogermyl complexes.[3] The obtained molybdenum and tungsten complexes $(\eta^5\text{-}C_5R_5)M(CO)_{3-n}(L)_nGeCl_{3-m}H_m$ (R = H or Me; M = Mo or W; n, m = 0 or 1; L = PMe_3 or EtNC) are attractive precursors for compounds with a metal–germanium multiple bond[4] and contain two reactive sites for further functionalization, the transition-metal and the germanium centers. Using the manifold reactivity of the trichlorogermyl complexes $(\eta^5\text{-}C_5R_5)M(CO)_3GeCl_3$ (**3a**, **3c** M = Mo, R = H or Me; **3b** M = W, R = H) we have now prepared several dimetallagermanes and describe their structures and properties.

Results and Discussion

Treatment of the trichlorogermyl complexes $CpM(CO)_3GeCl_3$ **3a** or **3b** with the carbonyl metallates $Li[CpM(CO)_3]$ (**2a** M = Mo; **2b** M = W), which were obtained by deprotonation of the hydrido complexes $CpM(CO)_3H$ **1a** or **1b** with 1 equivalent of $LiBu^n$, affords in refluxing THF the dimetalladichlorogermanes **4a** and **4b**, respectively [equation (1)]. Evidence for the selective transformation of **3a** to **4a** and **3b** to **4b** was given by the IR spectra of the reaction solutions, which revealed that the ν(CO) absorptions of the trichlorogermyl complexes at 2047, 1981 and 1961 cm^{-1} (**3a**) and 2040, 1969 and 1950 cm^{-1} (**3b**) and of the carbonyl metallates at 1905, 1806, 1782 and 1718 cm^{-1} (**2a**) and 1900, 1801, 1779 and 1716 cm^{-1} (**2b**) had been replaced at the end of the reaction by those of the products **4a** and **4b** (Table 1). After evaporation of the solvent and extraction of the solubles with CH_2Cl_2, the dimetallagermanes **4a** and **4b** were isolated as ocherous solids in 78 and 85% yields, respectively. Both compounds are soluble in CH_2Cl_2 and THF, sparingly soluble in Et_2O and insoluble in pentane. They are not sensitive to air and moisture and show a surprising thermal stability, melting at 192 and 212 °C, respectively. The method employed to prepare **4a** and **4b** was also used to obtain the dimetallagermane $[Cp^*Mo(CO)_3]_2GeCl_2$ **4c** ($Cp^* = C_5Me_5$) having a more crowded ligand sphere around the germanium atom. The synthesis of **4c** was achieved in three steps starting from $Cp^*Mo(CO)_3H$ **1c** and is outlined in Scheme 1.





Scheme 1 diox = 1,4-Dioxane

In the first step the hydrido complex **1c** was treated with 1 equivalent of $GeCl_2(diox)$ (diox = 1,4-dioxane) in toluene at ambient temperature to afford exclusively the dichlorogermyl complex $Cp^*Mo(CO)_3GeCl_2H$ **5c**. Evidence for the fast and selective insertion of $GeCl_2$ into the Mo–H bond of **1c** was given by the IR spectrum of the reaction solution, which revealed that the two ν(CO) absorptions of **1c** at 2010 and 1920 cm^{-1} had been replaced after 1 h by those of **5c** at 2027, 2018, 1954 and 1937 cm^{-1} (Table 1). Complex **5c** was isolated after

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† Dedicated to Professor Dr. P. Royo on the occasion of his 60th birthday on 12th January 1998.

Table 1 The ν(CO) absorptions of the complexes **1a**–**7a**

Complex	ν(CO)/cm^{-1}	Solvent
1a CpMo(CO)$_3$H	2030s, 1947vs	*a*
	2024s, 1932vs	*b*
	2023s, 1933vs	*c*
1b CpW(CO)$_3$H	2027s, 1939vs	*a*
	2020s, 1923vs	*b*
	2019s, 1926vs	*c*
1c Cp*Mo(CO)$_3$H	2015s, 1932vs	*a*
	2009s, 1916vs	*b*
	2010s, 1920vs	*c*
2a Li[CpMo(CO)$_3$]	1905s, 1806vs, 1782s, 1718s	*d*
2b Li[CpW(CO)$_3$]	1900s, 1801vs, 1779s, 1716s	*d*
2c K[Cp*Mo(CO)$_3$]	1884vs, 1773vs, 1736vs	*d*
3a CpMo(CO)$_3$GeCl$_3$	2051s, 1988m, 1965vs	*b*
	2047s, 1981m, 1961vs	*d*
3b CpW(CO)$_3$GeCl$_3$	2046s, 1975m, 1954vs	*b*
	2040s, 1969m, 1950vs	*d*
3c Cp*Mo(CO)$_3$GeCl$_3$	2037s, 1968 (sh), 1957vs	*b*
	2035s, 1955vs	*d*
4a [CpMo(CO)$_3$]$_2$GeCl$_2$	2035vs, 2013s, 1956vs, 1947vs (sh), 1922m	*b*
	2033vs, 2010s, 1956vs, 1944vs, 1920m	*c*
	2032vs, 2010s, 1956vs, 1943s, 1918m	*d*
4b [CpW(CO)$_3$]$_2$GeCl$_2$	2031vs, 2009s, 1945vs, 1937vs (sh), 1914m	*b*
	2029vs, 2006s, 1946vs, 1934s, 1910m	*d*
4c [Cp*Mo(CO)$_3$]$_2$GeCl$_2$	2020s, 1993m, 1947s, 1933vs, 1902m	*b*
5c Cp*Mo(CO)$_3$GeCl$_2$H	2029s, 1957s, 1938vs	*b*
	2027s, 2018m, 1954s, 1937vs	*c*
6a [Cp(CO)$_3$Mo(μ-GeCl$_2$)-{*trans*-Mo(CO)$_2$(PMe$_3$)Cp}]	2013s, 1941vs, 1923s, 1862s	*b*
	2010s, 1940vs, 1921s, 1863s	*c*
7a [CpMo(CO)$_3$]$_2$GeH$_2$	2017s, 1993vs, 1925vs (sh), 1913vs, 1895s (sh)	*b*
	2018s, 1994vs, 1933vs (sh), 1918vs, 1903s (sh)	*e*
	2015s, 1990vs, 1926vs (sh), 1913vs, 1898s (sh)	*f*

[a] In pentane. [b] In CH$_2$Cl$_2$. [c] In toluene. [d] In THF. [e] In Et$_2$O. [f] In benzene.

Table 2 The ^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectroscopic data of complexes **3c**, **4a**–**4c**, **5c**, **6a** and **7a** at 20 °C[a]

	δ_H					δ_C				
Complex	P(CH$_3$)$_3$	C$_5$(CH$_3$)$_5$	Ge-H	C$_5$H$_5$	δ_P	C$_5$(*C*H$_3$)$_5$	P(CH$_3$)$_3$	C$_5$H$_5$, *C*$_5$(CH$_3$)$_5$	CO	Solvent
3c	—	2.10 (15, s)	—	—	—	10.9	—	108.1	226.3, 230.3	*b*
4a	—	—	—	5.59 (10, s)	—	—	—	94.8	227.0, 231.9	*b*
4b	—	—	—	5.70 (10, s)	—	—	—	93.5	217.8, 219.5	*b*
4c	—	2.05 (30, s)	—	—	—	11.1	—	107.2	231.1, 231.2	*b*
5c	—	1.50 (15, s)	7.99 (1, s)	—	—	10.1	—	106.0	226.0, 231.7	*c*
6a	1.60 [9, d, ^2J(PH) 9.7]	—	—	5.26 [5, d, ^3J(PH) 1.2], 5.57 (5, s)	24.0	—	20.1 [d, ^1J(PC) 33.2]	92.9, 95.0	227.5, 233.7, 235.3 [d, ^2J(PC) 27.3]	*b*
7a	—	—	4.10 (2, s)	5.36 (10, s)	—	—	—	92.3	227.1, 232.9	*b*
7a	—	—	4.44 (2, s)	4.62 (10, s)	—	—	—	91.9	227.1, 233.0	*c*

[a] Relative intensities and multiplicities of signals in parentheses, coupling constants in Hz. [b] In CD$_2$Cl$_2$. [c] In C$_6$D$_6$.

work-up of the reaction solution as a yellow, air-sensitive solid in 75% yield, it is soluble in CH$_2$Cl$_2$ and toluene, but sparingly soluble in Et$_2$O and insoluble in *n*-pentane and shows a higher thermal stability than the cyclopentadienyl derivative CpMo(CO)$_3$GeCl$_2$H **5a** (decomp.: 87 °C)[3b] decomposing at 174 °C, when heated in a sealed capillary under argon.

Complex **5c** shows a similar reactivity pattern to **5a** and is very slowly chlorinated by CH$_2$Cl$_2$ and GeCl$_2$(diox) to afford the trichlorogermyl complex Cp*Mo(CO)$_3$GeCl$_3$ **3c**. Chlorination of **5c** is accelerated if CCl$_4$ is used as the chlorinating agent and was employed in the second step of the synthesis of **4c** in order to convert **5c** selectively to **3c** (Scheme 1). Complex **3c** was thereby isolated as a thermally stable yellow solid, which melts at 174 °C and is soluble in CH$_2$Cl$_2$ and THF, but is sparingly soluble in Et$_2$O and insoluble in *n*-pentane. In the last step of the route leading to **4c**, the carbonyl metallate K[Cp*-Mo(CO)$_3$] **2c** was first prepared *in situ* upon refluxing a mixture of Mo(CO)$_6$ and KCp* in THF and then added at ambient temperature to a solution of the trichlorogermyl complex **3c** in THF. Again IR monitoring of this reaction revealed a clean conversion of the starting materials to **4c** after 17 h. Work up of the reaction solution afforded complex **4c** as a brown solid in 84% overall yield (relative to **1c**). Complex **4c** has similar properties to **4a** and **4b** and decomposes upon heating at 215 °C.

The new complexes **3c**–**5c** were fully characterized (Tables 1 and 2). Thus, the IR spectra of **3c** and **5c** in CH$_2$Cl$_2$ show three ν(CO) absorption bands, which can be assigned on the basis of group theory to the two symmetric A′ and the one antisymmetric A″ stretching vibration, respectively.[5] The ν(CO) absorption bands of **3c** appear at higher wavenumbers than those of **5c** suggesting that the trichlorogermyl group is a stronger electron-withdrawing ligand than the dichlorogermyl group (Table 1).[6] Furthermore, the ν(CO) absorption bands of **5c** appear at higher wavenumbers than those of **1c** indicating in full agreement with earlier observations that insertion of GeCl$_2$ into a M–H bond reduces the electron density at the metal center and thereby weakens the metal d$_\pi$–CO (π*) back bonding.[3b] The higher energy absorption of the symmetric A′ CO stretching vibration gives rise to one band in the IR spectrum of **5c** in CH$_2$Cl$_2$ at 2029 cm^{-1}. This band is split into two com-

Table 3 Selected bond lengths (pm) and bond angles (°) with estimated standard deviations (e.s.d.s) for complexes **4a** and **4b**

	M = Mo	M = W
M1–C1	233.5(5)	231.1(12)
M1–C2	235.4(5)	233.2(11)
M1–C3	235.1(4)	235.0(10)
M1–C4	231.8(4)	233.5(11)
M1–C5	230.5(5)	230.7(11)
M1–C6	200.0(5)	199.6(11)
M1–C7	199.1(5)	199.1(9)
M1–C8	197.8(5)	198.4(11)
M2–C9	233.7(5)	234.8(12)
M2–C10	235.5(5)	233.6(10)
M2–C11	232.3(5)	232.9(12)
M2–C12	231.8(4)	230.1(12)
M2–C13	231.8(5)	229.4(11)
M2–C14	198.9(5)	199.5(10)
M2–C15	199.8(5)	200.1(11)
M2–C16	200.0(5)	197.5(10)
M1–Ge	266.68(6)	266.5(1)
M2–Ge	265.36(7)	265.7(1)
Ge–Cl1	226.7(1)	226.1(3)
Ge–Cl2	225.9(1)	225.8(3)
M1–Ge–M2	131.34(2)	131.38(4)
Cl1–Ge–Cl2	95.29(5)	95.1(1)
M1–Ge–Cl1	107.09(4)	107.25(8)
M1–Ge–Cl2	104.13(4)	104.16(9)

ponents, when the IR spectrum of **5c** is recorded in toluene [ν(CO), 2027 and 2018 cm^{-1}] (Table 1). This splitting is also observed in the IR spectra of other dichlorogermyl complexes in toluene [*e.g.* $CpMo(CO)_3GeCl_2H$, ν(CO) 2038, 2030 cm^{-1}; $Cp^*W(CO)_3GeCl_2H$, ν(CO) 2023, 2014 cm^{-1}][3b,7] and can be explained by the presence of rotational isomers with respect to the metal–germanium bond.[8] In polar solvents such as CH_2Cl_2 this splitting is not resolved due to substantial band broadening. The solution IR spectra of the dimetalladichlorogermanes **4a**–**4c** show in the region of 2200–1600 cm^{-1} five ν(CO) absorption bands (Table 1). If one assumes that **4a** and **4b** retain in solution the C_1 symmetric conformation adopted by these molecules in the solid state (see crystal structures of **4a** and **4b**) then six carbonyl stretching modes would be expected to be infrared active. Therefore, we assume that two of the six ν(CO) absorption bands overlap in the solution IR spectra of **4a** and **4b**. The ν(CO) frequencies decrease in the series $(\eta^5\text{-}C_5R_5)M(CO)_3GeCl_3$ > $(\eta^5\text{-}C_5R_5)M(CO)_3GeCl_2H$ > $[(\eta^5\text{-}C_5R_5)M(CO)_3]_2GeCl_2$ indicating that substitution of a chloro substituent at the germanium atom by a more electropositive group strengthens the metal (d_π)–CO (π^*) back bonding and thereby weakens the C–O bond.[3]

The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **3c**–**5c** also support the structures proposed for these compounds (Table 2). Thus, all spectra display the resonances expected for a Cp or Cp* ligand. In addition, the ^1H NMR spectrum of **5c** shows a singlet resonance for the germanium-bonded hydrogen atom at δ 7.99. The chemical shift of this proton is similar to that of $HGeCl_3$ (δ_H 7.6)[9] and characteristic of a dichlorogermyl ligand [*e.g.* $CpW(CO)_3GeCl_2H$, δ(Ge–H) 7.91 (CD_2Cl_2, 20 °C); $Cp^*W(CO)_3GeCl_2H$, δ(Ge–H) 8.14 (C_6D_6, 20 °C)].[3b,7] Furthermore, the $^{13}C\text{-}\{^1H\}$ NMR spectra of **3c**–**5c** display two carbonyl-carbon resonances. The higher-field and more intense carbonyl-carbon resonance is assigned to the two carbonyl ligands, which are in the *cis*-position relative to the germyl ligand. The carbonyl-carbon resonances of the dimetalladichlorogermanes **4a**–**4c** appear at lower-field than those of the trichlorogermyl complexes **3a**–**3c** indicating, in agreement with the IR spectra, a stronger metal–carbonyl back bonding in complexes **4a**–**4c** than in **3a**–**3c**.[3a,10] The solid-state structures of **4a** and **4b** were determined by single-crystal X-ray diffraction studies. Suitable single crystals were obtained after slow evaporation of a CH_2Cl_2 solution of **4a** or **4b** at room temperature. Both compounds are isostructural and therefore only a ZORTEP plot of a single molecule of **4a** is shown in Fig. 1. Selected bond lengths and angles of **4a** and **4b** are listed in Table 3.

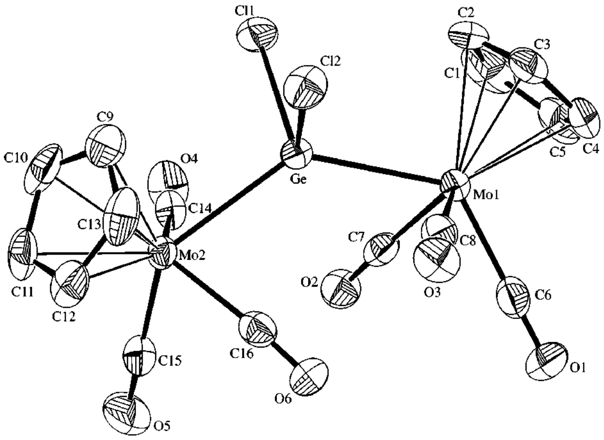


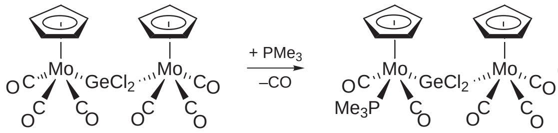
Fig. 1 The ZORTEP plot of the molecular structure of complex **4a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

Compounds **4a** and **4b** are composed of two $CpM(CO)_3$ fragments linked by a $GeCl_2$ bridge. Both molecules adopt in the solid state a conformation of low symmetry (C_1) in which the two metal fragments are twisted relative to each other as shown by the dihedral angle of 33.38° (**4a**) and 33.41° (**4b**) between the planes defined by the atoms Ge, M1 and Cp1 and Ge, M2 and Cp2, respectively (M = Mo or W; Cp1 and Cp2 denote the centers of the cyclopentadienyl rings C1–C5 and C9–C13, respectively). This conformation is probably adopted to minimize the steric repulsion between the $CpM(CO)_3$ fragments, which increases according to molecular models in conformations of higher symmetry (C_{2v} or C_s). The co-ordination geometry of the transition-metal centers in **4a** and **4b** is frequently observed for a 'four-legged piano-stool' complex of the type $(\eta^5\text{-}C_5R_5)M(CO)_3X$ (R = H or Me; M = Mo or W; X = le-donor ligand).[11] It can be described as square pyramidal with the Cp ligand occupying one co-ordination site at the apex of the pyramid and the carbonyl ligands and the $GeCl_2$ bridge lying at the corners of the basal plane. The $M\text{–}C_{ring}$ bond lengths in **4a** range from 230.5(5) to 235.4(5) pm and in **4b** from 229.4(11) to 235.0(10) pm. They have average values of 233.1(5) pm (**4a**) and 232.4(11) pm (**4b**), which are very close to those of $CpMo(CO)_3GeCl_3$ **3a** [average $Mo\text{–}C_{ring}$ 231.5(9) pm] and $CpW(CO)_3GeCl_3$ **3b** [average $W\text{–}C_{ring}$ 229.8(11) pm], respectively.[3a,7] Similarly, the M–CO bond lengths of the dimetalladichlorogermanes have average values of 199.3(5) (**4a**) and 199.0(10) pm (**4b**), which are very close to those of the trichlorogermyl complexes **3a** [average Mo–CO 199.8(9) pm] and **3b** [average W–CO 199.4(9) pm], respectively.[3a,7]

The tetrahedral environment of the germanium atom is strongly distorted as shown by the Cl–Ge–Cl bond angle [**4a**, 95.29(5); **4b**, 95.1(1)°], which is much smaller than that of a regular tetrahedron, and the M–Ge–M bond angle [**4a**, 131.34(2); **4b**, 131.38(4)°], which is considerably larger than that of a regular tetrahedron. In addition, a comparison of the structures of $GeCl_4$,[12] $CpM(CO)_3GeCl_3$ **3a** or **3b**,[3a,7] $CpW(CO)_3GeCl_2H$ **5b**[7] and $[CpM(CO)_3]_2GeCl_2$ **4a** or **4b** reveals the following trends as a chloro group is replaced successively by a more electropositive substituent: (a) the mean Cl–Ge–Cl bond angles decrease [$GeCl_4$, 109.5; **3a**, 101.4(1); **3b**, 101.3(1); **5b**, 101.2(1); **4a**, 95.29(5); **4b**, 95.1(1)°]; (b) the mean Ge–Cl bond lengths increase [$GeCl_4$, 211.3(3); **3a**, 217.6(2); **3b**, 217.8(3); **5b**, 219.2(3); **4a**, 226.3(1); **4b**, 226.0(3) pm] and (c) the M–Ge bonds become longer [**3a**, 254.6(1); **3b**, 254.37(9); **5b**, 255.9(1); **4a**, average Mo–Ge 266.02(6); **4b**, average W–Ge 266.1(1) pm]. All these trends can be explained using the atom rehybridization model of Bent.[13] According to this model in compounds of type AX_nY_{4-n}, in which A uses sp^3 hybrid orbitals and the X group is more electronegative than the Y group, the atom A rehybridizes in a manner such as to increase the p character of its orbitals directed towards the more electronegative substituent X. This causes, in the absence of any steric effects, a continuous decrease of the X–A–X and the Y–A–Y bond angles and a continuous increase of the A–X and the A–Y bond lengths, as X is successively replaced by Y. In the complexes **4a** and **4b** this electronic effect is probably superimposed by the steric pressure of the CpM(CO)$_3$ groups resulting in the same structural changes.

The dimetalladichlorogermanes **4a**–**4c** are homologous to the tin derivatives [CpM(CO)$_3$]$_2$SnX$_2$ (M = Cr, Mo or W; X = F, Cl, Br or I).[14] The tin compounds were previously prepared by electrophilic cleavage of the tin–carbon bonds of [CpM(CO)$_3$]$_2$-SnPh$_2$ with HX[15] or the insertion of SnX$_2$ into the metal–metal bond of [CpM(CO)$_3$]$_2$.[16] The molybdenum complex [CpMo(CO)$_3$]$_2$SnCl$_2$ has also been obtained with the trichlorostannyl complex CpMo(CO)$_3$SnCl$_3$ from the reaction of Hg[CpMo(CO)$_3$]$_2$ and SnCl$_2$.[17] However, attempts to extend this chemistry to germanium have not been reported so far or have failed. For example, reaction of [CpMo(CO)$_3$]$_2$ with GeBr$_2$, gave not the insertion product [CpMo(CO)$_3$]$_2$GeBr$_2$, but only the tribromogermyl complex CpMo(CO)$_3$GeBr$_3$ in low yield.[18] In this context, we tried to prepare the tungsten complex **4b** from [CpW(CO)$_3$]$_2$ and GeCl$_2$(diox). However, no reaction was observed at ambient temperature in CH$_2$Cl$_2$. When these compounds were heated in refluxing toluene a slow reaction occurred, which proceeded to completion only with excess of GeCl$_2$(diox), and led to a mixture of products, of which the hydrido complex **1b** and the trichlorogermyl complex **3b** were identified by IR and NMR spectroscopy. Another conceivable approach to **4a**–**4c** involves the reaction of GeCl$_4$ with the metallates **2a**–**2c**. However, the observation that GeCl$_4$ acts as an oxidizing agent towards Group 6 transition-metal anions limits the scope of such an approach.[3a,7] All these results show that the nucleophilic displacement reactions of the trichlorogermyl complexes **3a**–**3c** with the metallates **2a**–**2c** [equation (1) and Scheme 1] are a very useful approach to the dimetalladichlorogermanes **4a**–**4c**. Furthermore, these reactions are selective and allow a fast isolation of **4a**–**4c** in high yield. These advantages enabled us to carry out preliminary reactivity studies on complexes **4a**–**4c**.

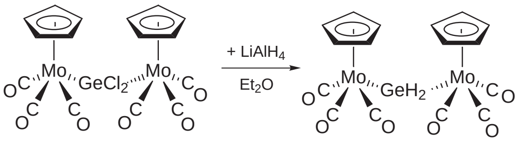
We found that complexes **4a**–**4c** contain two reactive sites for further functionalization, the transition-metal centers and the germanium atom. Thus, treatment of **4a** with PMe$_3$ in toluene at ambient temperature afforded the CO substitution product [Cp(CO)$_3$Mo(μ-GeCl$_2$){*trans*-Mo(CO)$_2$(PMe$_3$)Cp}] **6a**, which was isolated as a yellow solid in 45% yield [equation (2)].



(2)

4a **6a**

Complex **6a** is soluble in CH$_2$Cl$_2$, THF and toluene, moderately soluble in Et$_2$O, but insoluble in pentane and decomposes upon heating at 175 °C. Infrared monitoring of the reaction of **4a** with PMe$_3$ revealed, that more than 2 equivalents of PMe$_3$ were necessary for the complete consumption of **4a** and suggested the formation of a second product. This was easily separated from **6a** due to its insolubility in Et$_2$O and was identified by IR and NMR spectroscopy to be *trans*-[CpMo(CO)$_2$(PMe$_3$)$_2$]Cl.[3a] Attempts to achieve thermally a CO/PMe$_3$ ligand exchange at the other molybdenum center in **6a** in order to prepare the dimetalladichlorogermane *trans*-[CpMo(CO)$_2$(PMe$_3$)]$_2$GeCl$_2$ failed, the reaction of **6a** with PMe$_3$ always resulted in the formation of *trans*-[CpMo(CO)$_2$(PMe$_3$)$_2$]Cl. The germanium center of **4a** is also accessible to nucleophiles as demonstrated by the reaction of **4a** with LiAlH$_4$ to give the dimetallagermane [CpMo(CO)$_3$]$_2$GeH$_2$ **7a** [equation (3)]. The hydrido complex **1a** was also formed in this reaction indicating that cleavage of the Mo–Ge bonds of **4a** is a considerable side reaction. However, complex **7a** could be easily purified taking advantage of its low solubility in pentane and was isolated as a light brown solid in 22% yield.



(3)

4a **7a**

Complex **7a** is considerably more sensitive to oxygen than **4a** and more soluble in less polar solvents such as toluene, benzene and Et$_2$O. It reacts with chlorinated solvents particularly when exposed to daylight to give **4a**. However, chlorination of **7a** by CH$_2$Cl$_2$ is too slow at ambient temperature to hinder the spectroscopic characterization of **7a** in this solvent. Complexes **6a** and **7a** were fully characterized (Tables 1 and 2). Thus, the IR spectra of **6a** and **7a** show in the region of 2200–1600 cm^{-1} four and five ν(CO) absorption bands, respectively (Table 1). These absorptions appear at lower wavenumbers than those of **4a** as expected for more electron-rich complexes. Furthermore, the ^{1}H NMR spectrum of **6a** in CD$_2$Cl$_2$ displays a doublet resonance for the PMe$_3$ ligand protons at δ 1.60 and a doublet and a singlet resonance for the cyclopentadienyl protons of the CpMo(CO)$_2$PMe$_3$ and CpMo(CO)$_3$ fragments at δ 5.26 and 5.57, respectively (Table 2). In the ^{1}H NMR spectrum of **7a** in CD$_2$Cl$_2$ the germanium-bonded hydrogen atoms give rise to a singlet resonance at δ 4.10. In addition, the ^{13}C-{^{1}H} NMR spectrum of **6a** shows, besides the expected resonances for the PMe$_3$ and Cp ligands, three carbonyl-carbon resonances. The higher-field singlet resonances appearing at δ 227.5 and 233.7 in the approximate ratio of 2:1 are assigned to the carbonyl groups of the CpMo(CO)$_3$ fragment and the lower-field doublet resonance at δ 235.5 to the equivalent carbonyl groups of the CpMo(CO)$_2$PMe$_3$ fragment. These resonances are observed at lower field than those of CpMo(CO)$_3$GeCl$_3$ **3a** [δ(CO) 222.7, 226.4 (CD$_2$Cl$_2$, 20 °C)][3a] and of *trans*-CpMo(CO)$_2$(PMe$_3$)GeCl$_3$ [δ(CO) 231.4, (CD$_2$Cl$_2$, 20 °C)],[3a] respectively, indicating that replacement of a chloro group by the more electropositive CpMo(CO)$_2$PMe$_3$ or CpMo(CO)$_3$ substituent enhances the electron density at the metal center and thereby strengthens the M (d$_\pi$)–CO (π*) back bonding.[3a]

The crystal structure of **6a** was determined by a single-crystal X-ray diffraction study. Suitable crystals were obtained upon slow evaporation of a CH$_2$Cl$_2$ solution of **6a** at ambient temperature. A ZORTEP plot of one of the two independent molecules in the unit cell is shown in Fig. 2 and selected bond lengths and angles of this molecule are listed in Table 4. Discussion of the structural parameters is based on the average values of the bond lengths and angles of both molecules.

Complex **6a** adopts (as in the case of complexes **4a** and **4b**) a conformation of low symmetry (C_1) in which the CpMo(CO)$_3$ and CpMo(CO)$_2$PMe$_3$ fragments are twisted relative to each other. The twist angle between the planes defined respectively by the atoms Ge1, Mo1 and Cp1 and Ge1, Mo2 and Cp2 is 88.7° (Cp1 and Cp2 denote the centers of the cyclopentadienyl rings C11–C15 and C21–C25, respectively). As in **4a** and **4b** this conformation is probably adopted to minimize the steric repulsion between the sterically demanding metal fragments. The spatial arrangement of the ligands around the molybdenum atoms is that typically observed for 'four-legged piano-stool'

Table 4 Selected bond lengths (pm) and bond angles (°) with e.s.d.s for one of the two molecules of complex **6a** in the asymmetric unit

Mo1–C1	198.2(5)
Mo1–C2	198.5(5)
Mo1–C3	199.2(5)
Mo1–C11	235.1(5)
Mo1–C12	233.0(4)
Mo1–C13	231.4(4)
Mo1–C14	231.4(4)
Mo1–C15	232.7(5)
Mo2–C4	197.9(5)
Mo2–C5	196.9(5)
Mo2–C21	232.1(4)
Mo2–C22	233.0(4)
Mo2–C23	233.5(5)
Mo2–C24	234.5(4)
Mo2–C25	232.4(4)
Mo1–Ge1	265.09(6)
Mo2–Ge1	259.28(7)
Mo2–P1	246.1(1)
Ge1–Cl1	230.8(1)
Ge1–Cl2	227.7(1)
Mo1–Ge1–Mo2	132.79(2)
Cl1–Ge1–Cl2	94.55(5)
Mo1–Ge1–Cl1	101.59(4)
Mo1–Ge1–Cl2	104.35(3)
Mo2–Ge1–Cl1	109.35(4)
Mo2–Ge1–Cl2	107.67(4)

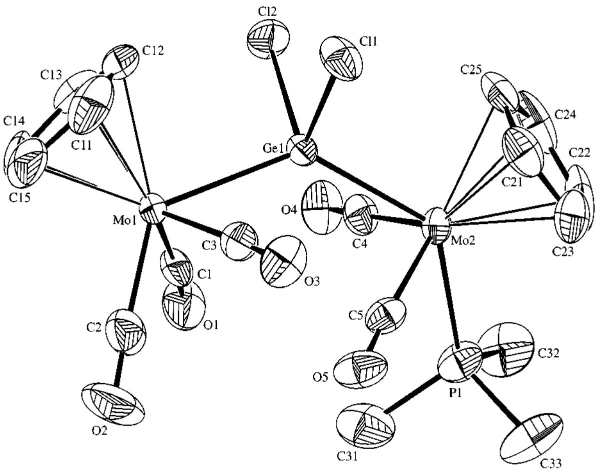


Fig. 2 The ZORTEP plot of one of the two molecules of complex **6a** in the asymmetric unit. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The second molecule of **6a** in the asymmetric unit contains the atoms Mo3, Mo4, Ge2, Cl3–Cl4A, P2, C6–C10, O6–O10, C41–C45, C51–C55 and C61–C63.

complexes[11] with the trimethylphosphane ligand bonded to Mo2 (Mo4) and occupying a *trans* co-ordination site relative to the $GeCl_2$ bridge. The average $Mo-C_{ring}$ bond length of the $CpMo(CO)_3$ and $CpMo(CO)_2PMe_3$ fragment is 232.9(5) and 232.6(4) pm, respectively. These values are very close to those of **4a** [average $Mo-C_{ring}$ 233.1(5) pm] and *trans*-$CpMo(CO)_2(PMe_3)GeCl_3$ [average $Mo-C_{ring}$ 231.8(6) pm], respectively.[3a] The Mo–CO bonds in the $CpMo(CO)_3$ fragment [average Mo–CO 197.5(5) pm] and $CpMo(CO)_2PMe_3$ fragment of **6a** [average Mo–CO 196.3(5) pm] are slightly shorter than those in $CpMo(CO)_3GeCl_3$ **3a** [average Mo–CO 199.8(9) pm][3a] and *trans*-$CpMo(CO)_2(PMe_3)GeCl_3$ [average Mo–CO 197.6(6) pm],[3a] respectively. This suggests, in full agreement with the IR and NMR spectroscopic data, a stronger metal–carbonyl back bonding in **6a** than in the trichlorogermyl complexes. The two molybdenum and two chlorine atoms form a strongly distorted tetrahedron around the germanium center as already observed for **4a** and **4b**. This is shown by the small average Cl–Ge–Cl bond angle of 94.3° and the large average Mo–Ge–Mo bond angle of 132.1°. Furthermore, the Ge–Cl bonds of **6a** are considerably longer than those of **3a** [average Ge–Cl 217.6(2) pm][3a] or *trans*-$CpMo(CO)_2(PMe_3)GeCl_3$ [average Ge–Cl 219.3(2) pm][3a] and the average lengths of the Mo–Ge bonds in **6a** [266.13(7) and 260.13(7) pm] are considerably longer than those in **3a** [Mo–Ge 254.6(1) pm][3a] and *trans*-$CpMo(CO)_2(PMe_3)GeCl_3$ [average Mo–Ge 250.57(6) pm],[3a] respectively. All these structural trends can be explained using the atom rehybridization model of Bent (see also discussion of the crystal structures of **4a** and **4b**).[13]

Conclusion

Convenient high-yield syntheses were developed for the dimetalladichlorogermanes $[(\eta^5-C_5R_5)M(CO)_3]_2GeCl_2$ (R = H or Me; M = Mo or W) starting from the easily accessible hydrido or chloro complexes $(\eta^5-C_5R_5)M(CO)_3X$ (X = H or Cl). The crystal structures of these compounds show a strong deformation of the tetrahedral environment around the germanium center, which originates from the difference in the electronegativity of the substituents and suggests that these compounds might be used in chlorine-abstraction reactions to prepare compounds with a transition metal–germanium multiple bond.[4] The dimetalladichlorogermanes contain two reactive sites for further functionalization, the transition-metal centers and the germanium atom.

Experimental

Standard inert-atmosphere techniques were used for all synthesis and sample manipulations. The solvents were dried by standard methods (pentane over CaH_2; Et_2O, THF, benzene and toluene over Na–benzophenone; CH_2Cl_2 over P_2O_5 and Na–Pb alloy and CCl_4 over P_2O_5), 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. Solution IR spectra were recorded on a Bruker IFS-55 spectrometer using a CaF_2 cell. Proton, $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectra were recorded on a Bruker AM-300 spectrometer in dry deoxygenated CD_2Cl_2 or C_6D_6 at 20 °C. The ^1H and $^{13}C-\{^1H\}$ NMR spectra were calibrated against the solvent signals (CD_2Cl_2, δ_H 5.32 and δ_C 53.8; C_6D_6, δ_H 7.15 and δ_C 128.0 and the $^{31}P-\{^1H\}$ 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, ^{184}W, ^{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 under argon in capillary tubes and heated with a rate of 1 K min^{-1}, IR spectra of the heated samples were recorded and compared with those of authentic samples to determine if the compounds had decomposed.

The methods for the synthesis of the complexes $CpM(CO)_3H$ (**1a**–**1c**)[19] were modified as following: the metallates $Na[CpM(CO)_3]$ (M = Mo or W) and $K[Cp^*Mo(CO)_3]$ **2c** were prepared *in situ* upon treatment of $M(CO)_6$ with NaCp and KCp* in boiling DME (1,2-dimethoxyethane)[20] and reacted subsequently with a 38% aqueous solution of HCl to give complexes **1a**–**1c** in 76, 93 and 86% yields, respectively. The complexes $CpM(CO)_3GeCl_3$ (**3a**, M = Mo; **3b**, M = W) were obtained as described recently.[3a] The compounds $GeCl_2$(diox) and PMe_3 were prepared following the literature procedures,[21,22] KCp* was obtained from KH and Cp*H.[23] All other chemicals were commercially available.

Syntheses

$Cp^*Mo(CO)_3GeCl_3$ 3c. A solution of 696 mg (1.51 mmol) of $Cp^*Mo(CO)_3GeCl_2H$ **5c** in 30 ml of CH_2Cl_2 was treated with

2.50 ml (25.91 mmol) of CCl_4 and stirred at ambient temperature. The reaction was monitored by IR spectroscopy and was complete after 2 h. The yellow solution was evaporated to dryness and the residue was washed twice with 10 ml of pentane to give **3c** as a yellow solid. Yield 736 mg (98%). M.p. 174 °C [Found: C, 30.97; H, 3.23; Cl, 21.52. Calc. for $C_{13}H_{15}Cl_3GeMoO_3$ (494.17): C, 31.60; H, 3.06; Cl, 21.52%]. EI-MS [70 eV (eV ≈ 1.602×10^{-17} J)]: $m/z = 496$ $[M]^+$, 461 ($[M - Cl]^+$), 433 ($[M - Cl - CO]^+$), 377 ($[M - Cl - 3CO]^+$), 352 ($[M - GeCl_2]^+$), 324 ($[M - GeCl_2 - CO]^+$), 296 ($[M - GeCl_2 - 2CO]^+$), 268 ($[M - GeCl_2 - 3CO]^+$) (base peak).

$[CpMo(CO)_3]_2GeCl_2$ 4a. A solution of 320 mg (1.30 mmol) of $CpMo(CO)_3H$ **1a** in 30 ml of pentane was treated at −40 °C with 0.65 ml (1.30 mmol) of a 2 M solution of $LiBu^n$ in pentane. Instantaneous precipitation of a white solid was observed. The resulting suspension was warmed to room temperature, stirred for 15 min and evaporated to dryness. The residue was washed once with a minimum amount of pentane and dried *in vacuo* to give the lime-coloured solid of $Li[CpMo(CO)_3]$ **2a**. This was dissolved in 20 ml of THF and the yellow-brown solution was added dropwise to a yellow solution of 544 mg (1.28 mmol) of **3a** in 20 ml of THF. The reaction mixture was refluxed for 5 h until reaction was complete (IR monitoring). The solvent was then removed *in vacuo*, the residue washed twice with 10 ml of pentane and dissolved in 30 ml of CH_2Cl_2. The solution was separated from LiCl through a filter cannula and the dark red filtrate evaporated to dryness. The residue was washed twice with 10 ml of pentane and dried *in vacuo* to give **4a** as an ocherous solid. Yield 633 mg (78% relative to **3a**). M.p. 192 °C [Found: C, 30.21; H, 1.54; Cl, 11.03. Calc. for $C_{16}H_{10}Cl_2GeMo_2O_6$ (633.65): C, 30.33; H, 1.59; Cl, 11.19%]. EI-MS (70 eV): $m/z = 610$ ($[M - CO]^+$), 582 ($[M - 2CO]^+$), 554 ($[M - 3CO]^+$), 526 ($[M - 4CO]^+$), 498 ($[M - 5CO]^+$), 470 ($[M - 6CO]^+$), 434 ($[M - 6CO - HCl]^+$).

$[CpW(CO)_3]_2GeCl_2$ 4b. Following the procedure described above for the synthesis of **4a**, 1.44 mmol of $Li[CpW(CO)_3]$ **2b** was prepared from 481 mg (1.44 mmol) of $CpW(CO)_3H$ **1b** and 0.72 ml (1.44 mmol) of a 2 M solution of $LiBu^n$ in pentane, dissolved in 20 ml of THF and the yellow-brown solution formed was added to a yellow solution of 730 mg (1.43 mmol) of $CpW(CO)_3GeCl_3$ **3b** in THF. The reaction mixture was refluxed for 6 h and completion of the reaction was confirmed by IR spectroscopy. Work-up of the resulting suspension as described for the preparation of **4a** afforded **4b** as an ocherous solid. Yield 986 mg (85% relative to **3b**). M.p. 212 °C [Found: C, 23.69; H, 1.19; Cl, 9.32. Calc. for $C_{16}H_{10}Cl_2GeO_6W_2$ (809.47): C, 23.74; H, 1.25; Cl, 8.76%]. EI-MS (70 eV): $m/z = 782$ ($[M - CO]^+$), 754 ($[M - 2CO]^+$), 698 ($[M - 4CO]^+$), 670 ($[M - 5CO]^+$), 642 ($[M - 6CO]^+$), 606 ($[M - 6CO - HCl]^+$), 477 ($[M - CpW(CO)_3]^+$), 449 ($[M - CpW(CO)_3 - CO]^+$), 421 ($[M - CpW(CO)_3 - 2CO]^+$), 393 ($[M - CpW(CO)_3 - 3CO]^+$), 333 ($[M - CpW(CO)_3 - GeCl_2]^+$).

$[Cp^*Mo(CO)_3]_2GeCl_2$ 4c. The metallate $K[Cp^*Mo(CO)_3]$ **2c** (1.30 mmol) was prepared *in situ* upon refluxing a mixture of 343 mg (1.30 mmol) of $Mo(CO)_6$ and 230 mg (1.32 mmol) of KCp* in 30 ml of THF for 17 h. The THF solution of **2c** was added slowly *via* a cannula to a yellow solution of 598 mg (1.21 mmol) of **3c** in 30 ml of THF and the reaction mixture was stirred for 16 h at ambient temperature. Completion of the reaction was confirmed by IR spectroscopy. The resulting suspension was worked up as described above for the preparation of **4a** to afford **4c** as a brown solid. Yield 785 mg (84% relative to **3c**). M.p. 215 °C (decomp.) [Found: C, 40.87; H, 4.10; Cl, 8.25. Calc. for $C_{26}H_{30}Cl_2GeMo_2O_6$ (773.91): C, 40.35; H, 3.91; Cl, 9.16%]. EI-MS (70 eV): $m/z = 610$ ($[M - 6CO]^+$), 575 ($[M - 6CO - Cl]^+$), 459 ($[M - Cp^*Mo(CO)_3 - H_2]^+$).

$Cp^*Mo(CO)_3GeCl_2H$ 5c. A solution of 350 mg (1.11 mmol) of $Cp^*Mo(CO)_3H$ **1c** was added to 256 mg (1.11 mmol) of $GeCl_2(diox)$ and the mixture was stirred for 1 h at ambient temperature. During this time the colour of the solution changed to yellow. Completion of the reaction after 1 h was confirmed by IR spectroscopy. The solution was then filtered off from some insoluble material through a filter cannula and the filtrate was evaporated to dryness. The residue was washed twice with 20 ml of pentane to afford **5c** as a yellow solid. Yield 381 mg (75%). M.p. 174 °C (decomp.) [Found: C, 33.22; H, 3.79; Cl, 14.69. Calc. for $C_{13}H_{16}Cl_2GeMoO_3$ (459.72): C, 33.96; H, 3.51; Cl, 15.42%] EI-MS (70 eV): $m/z = 461$ $[M - H]^+$, 433 ($[M - H - CO]^+$), 406 ($[M - 2CO]^+$), 376 ($[M - 3CO - H_2]^+$).

$[Cp(CO)_3Mo(\mu\text{-}GeCl_2)\{$*trans*$\text{-}Mo(CO)_2(PMe_3)Cp\}]$ 6a. A solution of 367 mg (0.58 mmol) of **4a** in 40 ml of toluene was treated with 0.060 ml (0.58 mmol) of PMe_3. Gas evolution (CO) was observed immediately and the solution became cloudy. The reaction mixture was stirred for 3.5 h at ambient temperature until gas evolution stopped. An IR spectrum of the solution revealed the presence of unreacted starting material. The reaction mixture was therefore treated with additional 0.05 ml (0.48 mmol) of PMe_3 and after 2 h with 0.03 ml (0.29 mmol) of PMe_3. Each addition of PMe_3 caused an immediate gas evolution. Completion of the reaction after 15 h stirring at ambient temperature was revealed by IR spectroscopy. The cloudy solution was filtered through a filter cannula and the filtrate evaporated to dryness to give complex **6a** as a yellow solid, that was shown by ^1H and ^{31}P NMR spectroscopy to be contaminated to 10% with *trans*-$[CpMo(CO)_2(PMe_3)_2]Cl$. Crude yield 318 mg (80%). In order to obtain an analytically pure sample of **6a**, the crude product was suspended in 20 ml of Et_2O, the ether solution filtered and the yellow filtrate evaporated to dryness. The residue was extracted three times with 10 ml of Et_2O, the combined extracts were filtered and evaporated to dryness to afford a yellow solid. Yield 194 mg (49%). M.p. 175 °C (decomp.) [Found: C, 32.70; H, 2.90; Cl, 9.79; P, 4.17. Calc. for $C_{18}H_{19}Cl_2GeMo_2O_5P$ (681.71): C, 31.71; H, 2.81; Cl, 10.40; P, 4.54%]. EI-MS (70 eV): $m/z = 658$ ($[M - CO]^+$), 630 ($[M - 2CO]^+$), 602 ($[M - 3CO]^+$), 574 ($[M - 4CO]^+$), 546 ($[M - 5CO]^+$), 470 ($[M - 5CO - PMe_3]^+$), 439 ($[M - CpMo(CO)_3]^+$), 411 ($[M - CpMo(CO)_3 - CO]^+$), 383 ($[M - CpMo(CO)_3 - 2CO]^+$), 295 ($[M - CpMo(CO)_3 - GeCl_2]^+$).

$[CpMo(CO)_3]_2GeH_2$ 7a. A suspension of 1.25 g (1.97 mmol) of **4a** in 30 ml of Et_2O was treated with 100 mg (2.63 mmol) of $LiAlH_4$ and stirred at ambient temperature. The reaction was monitored by IR spectroscopy. After 10 h the IR spectrum of the reaction solution revealed only the presence of **7a** and **1a**. The suspension was then evaporated to dryness and the oily red residue was washed three times with 10 ml of pentane and treated with 30 ml of benzene. The benzene solution was filtered through a filter cannula, the filtrate was concentrated *in vacuo* to a few ml and pentane was added to precipitate complex **7a**. The supernatant solution was decanted off and the precipitate was washed with 10 ml of pentane and dried *in vacuo* to give **7a** as a light brown solid. Yield 249 mg (22%). M.p. 142 °C (decomp.) [Found: C, 32.75; H, 2.34. Calc. for $C_{16}H_{12}GeMo_2O_6$ (564.76): C, 34.03; H, 2.14%] EI-MS (70 eV): $m/z = 540$ ($[M - CO - H_2]^+$), 484 ($[M - 3CO - H_2]^+$), 456 ($[M - 4CO - H_2]^+$), 400 ($[M - 6CO - H_2]^+$).

Crystallography

A summary of the crystal data, data collection and refinement for complexes **4a**, **4b** and **6a** is given in Table 5. Data collection for **4a** and **6a** was performed on a STOE IPDS area detector equipped with a low-temperature device and graphite-monochromated MoKα radiation (λ = 0.710 73 Å). Lattice parameters were refined from 2000 reflections after data

Table 5 Summary of crystallographic data for the complexes **4a**, **4b** and **6a**

	4a	**4b**	**6a**
Empirical formula	$C_{16}H_{10}Cl_2GeMo_2O_6$	$C_{16}H_{10}Cl_2GeO_6W_2$	$C_{18}H_{19}Cl_2GeMo_2O_5P$
M	633.63	809.45	681.69
T/K	200(2)	293(2)	200(2)
Crystal color	Yellow	Orange-yellow	Yellow
Crystal size/mm	0.53 × 0.34 × 0.30	0.76 × 0.53 × 0.30	0.30 × 0.23 × 0.19
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	*Pbca* (no. 61)	$P2_1/n$ (no. 14)
a/Å	11.295(2)	11.370(3)	17.876(3)
b/Å	14.832(3)	14.848(4)	15.859(3)
c/Å	23.680(6)	23.811(9)	18.691(3)
β/°			116.203(12)
U/Å^3	3967(1)	4020(2)	4754(1)
Z	8	8	8
D_c/g cm^{-3}	2.122	2.675	1.905
μ(Mo-Kα)/mm^{-1}	2.892	12.693	2.482
F(000)	2432	2944	2656
2θ Minimum, maximum (°)	5, 52	4, 50	4, 52
hkl Ranges	0–13, 0–18, 0–29	0–13, 0–17, 0–28	−21 to 19, 0–19, 0–23
Total data	28 391	3989	33 291
Unique data (R_{int})	3968 (0.0793)	3532	9213 (0.0669)
Minimum, maximum density/e Å^{-3}	0.706, −0.720	0.940, −2.226	1.717, −1.639
No. parameters refined	245	244	542
Extinction coefficient[a]	0.001 54(13)		
$R1$[b] [$I > 2\sigma(I)$]	0.0367	0.0391	0.0328
$wR2$[c]	0.0855	0.0969	0.0707
S[d]	0.939	1.028	0.917

[a] $F_{c*} = kF_o[1 + 0.001\ F_c^2\lambda^3/\sin(2\theta)]^{-\frac{1}{4}}$. [b] $R1 = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$.

collection. The crystal of **4a** was rotated in 1.8° steps to yield 111 exposures and each of them was exposed for 2.5 min, whereas data on **6a** were collected in the oscillation mode with 1° steps to yield 180 exposures, which were each exposed for 3 min. Intensity data were integrated and converted into a SHELX *hkl* file with the STOE IPDS software.[24] Data collection for **4b** was performed on a STOE STADI4 four-circle diffractometer at ambient temperature and with graphite-monochromated MoKα radiation ($\lambda = 0.710\,73$ Å). Lattice parameters were determined from the setting angles of 46 reflections in the range of $27° \leqslant 2\theta \leqslant 30°$. Data were collected in the ω–2θ 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. The input files for the SHELX programs were prepared with the program UTILITY.[25] Structure solution was performed with the Patterson method (SHELXS 86)[26] and subsequent Fourier-difference synthesis (SHELXL 93).[27] Refinement on F^2 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 $d(\text{C–H}) = 0.96$ Å and $U_{iso} = 0.08$ Å^2. Neutral atom scattering factors were taken from Cromer and Mann.[28] Geometrical calculations and illustrations were performed with PLATON[29] and ZORTEP.[30]

In the final stages of the refinement, data for **4a** were corrected for secondary extinction effects. Complex **6a** crystallizes with two independent molecules in the asymmetrical unit. A split atom model was successfully employed in the second independent molecule for atoms C13 and C14 attached to atom Ge2 leading to a ratio of 1:1. Atoms C13, C13A, C14 and C14A could be refined anisotropically.

CCDC reference number 186/987.

See http://www.rsc.org/suppdata/dt/1998/2029/ for crystallographic files in .cif format.

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