Organometallics **2002,** *21,* 653−661

Molybdenum and Tungsten Germylyne Complexes of the General Formula *trans*-[X(dppe)$_2$M≡Ge-(η^1-Cp*)] (X = Cl, Br, I; dppe = $Ph_2PCH_2CH_2PPh_2$; Cp* = C_5Me_5): Syntheses, Molecular Structures, and Bonding Features of the Germylyne Ligand

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Received August 28, 2001

The halogermylenes $(Cp^*GeX)_n$ (**1a**, X = Cl, n = 1; **1b**, X = Br, n = 2; Cp* = pentamethylcyclopentadienyl) were prepared in high yield by a redistribution reaction of $GeCp^*_2$ with GeX_2(1,4-dioxane). The ionic compounds [Cp*Ge][GeX_3] (**2a**, X = Cl; **2b**, X = Br) were also formed to a small extent in this reaction. Treatment of *trans*-[Mo(dppe)$_2$(N_2)$_2$] (**3**) (dppe = $Ph_2PCH_2CH_2PPh_2$) with 1 equiv of **1a**,**b** affords in refluxing toluene the germylyne complexes *trans*-[X(dppe)$_2$Mo≡Ge−(η^1-Cp*)] (**4a**, X = Cl; **4b**, X = Br). Concomitant formation of $GeCp^*_2$ and the dihalo complexes *trans*-[Mo(dppe)$_2$(X)$_2$] (**5a**, X = Cl; **5b**, X = Br) is observed in this reaction. In comparison, the reactions of *trans*-[W(dppe)$_2$(N_2)$_2$] (**6**) with **1a**,**b** and $(Cp^*GeI)_\infty$ (**1c**) afford selectively the germylyne complexes *trans*-[X(dppe)$_2$W≡Ge−(η^1-Cp*)] (**7a**−**c**). The molecular structures of **4a**·0.5pentane and **4b**·0.5pentane reveal very short Mo−Ge bonds, almost linear Mo−Ge−C(Cp*) sequences, and an η^1-bonded Cp* substituent indicating the presence of a molybdenum−germanium triple bond. The structural features of the germylyne ligand in **4a** and **4b** are compared with those in the corresponding tungsten complexes *trans*-[X(dppe)$_2$W≡Ge−(η^1-Cp*)] (**7a**−**c**), and the bonding parameters of the Cp* substituent are shown to be similar to those in the germanes (η^1-Cp*)GeI_3 (**8**) and (η^1-Cp*)$_2$-$GeCl_2$ (**9**).

Introduction

Numerous transition metal carbyne complexes have been prepared and their reactions studied in detail.[1] In comparison, complexes containing a triple bond between a transition metal and a group 14 element that is heavier than carbon are very rare. In fact, silylyne, stannylyne, and plumbylyne complexes are presently unknown, and in the case of germanium only two classes of compounds have been described so far.[2] The first one includes the dicarbonyl complexes [(η^5-C_5H_5)(CO)$_2$-M≡Ge−R] (M = Cr, Mo, W), bearing a sterically very demanding substituent R at the germanium atom (R = C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-$i$$Pr_3$), C_6H_3-2,6-Mes_2 (Mes = C_6H_2-2,4,6-Me_3)).[3] The second class form the tungsten diphosphane complexes *trans*-[X(dppe)$_2$-W≡Ge−(η^1-Cp*)] (X = Cl, Br, I), in which the Cp* substituent as potential leaving group is bonded to germanium.[4] In continuation of our work in this field we report here on the syntheses and molecular structures of the molybdenum germylyne complexes *trans*-[X(dppe)$_2$Mo≡Ge−(η^1-Cp*)] (**4a**, X = Cl; **4b**, X = Br). The structural features of the germylyne ligand in **4a** and **4b** are compared with those in the tungsten congeners *trans*-[X(dppe)$_2$W≡Ge−(η^1-Cp*)] (X = Cl, Br, I) (**7a**−**c**) and the dicarbonyl complexes [(η^5-C_5H_5)-(CO)$_2$M≡Ge−R]. The molecular structures of (η^1-Cp*)-GeI_3 (**8**) and (η^1-Cp*)$_2GeCl_2$ (**9**) are reported and the bonding mode of the Cp* group in **4a**,**b** and **7a**−**c** compared with that in **8** and **9**.

Results and Discussion

Starting materials for the reactions described below were the halogermylenes $(Cp^*GeX)_n$ (**1a**, X = Cl, n = 1; **1b**, X = Br, n = 2; **1c**, X = I, n = ∞)[5−7] and the dinitrogen complexes *trans*-[M(dppe)$_2$(N_2)$_2$] (**3**, M = Mo; **6**, M = W).[8] For the synthesis of the halogermylenes **1a** and **1b** a redistribution reaction of $GeCp^*_2$[9] with

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(7) Compound **1b** is composed in the solid state of Br-bridged dimers, whereas **1c** forms an I-bridged coordination polymer with a ladder structure (ref 6). Ebullioscopic measurements show, however, that **1b** and **1c** are dissociated into monomers in CH_2Cl_2. Therefore all subsequent remarks and calculations in this publication are based on the monomers.

10.1021/om010785x CCC: $22.00
Publication on Web 01/24/2002

GeX_2(1,4-dioxane) (X = Cl, Br)[10] was used (eq 1). Compounds **1a** and **1b** were thereby obtained as pale

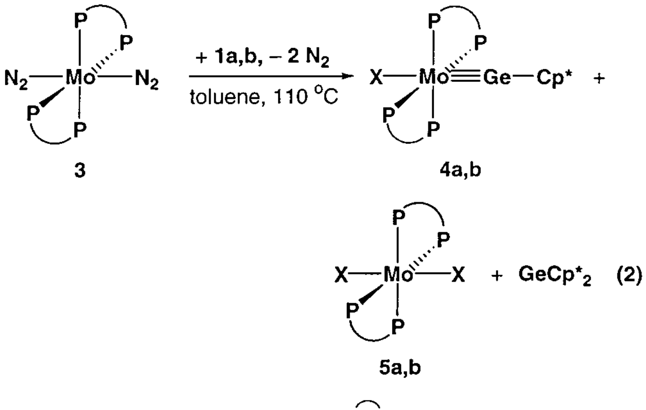
$$\mathrm{GeCp^*_2 + GeX_2(1,4\text{-}dioxane)} \xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{2\ Cp^*GeX} \quad (1)$$

1a,b

a: X = Cl; b: X = Br

green-yellow (**1a**) and white (**1b**) microcrystalline solids in 90 and 88% yields, respectively, and were identified by comparison of their NMR spectra with those of analytically pure samples obtained as described previously.[5,6] Both compounds are very air-sensitive, discoloring in air rapidly to yellow and then to brown, and are thermally very stable. Thus, no evidence for decomposition was found by NMR spectroscopy when **1a**,**b** were heated under rigorous exclusion of air for 15 min at 110 °C in toluene-d_8. The ionic compounds [Cp*Ge][$GeCl_3$] (**2a**)[5] and [Cp*Ge][$GeBr_3$] (**2b**) were also formed to a small extent in the reaction of $GeCp^*_2$ with GeX_2(1,4-dioxane) (X = Cl, Br). These were easily separated from **1a**,**b** taking advantage of their insolubility in pentane and isolated as white solids in 5 and 6% yields, respectively. Compound **2b** is a moderately air-sensitive solid that is soluble in CH_2Cl_2 but insoluble in diethyl ether and melts at 134−140 °C. The ^1H NMR spectrum of **2b** displays in CD_2Cl_2 at ambient temperature one singlet resonance for the methyl protons at δ 2.17, and the $^{13}C\{^1H\}$ NMR spectrum one singlet resonance for the methyl and the ring carbon nuclei at δ 9.8 and 121.8, respectively. The methyl proton resonance appears at lower field than that of **1b** (δ = 2.00 (CD_2Cl_2, RT)) and at a position close to that found for other salts bearing the $[Cp^*Ge]^+$ cation (δ_{Me} (CD_2Cl_2, RT): **2a**, 2.16; [Cp*Ge][BF_4], 2.16; [Cp*Ge][$InCl_4$], 2.21).[11] The ionic character of **2a** and **2b** was confirmed by single-crystal X-ray structural analyses.[11]

Heating of an equimolar mixture of *trans*-[Mo(dppe)$_2$(N_2)$_2$] (**3**) and **1a**,**b** in boiling toluene resulted in the formation of the germylyne complexes *trans*-[X(dppe)$_2$Mo≡Ge−(η^1-Cp*)] (**4a**, X = Cl; **4b**, X = Br) (eq 2).



a: X = Cl, b: X = Br; $\overset{\frown}{P\ P}$= dppe

Evidence for a fast reaction was given by the IR spectra of the reaction solutions, which revealed that the $\nu(N_2)$ absorptions of **3** at 2040 and 1977 cm^{-1} have disappeared within a few minutes. No intermediates could be observed by IR or $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ spectra of the crude products, which were obtained after evaporation of the solvent, showed in C_6D_6 that the singlet resonance of the starting material at δ 66.4 had been replaced by one singlet resonance (**4a**, δ 66.7; **4b**, δ 65.0), suggesting at first glance the exclusive formation of the molybdenum germylyne complexes.[12] However, the ^1H NMR spectra of the crude products revealed the presence of two other compounds, which by comparison with authentic samples were idendified to be *trans*-[Mo(dppe)$_2$(X)$_2$] (**5a**, X = Cl; **5b**, X = Br)[13] and $GeCp^*_2$,[9] respectively (eq 2).[14] The molar ratio of **4a**/**5a**/$GeCp^*_2$ and of **4b**/**5b**/$GeCp^*_2$ was found by ^1H NMR spectroscopy to be approximately 12/1/1.3 and 5.1/1/1.1, respectively. $GeCp^*_2$ could be easily removed upon washing the crude products with pentane. Separation of **4a**,**b** from **5a**,**b** proved however difficult, the germylyne complexes **4a** and **4b** enhancing the solubility of the less soluble dihalides **5a** and **5b** in THF, toluene, and diethyl ether. This was finally achieved by repeated fractional crystallization from hot toluene to afford the germylyne complexes as orange-brown, very air-sensitive solids, which contain 1 mol of toluene. Both compounds show a remarkable thermal stability and decompose upon melting at 236 and 224 °C, respectively. They are soluble in THF and warm toluene to give dark red solutions, which brighten rapidly upon exposure to air. The oxidation results in a mixture of presently unknown products. The IR spectra of **4a·toluene** and **4b·toluene** are essentially identical in the region 4000−400 cm^{-1} as expected for isostructural complexes, and the $^{31}P\{^1H\}$ NMR spectra display in THF-d_8 one singlet resonance for the chemically equivalent dppe ligands at δ 66.6 and 64.9, respectively. Furthermore the ^1H NMR spectra show in THF-d_8 a double set of resonances for the diastereotopic methylene protons at δ 2.45 and 2.83 (**4a·toluene**) and δ 2.49 and 2.93 (**4b·toluene**), and the $^{13}C\{^1H\}$ NMR spectra display a double set of resonances for the diastereotopic phenyl substituents of each PPh_2 group (Experimental Section). All these spectroscopic data indicate the presence of diamagnetic complexes of the general formula *trans*-[Mo(dppe)$_2$(L)(L′)]. Finally, one singlet resonance is observed for the methyl protons of the Cp* group in

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[12] When the reactions of **3** with **1a**,**b** were carried out in toluene, which after drying with Na/benzophenone and deoxygenation was stored under inert gas for several days over 4 Å sieves in Schlenk flasks with a plastic stopper, the $^{31}P\{^1H\}$ NMR spectrum of the crude product in C_6D_6 displayed an additional singlet at δ 68.5 (in the case of **3a**) and 67.2 (in the case of **3b**), indicating the formation of a second diamagnetic product. This product did not contain a Cp* group according to ^1H NMR spectroscopy and is probably the result of oxidation/hydrolysis of the germylyne complexes **4a** and **4b**.

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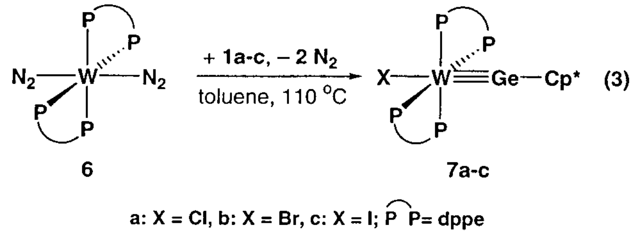
[14] ^1H NMR data of $GeCp^*_2$ and **4a**,**b** in C_6D_6 at room temperature: $GeCp^*_2$, δ 1.94 (s, 15H, C_5Me_5); **4a**, δ 8.01 (s, 8H), 8.75 (s, $\Delta\nu_{1/2}$ = 25 Hz, 8H), 8.94 (s, $\Delta\nu_{1/2}$ = 32 Hz, 16H), 15.23 (s, $\Delta\nu_{1/2}$ = 227 Hz, 16H) ($\Delta\nu_{1/2}$ of the solvent signal = 12 Hz); **4b**, δ 8.85 (s, $\Delta\nu_{1/2}$ = 13 Hz, 8H), 9.12 (s, $\Delta\nu_{1/2}$ = 14 Hz, 16H), 9.40 (s, $\Delta\nu_{1/2}$ = 34 Hz, 8H), 17.72 (s, $\Delta\nu_{1/2}$ = 45 Hz, 16H) ($\Delta\nu_{1/2}$ of the solvent signal = 3.6 Hz). No ^{31}P NMR signals were observed for the paramagnetic complexes **4a** and **4b**.

the ^1H NMR spectra of **4a**·toluene ($\delta = 1.41$ (THF-d_8); $\delta = 1.50$ (C_6D_6)) and **4b**·toluene ($\delta = 1.36$ (THF-d_8); $\delta = 1.46$ (C_6D_6)) at room temperature. This reveals a fast haptotropic shift of the Cp* substituent on the NMR time scale, if one takes into account the solid-state molecular structures of **4a** and **4b** (vide infra). The activation energy for this process should be low given the fact that the static structures of **4a**·toluene and of **4b**·toluene cannot be frozen out in toluene-d_8 at −73 °C (300 MHz spectrometer). This agrees fully with the results of density functional theory (DFT) calculations on the related model compounds *trans*-[Cl(L)$_4$W≡Ge−(η^1-Cp)] (L = CO, PH$_3$; Cp = C$_5$H$_5$).[4] The energy barrier for the haptotropic shift involving a transition state structure with an η^2-bonded Cp group is at 3.7 kJ/mol (L = CO) and 10.8 kJ/mol (L = PH$_3$), which is considerably smaller than that of cyclopentadienyl germanes.[15]

The reactions of the corresponding tungsten compound *trans*-[W(dppe)$_2$(N$_2$)$_2$] (**6**) with the halogermylenes **1a**−**c**[7] are much more selective than those of the molybdenum complex **3** mentioned above and afford the tungsten germylyne complexes *trans*-[X(dppe)$_2$-W≡Ge−(η^1-Cp*)] (**7a**, X = Cl; **7b**, X = Br; **7c**, X = I) in good yields (eq 3).[4] Only a tiny amount of *trans*-[W(dppe)$_2$(X)$_2$] (X = Cl, Br, I) and GeCp*$_2$ were formed in these reactions according to ^1H NMR spectroscopy, and no intermediates could be detected by IR or $^{31}P\{^1H\}$ NMR spectroscopy as in the molybdenum case (vide supra). The germylyne complexes **7a**−**c** were isolated as orange-brown (**7a**,**b**) and red-brown (**7c**) solids, which are less air-sensitive and thermally more stable than their molybdenum congeners **4a** and **4b**. **7a**−**c** have spectroscopic properties similar to **4a** and **4b** (Experimental Section).[4]



The solid-state structures of the germylyne complexes **4a**·0.5pentane, **4b**·0.5pentane, **7b**·0.5pentane, and **7c**·toluene were determined by single-crystal X-ray diffraction. Suitable dark red crystals of **4a**·0.5pentane, **4b**·0.5pentane, and **7b**·0.5pentane were obtained upon diffusion of pentane into a toluene solution (**4a**) or a THF solution (**4b**, **7b**) at 4 and 20 °C, respectively. Red-brown crystals of **7c**·toluene were grown upon slow cooling of a hot saturated toluene solution of **7c** to room temperature. The pentane hemisolvates of **4a**, **4b**, and **7b** are isostructural and crystallize in the space groups *I*2/*a* (**4a**, **4b**) and *C*2/*c* (**7b**). Similarly, the toluene solvates of **7a** and **7c** are isostructural and crystallize in the space group *P*$\bar{1}$. The molecular structures of **4b** and **7c** are depicted in Figures 1 and 2, and selected bond lengths and angles of all germylyne complexes are listed in Table 1 including those of **7a**·toluene[4] for comparison reasons.

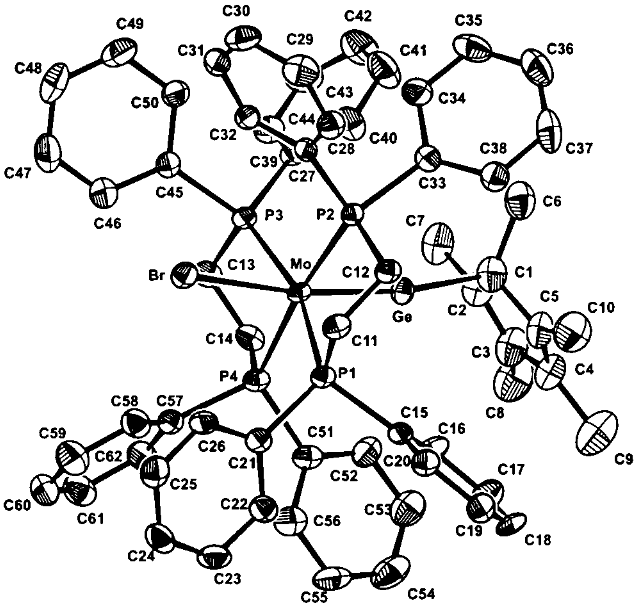


Figure 1. DIAMOND plot of the molecular structure of *trans*-[Br(dppe)$_2$Mo≡Ge−(η^1-Cp*)] (**4b**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

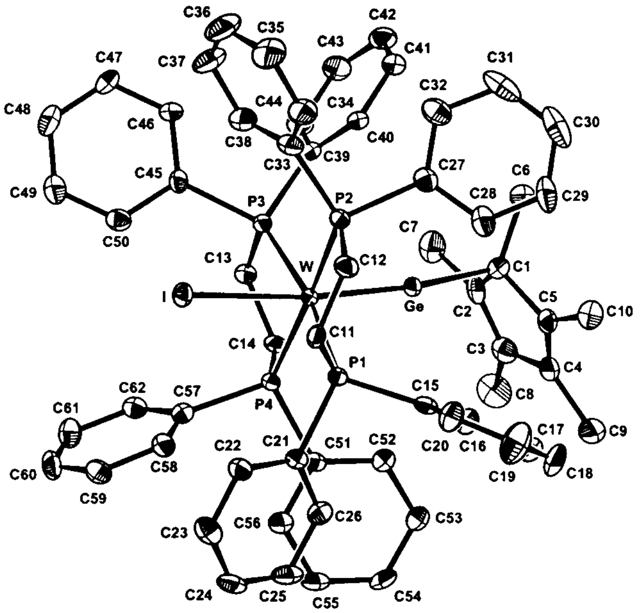


Figure 2. DIAMOND plot of the molecular structure of *trans*-[I(dppe)$_2$W≡Ge−(η^1-Cp*)] (**7c**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

All germylyne complexes reveal a distorted octahedral coordination geometry, in which the halogen and the germylyne ligand occupy *trans* positions. This agrees fully with the results of the NMR studies in solution (vide supra). Complexes **4a**, **4b**, and **7b** differ from **7a** and **7c** in the conformation adopted by the Cp* substituent and the phenyl groups (Figure 3).

The Mo−Br distance of **4b**·0.5pentane (264.06(7) pm) is 9 pm shorter than that of the related carbyne complex *trans*-[Br(dppe)$_2$Mo≡C−SiMe$_3$] (Mo−Br = 273.1(2) pm)[16] and the W−Br distance of **7b**·0.5pentane (263.8(2) pm) 10.6 pm shorter than that of *trans*-[Br(dmpe)$_2$W≡C−Ph] (W−Br = 274.4(2) pm, dmpe = Me$_2$PCH$_2$CH$_2$-

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Table 1. Selected Bond Lengths (pm) and Angles (deg) with Estimated Standard Deviations of the Germylyne Complexes *trans*-[X(dppe)$_2$M≡Ge−(η^1-Cp*)] (4, M = Mo; 7, M =W; a, X = Cl; b, X = Br; c, X = I)

	4a·0.5pentane	**4b**·0.5pentane	**7a**·toluene	**7b**·0.5pentane	**7c**·toluene
M−Ge	231.85(6)	231.03(6)	230.2(1)	229.3(1)	230.60(9)
M−X	251.2(1)	264.06(7)	248.6(1)	263.8(2)	282.76(9)
M−P(1)	250.4(1)	249.7(1)	246.9(1)	248.0(3)	249.6(2)
M−P(2)	252.8(1)	253.1(1)	248.9(1)	250.6(3)	249.0(2)
M−P(3)	249.1(1)	248.8(1)	245.5(1)	247.0(3)	250.0(2)
M−P(4)	247.0(1)	247.8(1)	244.6(1)	245.9(4)	245.8(2)
(M−P)$_{av}$	249.8(1)	249.8(1)	246.5(1)	247.9(3)	248.6(2)
Ge−C(1)	204.9(4)	202.9(5)	203.8(5)	203.0(8)	204.9(6)
C(1)−C(2)	148.1(5)	149.6(7)	150.0(8)	149.6(10)	149.3(9)
C(2)−C(3)	135.4(6)	135.3(7)	136.7(8)	133.9(11)	137.1(9)
C(3)−C(4)	146.8(6)	146.2(7)	145.1(8)	146.0(12)	147.3(9)
C(4)−C(5)	136.0(6)	134.1(7)	137.2(7)	135.4(11)	133.5(9)
C(5)−C(1)	149.6(6)	150.8(7)	147.7(8)	148.6(11)	149.5(8)
M−Ge−C(1)	172.0(1)	171.6(2)	172.2(2)	172.4(2)	172.6(2)
Ge−M−X	171.36(3)	171.35(2)	174.04(3)	171.23(3)	173.90(2)
Ge−M−P(1)	101.67(3)	101.49(3)	101.81(4)	101.81(7)	100.96(4)
Ge−M−P(2)	87.82(3)	87.97(3)	94.16(5)	88.25(8)	93.81(4)
Ge−M−P(3)	91.31(3)	91.35(3)	87.80(4)	91.63(7)	87.46(4)
Ge−M−P(4)	89.64(3)	89.18(3)	92.11(5)	89.33(8)	92.47(4)
X−M−P(1)	81.52(3)	82.08(3)	81.85(5)	81.98(7)	82.96(4)
X−M−P(2)	84.83(3)	84.87(3)	81.87(5)	84.62(9)	82.36(4)
X−M−P(3)	86.50(3)	86.07(3)	88.91(5)	85.63(7)	88.95(4)
X−M−P(4)	98.16(3)	98.48(3)	92.17(5)	98.36(9)	91.73(4)
Ge−C(1)−C$_g$[a]	115.9	116.8	109.6	116.9	109.4
Ge−C(1)−C(2)	105.7(3)	107.0(3)	100.3(3)	105.9(5)	100.1(4)
Ge−C(1)−C(5)	105.4(3)	106.1(3)	105.2(3)	106.7(5)	105.6(4)
Ge−C(1)−C(6)	110.8(3)	111.4(3)	111.7(4)	110.7(5)	111.4(4)
C(2)−C(1)−C(5)	104.5(3)	103.7(4)	104.7(4)	103.8(6)	103.6(5)
C(2)−C(1)−C(6)	114.4(4)	114.0(4)	117.1(5)	114.2(7)	118.3(6)
C(5)−C(1)−C(6)	115.2(4)	114.1(4)	116.1(4)	114.7(7)	115.9(5)

[a] C$_g$ denotes the center of the C$_5$ ring.

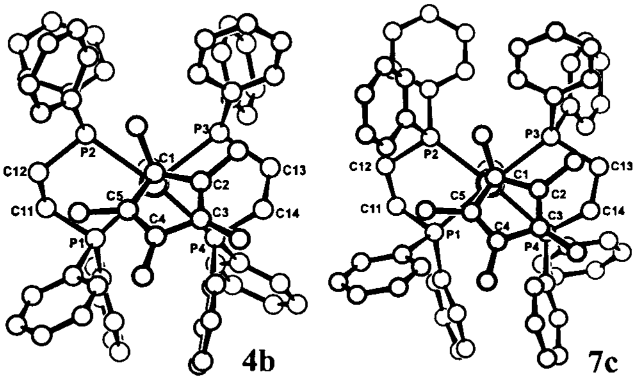

Figure 3. View of **4b** down the Ge−Mo−Br axis and of **7c** down the Ge−W−I axis showing the different conformations of the Cp* ring and the diphosphane ligands.

PMe$_2$).[17] Similarly, the Mo−Cl distance of **4a**·0.5pentane (251.2(1) pm) is 7.3 pm shorter than that of the electronically related carbyne complex *trans*-[Cl-{P(OMe)$_3$}$_4$Mo≡C−Ph] (Mo−Cl = 258.5(3) pm).[18] All these data indicate a weaker *trans* influence[19] of the germylyne ligand Ge(η^1-Cp*) than that of the carbyne ligands CPh and CSiMe$_3$. A comparison of the germylyne complexes *trans*-[X(P)$_4$M≡Ge−(η^1-Cp*)] (M = Mo, W; P = 0.5dppe, PMe$_3$; X = Cl, Br) with the bisdinitrogen complexes *cis*- or *trans*-[M(P)$_4$(N$_2$)$_2$][20] and the dihalides *trans*-[M(P)$_4$(X)$_2$][21] reveals an increase of the average M−P bond lengths in the series *cis*- or *trans*-[M(P)$_4$(N$_2$)$_2$] < *trans*-[X(P)$_4$M≡Ge−(η^1-Cp*)] < *trans*-[M(P)$_4$(X)$_2$] (Table 2), which indicates a weakening of the M−P bonds. This suggests in the absence of any steric effects a reduction of the electron density at the metal center and a decrease of the metal−phosphane back-bonding in the same series. Additional evidence that the M−P bonds of the germylyne complexes *trans*-[X(P)$_4$M≡Ge−(η^1-Cp*)] are weaker than those of the bisdinitrogen complexes *cis*- or *trans*-[M(P)$_4$(N$_2$)$_2$] is given by the ^1J(W,P) coupling constants of the complex pairs **7a**/**6** (^1J(W,P) = 258.8/320.8 Hz)[4,11] and *trans*-[Cl-(PMe$_3$)$_4$W≡Ge−(η^1-Cp*)]/*cis*-[W(PMe$_3$)$_4$(N$_2$)$_2$] (^1J(W,P) = 264.1/312, 314 Hz).[11,20b]

Striking features of the molecular structures of the germylyne complexes are however the very short M−Ge bonds, the almost linear M−Ge−C(Cp*) linkages, and the η^1-coordination of the Cp* substituent, which suggest in agreement with the results of theoretical calculations the presence of metal−germanium triple bonds in these compounds.[4] Thus, the Mo−Ge bond length of **4a**·0.5pentane is at 231.85(6) pm and that of **4b**·0.5pentane at 231.03(6) pm, which is considerably smaller than Mo−Ge single bond lengths. The latter range from 250 to 266 pm depending on the coordination sphere of molybdenum and the other substituents at the germanium atom, e.g., *trans*-[(η^5-Cp)Mo(CO)$_2$(PMe$_3$)-

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Table 2. Comparison of the M−P and M−X Bond Lengths of the Complexes *cis*- or *trans*-$[M(P)_4(N_2)_2]$, *trans*-$[X(P)_4M{\equiv}Ge\text{-}(\eta^1\text{-}Cp^*)]$, and *trans*-$[M(P)_4(X)_2]$ (M = Mo, W; P = 0.5dppe, PMe_3; X = Cl, Br)[a]

complex	M−P[b]	M−X	ref
trans-$[Mo(dppe)_2(N_2)_2]$ (**3**)	245.4(1)		20a
trans-$[Cl(dppe)_2Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ (**4a**)[c]	249.8(1)	251.2(1)	this work
trans-$[Mo(dppe)_2(Cl)_2]$ (**5a**)[d]	251.4(2)	243.4(2)	13c
trans-$[Br(dppe)_2Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ (**4b**)[c]	249.8(1)	264.06(7)	this work
trans-$[Mo(dppe)_2(Br)_2]$ (**5b**)	252.0(1)	256.9(1)	21a
cis-$[Mo(PMe_3)_4(N_2)_2]$	245.2(3)[e]		20b
trans-$[Cl(PMe_3)_4Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$[f]	247.9(2)	253.4(2)	11
trans-$[Mo(PMe_3)_4(Cl)_2]$	249.6(3)	242.0(6)	21b
trans-$[W(dppe)_2(N_2)_2]$ (**6**)	245.4(3)		20c
trans-$[Cl(dppe)_2W{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ (**7a**)[c]	246.5(1)	248.6(1)	4
trans-$[W(dppe)_2(Cl)_2]$[c]	250.1(1)	242.3(1)[b]	11

[a] Bond lengths are given in pm and estimated standard deviations in parentheses. [b] Average M−P and M−Cl bond lengths. [c] Bonding parameters of the hemipentane ($0.5C_5H_{12}$) solvates of **4a**, **4b** and *trans*-$[W(dppe)_2(Cl)_2]$ and the toluene solvate of **7a**. [d] Average M−P and M−Cl bond lengths of the hemipentane solvate and the ditetrahydrofurane solvate ($2C_4H_8O$) of **5a**. [e] The average Mo−P bond lengths of the *trans*- and *cis*-coordinated PMe_3 ligands do not differ significantly ($(Mo{-}P)_{trans}$ = 245.3(3) pm; $(Mo{-}P)_{cis}$ = 245.0(3) pm). [f] Average values of the two crystallographically independent molecules.

$(GeCl_3)]$ ($(Mo{-}Ge)_{av}$ = 250.57(6) pm),[22a] *trans*-$[(\eta^5\text{-}Cp)Mo(CO)_2(PMe_3)(GeCl_2H)]$ (Mo−Ge = 253.1(2) pm),[22b] $[(\eta^5\text{-}Cp)Mo(CO)_3(GeCl_3)]$ (Mo−Ge = 254.6(1) pm),[22a] $[(\eta^5\text{-}Cp)Mo(\eta^3\text{-}C_6H_{11})(NO)(GePh_3)]$ (Mo−Ge = 260.4(2) pm),[23] $[(\eta^5\text{-}Cp)Mo(CO)_2\{C(OEt)Ph\}(GePh_3)]$ (Mo−Ge = 265.8(2) pm),[24] and $[\{(\eta^5\text{-}Cp)Mo(CO)_3\}_2GeCl_2]$ ($(Mo{-}Ge)_{av}$ = 266.02(7) pm).[22c] The Mo−Ge triple bonds of **4a**,**b** are 3−5 pm longer than those of the dicarbonyl complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}R_2]$ (R = Mes, Mo−Ge = 227.1(1) pm; R = Trip, Mo−Ge = 227.2(8) pm)[3] and of germylyne complexes, which bear sterically less demanding and more basic phosphane ligands, such as *trans*-$[Br(depe)_2Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ (Mo−Ge = 227.98(5) pm, depe = $Et_2PCH_2CH_2PEt_2$)[11] and *trans*-$[Cl(PMe_3)_4Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ ($(Mo{-}Ge)_{av}$ = 228.1(1) pm (two crystallographically independent molecules in the solid state)).[11] The latter finding can be explained by the decrease in steric crowding around the metal center and the stronger molybdenum−germylyne ligand π bonding in the complexes *trans*-$[Br(depe)_2Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ and *trans*-$[Cl(PMe_3)_4Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$. Similarly, the W−Ge distances of the germylyne complexes **7a**·toluene, **7b**·0.5pentane, and **7c**·toluene range from 229.3(1) to 230.60(9) pm (Table 1) and are slightly longer than that of the dicarbonyl complex $[(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Mes_2]$ (W−Ge = 227.7(1) pm),[3b] but considerably smaller than W−Ge single bond lengths, which are found between 249 and 268 pm, e.g., (*spy*-5−13)-$[(\eta^5\text{-}Cp^*)W(CO)(EtNC)(PMe_3)GeCl_3]$ (W−Ge = 249.3(2) pm),[25] *cis*-$[(\eta^5\text{-}Cp^*)W(CO)_2\{C(H)NEt_2\}(GeCl_3)]$ (W−Ge = 252.69(9) pm),[25] $[(\eta^5\text{-}Cp)_2W(GeMe_2Cl)(SiMe_3)]$ (W−Ge = 254.2(1) pm),[26] *cis*-$[(\eta^5\text{-}Cp^*)W(CO)_2(PMe_3)(GeCl_3)]$ (W−Ge = 255.90(5) pm),[27] $W_2(GePh_3)_2(NMe_2)_4$ (W−Ge = 262.5(1) pm),[28] $[\{(\eta^5\text{-}Cp)(CO)_3W\}_2GeCl_2]$ ($(W{-}Ge)_{av}$ = 266.1(1) pm),[22c] and $[(\eta^5\text{-}Cp)W(CO)_3Ge(C_6H_3\text{-}2,6\text{-}Trip_2)]$ (W−Ge = 268.1(3) pm).[3b] Only a small influence of the metal center and the *trans*-arranged halogen ligand is observed on the M−Ge bond lengths of **4a**,**b** and **7a**−**c**. For example the W−Ge triple bonds are approximately 1.7 pm longer than the Mo−Ge triple bonds (Table 1), this value being close to the difference of the metallic radii of the two elements (0.8 pm).[29]

The M−Ge−C atom sequences in **4a**,**b** and **7a**−**c** deviate slightly from linearity, the angles at the germanium atom ranging from 171.6(2)° to 172.6(2)° (Table 1). The same phenomenon was observed in the dicarbonyl complexes $[(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}R_2]$ (M = Mo, W; R = Mes, Trip) (M−Ge−C = 170.9(3)−174.3(1)°)[3] and is apparently in the case of **4a**,**b** and **7a**−**c** the result of intramolecular steric repulsions between the Cp* substituent and the dppe ligands. For example, the M−Ge−C(Cp*) angles of the less crowded germylyne complexes *trans*-$[Cl(PMe_3)_4Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ and *trans*-$[Br(depe)_2Mo{\equiv}Ge{-}(\eta^1\text{-}Cp^*)]$ are 177.3(2)° (mean value of the two crystallographically independent molecules) and 177.46(8)°, respectively. These values are close to the expected 180° for a sp-hybridized germanium atom. Finally, the Cp* substituent is η^1-bonded to germanium, as evidenced by the Ge−C(1) bond lengths, the Ge−C(2)/C(5) and Ge−C(3)/C(4) distances, the $(C{-}C)_{ring}$ bond lengths, and the bond angles at the C(1) atom (Table 1). For example, the Ge−C(1) bond lengths, which range from 202.9(5) pm (**4b**·0.5pentane) to 204.9(6) pm (**7c**·toluene), compare well with those of Ge−C σ bonds in other two-coordinate, low-valent germanium compounds, such as the diarylgermylenes $GeMes^*_2$ ($(Ge{-}C)_{av}$ = 204.7(4) pm, Mes* = $C_6H_2\text{-}2,4,6\text{-}tBu_3$),[30] $Ge(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ (Ge−C = 203.3(4) pm),[31] and $Ge(C_6H_3\text{-}2,6\text{-}(1\text{-}naphthyl)_2)_2$ ($(Ge{-}C)_{av}$ = 203.3(2) pm)[32] or the dialkylgermylene $Ge[CH(SiMe_3)_2][C(SiMe_3)_3]$ (Ge−C = 201.2-

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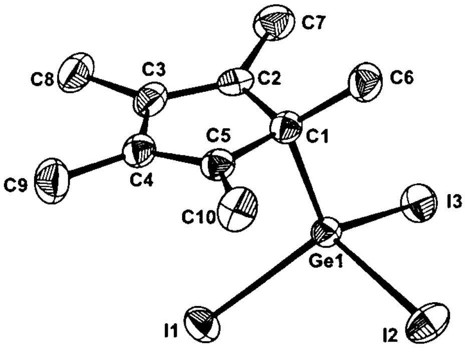

Figure 4. Structure of one of the two molecules of (η^1-Cp*)GeI_3 (**8**) in the asymmetric unit (DIAMOND plot). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms omitted for clarity.

(6) and 206.7(4) pm).[33] This suggests in agreement with the results of theoretical calculations a high p character of the germanium hybrid orbital used for the σ bond to carbon in the germylyne complexes.[4] In addition, the Ge−C(1) bonds of the germylyne complexes are considerably shorter than those of **1a** ($(Ge-C)_{av}$ = 221.7(3) pm), in which the Cp* group is η^2-bonded to germanium.[6] Furthermore, the Ge−C(2)/C(5) and Ge−C(3)/C(4) distances, which lie respectively in the range from 273.8 to 285.0 pm and from 350.3 to 367.4 pm, are too long to suggest any bonding interaction between these atoms. Moreover, an alternation of single and double C−C bonds is observed in the five-membered ring, which points to localized π bonds between the atoms C(2)−C(3) and C(4)−C(5), and the germanium atom is displaced beyond the periphery of the five-membered ring, as shown by the Ge−C(1)−C_g angle, which ranges from 109.4° (**7c**·toluene) to 116.9° (**7b**·0.5pentane) (Table 1). The C_5 rings are almost planar, the maximal deviation of one of the ring-carbon atoms from the least-squares plane is observed in **7a**·toluene and **7c**·toluene and ranges from −2.2 pm to 2.4 pm. The C(1)-attached methyl group is bent out of the ring plane in a direction away from the germanium atom by 39.4° (**7c**·toluene) to 47.8° (**4b**·0.5pentane), which indicates with the other bond angles at C(1) an sp^3 hybridization of this atom. Finally, similar bonding features are found for the η^1-bonded Cp* group in the germanes (η^1-Cp*)GeI_3 (**8**) and (η^1-Cp*)$_2GeCl_2$ (**9**) (vide infra), giving further unambiguous evidence for the η^1-bonding mode of the Cp* substituent in the germylyne complexes **4a**,**b** and **7a**−**c**. The molecular structures of **8** and **9** are depicted in Figures 4 and 5, respectively, and selected bond lengths and angles are listed in Table 3.

Two independent molecules of **8** with marginally different bonding parameters were found in the asymmetric unit. The following discussion is based on the average bond lengths and angles of the two molecules of **8**. Compound **9** reveals a crystallographically imposed C_2 symmetry. Both halogermanes are composed of distorted tetrahedral molecules, as revealed by the I−Ge−I angles of **8** (105.74(3)°, mean value) and the Cl(1)−Ge−Cl(1)#1 angle of **9** (98.98(11)°), which are more acute than that of a regular tetrahedron, or the C−Ge−I angles of **8** (112.98(12)°, mean value) and the C(1)−Ge−C(1)#1 angle of **9** (127.3(3)°), which are more obtuse than that of a regular tetrahedron. These distortions can be explained with the large steric demand of the Cp* group, to which an electronic effect is superimposed according to the Walsh/Bent rules.[34] For the same reasons the Ge−I bonds of **8** ($(Ge-I)_{av}$ = 253.37(9) pm) are longer than those of GeI_4 ($(Ge-I)_{av}$ = 250.0(1) pm),[35] the Ge−Cl bonds of **9** (218.61(18) pm) are longer than those of $GeCl_4$ (211.3(3) pm),[36] $MeGeCl_3$ (213.2(3) pm),[37] (η^1-Cp*)$GeCl_3$ ($(Ge-Cl)_{av}$ = 213.41(7)

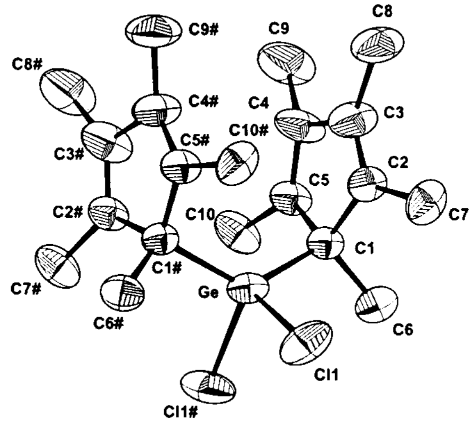

Figure 5. DIAMOND plot of the molecular structure of (η^1-Cp*)$_2GeCl_2$ (**9**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Bond Lengths (pm) and Bond Angles (deg) with Estimated Standard Deviations for (η^1-Cp*)GeI_3 (8) and (η^1-Cp*)$_2GeCl_2$ (9)

bond lengths		bond angles	
	Compound **8**[a]		
Ge(1)−C(1)	202.8(4)	C(1)−Ge(1)−I(1)	112.67(12)
C(1)−C(2)	150.0(5)	C(1)−Ge(1)−I(2)	111.90(12)
C(2)−C(3)	135.7(6)	C(1)−Ge(1)−I(3)	115.31(13)
C(3)−C(4)	146.6(6)	I(1)−Ge(1)−I(2)	108.59(4)
C(4)−C(5)	136.1(6)	I(1)−Ge(1)−I(3)	105.91(3)
C(5)−C(1)	151.2(6)	I(2)−Ge(1)−I(3)	101.67(3)
Ge(1)−I(1)	252.7(1)	Ge(1)−C(1)−C_g[b]	106.9
Ge(1)−I(2)	253.06(8)	Ge(1)−C(1)−C(2)	101.2(2)
Ge(1)−I(3)	254.73(9)	Ge(1)−C(1)−C(5)	101.3(3)
Ge(1)···C(2)	274.7[c]	Ge(1)−C(1)−C(6)	108.9(3)
Ge(1)···C(3)	342.7[c]	C(2)−C(1)−C(5)	104.2(3)
Ge(1)···C(4)	344.0[c]	C(2)−C(1)−C(6)	118.8(4)
Ge(1)···C(5)	275.7[c]	C(5)−C(1)−C(6)	119.5(3)
	Compound **9**		
Ge−C(1)	197.8(5)	C(1)−Ge−Cl(1)	107.14(15)
C(1)−C(2)	153.0(7)	C(1)−Ge−Cl(1)#1	106.36(14)
C(2)−C(3)	130.2(9)	C(1)−Ge−C(1)#1	127.3(3)
C(3)−C(4)	149.0(7)	Cl(1)−Ge−Cl(1)#1	98.98(11)
C(4)−C(5)	134.9(8)	Ge−C(1)−C_g[b]	120.7
Ge−Cl(1)	218.61(18)	Ge−C(1)−C(2)	109.4(3)
Ge···C(2)	287.4[c]	Ge−C(1)−C(5)	111.5(4)
Ge···C(3)	369.3[c]	Ge−C(1)−C(6)	108.5(4)
Ge···C(4)	369.2[c]	C(2)−C(1)−C(5)	101.7(4)
Ge···C(5)	290.0[c]	C(2)−C(1)−C(6)	112.7(5)
		C(5)−C(1)−C(6)	113.0(4)

[a] Bond lengths and angles of one of the two independent molecules. [b] C_g denotes the center of the C_5 ring. [c] Atomic distances.

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pm),[11] and Me_2GeCl_2 (214.3(4) pm),[37] and the Ge−C bonds of **9** (197.8(5) pm) (Table 3) are slightly longer than that of (η^1-Cp*)$GeCl_3$ (196.3(3) pm).[11]

Conclusion

Thermal elimination of dinitrogen from the complexes *trans*-[M(dppe)$_2$(N_2)$_2$] (M = Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$) affords in the presence of the germanium(II) halides (Cp*GeX)$_n$ (Cp* = C_5Me_5; X = Cl, n = 1; X = Br, n = 2; X = I, $n = \infty$) the mononuclear germylyne complexes *trans*-[X(dppe)$_2$M≡Ge−(η^1-Cp*)]. The spectroscopic data and the structural parameters provide experimental evidence for the presence of metal−germanium triple bonds in these complexes. The large number of known transition metal dinitrogen complexes[38] and the increasing number of isolable germanium(II) halides[39] let us suggest that the “dinitrogen elimination method” can become a very valuable route to germylyne complexes of variable ligand sphere allowing systematic reactivity studies. Preliminary work in this direction shows that the “dinitrogen elimination method” can be also used to prepare germylyne complexes bearing monodentate phosphane ligands, e.g., *trans*-[Cl(PMe_3)$_4$M≡Ge−(η^1-Cp*)] (M = Mo, W), which easily undergo oxidation reactions. Halogen exchange by pseudohalides is also possible in the case of tungsten to afford the germylyne complexes *trans*-[Y(dppe)$_2$W≡Ge−(η^1-Cp*)] (Y = NCO, N_3, NCS, CN).[11]

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk and glovebox techniques.[40] The solvents were dried by standard methods (pentane over CaH_2, toluene, THF, and diethyl ether over Na/benzophenone, CH_2Cl_2 over Sicapent (Merck) and Na/Pb alloy) and distilled under dinitrogen. The dried solvents were stored over $LiAlH_4$ (toluene and CH_2Cl_2 over CaH_2), trap-to-trap condensed, and deoxygenated immediately prior to use. The dinitrogen complexes **3** and **5** were prepared as reported in the literature[8] under an atmosphere of dinitrogen and recrystallized from THF, until the compounds were found by elemental analysis to be free of chlorine. Cp*GeI (**1c**) was prepared upon treatment of **1a** with an excess of NaI in diethyl ether,[11] Cp*GeI_3 (**8**)[41] upon oxidation of **7c** with iodine, and Cp*$_2GeCl_2$ (**9**) as described previously.[42] Elemental analyses were obtained from the Central Analytical Group of the Chemistry Department of the Humboldt-Universität zu Berlin. Solution IR spectra were recorded in the region 2300−1500 cm^{-1} on a Bruker IFS-55 spectrometer and IR spectra of the products in the region 4000−400 cm^{-1} as KBr pellets. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AM-300 spectrometer in dry deoxygenated tetrahydrofurane-d_8, benzene-d_6, toluene-d_8, or methylene-d_2 chloride. The ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated against the internal residual proton and natural abundance ^{13}C resonances of the deuterated solvent (tetrahydrofurane-d_8, δ_H 1.73 and δ_C 25.3 ppm; benzene-d_6, δ_H 7.15 and δ_C 128.0 ppm; toluene-d_8, δ_{Me} 2.09 and δ_{Me} 20.4 ppm; methylene-d_2 chloride δ_H 5.32 and δ_C 53.8 ppm). The ^{31}P{^{1}H} NMR spectra were calibrated against an external 85% aqueous H_3PO_4 solution. The following abbreviations were used for the signal multiplicities: s = singlet, m = multiplet. Melting points were determined using a Büchi 530 melting point apparatus and are corrected. The samples were sealed under vacuum in capillary tubes.

1. Preparation of Cp*GeCl (1a) and [Cp*Ge][$GeCl_3$] (2a) from GeCp*$_2$ and $GeCl_2$(1,4-dioxane). A solution of GeCp*$_2$ (1.647 g, 4.801 mmol) in 40 mL of CH_2Cl_2 was cooled to −70 °C and added without stirring to a suspension of $GeCl_2$(1,4-dioxane) (1.123 g, 4.848 mmol) in 35 mL of CH_2Cl_2, which was kept at −70 °C. Stirring was then started, and the reaction mixture was allowed to warm to ambient temperature within approximately 0.5 h. During this time all $GeCl_2$(1,4-dioxane) dissolved and a slight cloudy, pale yellow-green solution resulted. After stirring for 10 min at ambient temperature the solvent was removed in vacuo, and the residue was dried briefly and extracted three times with 60 mL of pentane. The combined pentane extracts were evaporated to dryness to afford **1a** as a pale green-yellow, microcrystalline solid of characteristic smell, which can be stored for several months in the freezer (−28 °C) without sign of decomposition: yield 2.094 g (90% based on GeCp*$_2$); mp 76 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 1.65 (s, 15H, C_5Me_5). ^{1}H NMR (300 MHz, toluene-d_8): δ 1.66 (s, 15H, C_5Me_5). ^{1}H NMR (300 MHz, THF-d_8): δ 2.00 (s, 15H, C_5Me_5). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.02 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 9.4 (s, C_5Me_5), 120.1 (s, C_5Me$_5$). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d_8): δ 9.3 (s, C_5Me_5), 120.2 (s, C_5Me$_5$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 9.8 (s, C_5Me_5), 120.7 (s, C_5Me$_5$).

The pentane-insoluble fraction was treated with CH_2Cl_2, and the solution was filtered from some insoluble yellow material. The filtrate was concentrated in vacuo to a few milliliters and treated with a diethyl ether/pentane mixture (1/1) to complete precipitation of **2a** as a white solid, which was dried in vacuo at ambient temperature: yield 167 mg (5% relative to GeCp*$_2$). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.16 (s, ^1J(C,H) = 129.4 Hz, 15H, C_5Me_5). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 9.6 (s, C_5Me_5), 121.7 (s, C_5Me$_5$).

2. Preparation of Cp*GeBr (1b) and [Cp*Ge][$GeBr_3$] (2b) from GeCp*$_2$ and $GeBr_2$(1,4-dioxane). A sample of GeCp*$_2$ (423 mg, 1.23 mmol) was mixed at −78 °C with a sample of $GeBr_2$(1,4-dioxane) (415 mg, 1.29 mmol), and the mixture was treated with 20 mL of cold (−78 °C) toluene. The suspension was stirred and allowed to warm to room temperature. After stirring for 0.5 h at ambient temperature an orange suspension resulted, which was evaporated to dryness and dried in vacuo for 1 h. The residue was extracted twice with 50 mL of pentane and the insoluble portion worked up as described below. The combined pentane extracts were concentrated under vacuum to approximately 5 mL, and the resulting suspension was cooled to −78 °C to complete crystallization of **1b**. The supernatant solution was decanted and the precipitate was dried for 0.5 h in vacuo at ambient temperature to afford **1b** as a white, microcrystalline solid: yield 621 mg (88% based on GeCp*$_2$). ^{1}H NMR (300 MHz, C_6D_6): δ 1.65 (s, ^1J(C,H) = 127.1 Hz, 15H, C_5Me_5). ^{1}H NMR (300 MHz, toluene-d_8): δ 1.66 (s, 15H, C_5Me_5). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.00 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 9.6 (s, C_5Me_5), 119.9 (s, C_5Me$_5$). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d_8): δ 9.5 (s, C_5Me_5), 120.0 (s, C_5Me$_5$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 9.9 (s, C_5Me_5), 120.1 (s, C_5Me$_5$).

The pentane-insoluble fraction was treated with CH_2Cl_2, and the solution was filtered from some insoluble orange material. The colorless filtrate was concentrated in vacuo to a few milliliters and treated with pentane to complete precipitation of **2b**. The precipitate was washed with pentane and dried under vacuum for 1 h to afford **2b** as a muddy-white solid: yield 72 mg (6% based on GeCp*$_2$); mp 134−140 °C. Anal. Calcd for $C_{10}H_{15}Br_3Ge_2$ (520.18): C, 23.09; H, 2.91; Br, 46.08. Found: C, 23.16; H, 3.12; Br, 45.81. ^{1}H NMR (300 MHz,

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C_6D_6): δ 1.41 (s, ^1J(C,H) = 129.2 Hz, 15H, C_5Me_5). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.17 (s, ^1J(C,H) = 129.3 Hz, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 8.9 (s, C_5Me_5), 120.6 (s, C_5-Me_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 9.8 (s, C_5Me_5), 121.8 (s, C_5Me_5).

3. Preparation of *trans*-[Cl(dppe)$_2$Mo≡Ge−(η^1-Cp*)]·toluene (4a·toluene). A mixture of **3** (385 mg, 0.406 mmol) and Cp*GeCl (**1a**) (100 mg, 0.411 mmol) was suspended in 80 mL of toluene, and the suspension was refluxed for 20 min. During this time all starting material dissolved to give an orange solution, which turned rapidly dark red to red-brown. Completion of the reaction was confirmed by IR and $^{31}P\{^1H\}$ NMR spectroscopy. The warm solution was filtered and the filtrate concentrated in vacuo to approximately 3 mL and cooled to −28 °C for 1 h to afford a precipitate, which was washed with a minimum amount of cold toluene and dried in vacuo. The solid was redissolved in hot toluene, the solution was filtered, and the filtrate was concentrated to a few milliliters and cooled to −28 °C. The resulting precipitate was washed with a minimum amount of cold toluene and recrystallized from toluene as described above to yield after drying under fine vacuum at ambient temperature **4a·**toluene as an analytically pure orange-brown, microcrystalline solid: yield 200 mg (40%); mp 237 °C (dec). Anal. Calcd for $C_{69}H_{71}ClGeMoP_4$ (1228.22): C, 67.48; H, 5.83; Cl, 2.89; N, 0. Found: C, 67.90; H, 5.87; Cl, 3.13; N, 0.00. ^{1}H NMR (300 MHz, THF-d_8, RT): δ 1.41 (s, 15H, C_5Me_5), 2.31 (s, 3H, Ph*Me*), 2.45 (m, 4H, 4 × H_ACH_B), 2.83 (m, 4H, 4 × H_ACH_B), 6.84−7.70 (m, 45H, 4 × P*Ph*$_2$ and *Ph*Me). ^{1}H NMR (300 MHz, C_6D_6, RT): δ 1.50 (s, 15H, C_5Me_5), 2.10 (s, Ph*Me*), 2.37 (m, 4H, 4 × H_ACH_B), 2.81 (m, 4H, 4 × H_ACH_B), 6.88−7.81 (m, 45H, 4 × P*Ph*$_2$ and *Ph*Me). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, RT): δ 66.6 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, RT): δ 66.7 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, RT): 12.7 (s, C_5Me_5), 21.5 (s, Ph*Me*), 33.3 (m, 4 × CH_2), 126.0 (s, *p-C*, *Ph*Me), 126.9 (s, C_5Me_5), 127.3 and 128.1 (m, *m-C*, 4 × Ph_APPh_B), 128.2 and 129.0 (s, *p-C*, 4 × Ph_APPh_B), 128.9 (s, *m-C*, *Ph*Me), 129.6 (s, *o-C*, *Ph*Me), 134.5 and 135.2 (m, *o-C*, 4 × Ph_APPh_B), 138.4 (s, *ipso-C*, *Ph*Me), 138.9 and 147.1 (m, *ipso-C*, 4 × Ph_APPh_B).

4. Preparation of *trans*-[Br(dppe)$_2$Mo≡Ge−(η^1-Cp*)]·toluene (4b·toluene). A mixture of **3** (340 mg, 0.358 mmol) and Cp*GeBr (**1b**) (103 mg, 0.358 mmol) was suspended in 50 mL of toluene, and the suspension was refluxed for 7 min in the glovebox. During this time all starting material dissolved to give an orange solution, which turned rapidly to red-brown. Completion of the reaction was confirmed by IR and $^{31}P\{^1H\}$ NMR spectroscopy. The warm solution was filtered and the filtrate concentrated in vacuo to a few milliliters and cooled for 1 h at −28 °C to afford a precipitate, which was washed with cold toluene and dried in vacuo at ambient temperature for 0.5 h. The dark orange solid was recrystallized three times from hot toluene as described above for the isolation of **4a·**toluene to afford complex **4b·**toluene as an orange-brown, microcrystalline solid: yield 82 mg (18%); mp 224 °C (dec). Anal. Calcd for $C_{69}H_{71}BrGeMoP_4$ (1272.68): C, 65.12; H, 5.62; Br, 6.28; N, 0. Found: C, 65.65; H, 6.03; Br, 6.72; N, 0.00. ^{1}H NMR (300 MHz, THF-d_8, RT): δ 1.36 (s, 15H, C_5Me_5), 2.31 (s, 3H, Ph*Me*), 2.49 (m, 4H, 4 × H_ACH_B), 2.93 (m, 4H, 4 × H_ACH_B), 6.86−7.73 (m, 45H, 4 × P*Ph*$_2$ and *Ph*Me). ^{1}H NMR (300 MHz, C_6D_6, RT): δ 1.46 (s, 15H, C_5Me_5), 2.10 (s, Ph*Me*), 2.42 (m, 4H, 4 × H_ACH_B), 2.91 (m, 4H, 4 × H_ACH_B), 6.89−7.84 (m, 45H, 4 × P*Ph*$_2$ and *Ph*Me). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, RT): δ 64.9 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, RT): δ 65.0 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, RT): 12.7 (s, C_5Me_5), 21.5 (s, Ph*Me*) 33.9 (m, 4 × CH_2), 126.0 (s, *p-C*, *Ph*Me), 126.9 (s, C_5Me_5), 127.1 and 128.2 (m, *m-C*, 4 × Ph_APPh_B), 128.3 and 129.0 (s, *p-C*, 4 × Ph_APPh_B), 128.9 (s, *m-C*, *Ph*Me), 129.6 (s, *o-C*, *Ph*Me), 134.4 and 135.4 (m, *o-C*, 4 × Ph_APPh_B), 138.4 (s, *ipso-C*, *Ph*Me), 139.2 and 147.9 (m, *ipso-C*, 4 × Ph_APPh_B).

5. Preparation of *trans*-[Br(dppe)$_2$W≡Ge−(η^1-Cp*)]·toluene (7b·toluene). A solution of **1b** (51 mg, 0.177 mmol) in 5 mL of toluene was added to a solution of **6** (184 mg, 0.177 mmol) in 40 mL of toluene, and the mixture was heated in a preheated oil bath (120 °C), so that the solvent boiled gently. The color of the solution turned from orange to red, and after 40 min an IR spectrum of the reaction solution was recorded, confirming the absence of any N_2-containing complexes. The solution was then concentrated in vacuo to a few milliliters and cooled overnight at −28 °C. The resulting suspension was treated with 30 mL of cold pentane (−28 °C) to complete precipitation of complex **7b·**toluene, which was washed with 10 mL of pentane and dried under fine vacuum for 3 h at ambient temperature. An orange-brown solid resulted, yield 188 mg (78%), mp 236 °C (dec). Anal. Calcd for $C_{69}H_{71}BrGeP_4W$ (1360.58): C, 60.91; H, 5.26; Br, 5.87. Found: C, 60.25; H, 5.37; Br, 6.49. ^{1}H NMR (300 MHz, THF-d_8, RT): δ 1.37 (s, 15H, C_5Me_5), 2.31 (s, 3H, Ph*Me*), 2.46 (m, 4H, 4 × H_ACH_B), 2.95 (m, 4H, 4 × H_ACH_B), 6.89−7.70 (m, 45H, 4 × P*Ph*$_2$ and *Ph*Me). ^{1}H NMR (300 MHz, C_6D_6, RT): δ 1.47 (s, 15H, C_5Me_5), 2.10 (s, 3H, Ph*Me*), 2.40 (m, 4H, 4 × H_ACH_B), 2.93 (m, 4H, 4 × H_ACH_B), 6.98−7.81 (m, 45 H, 4 × P*Ph*$_2$ and *Ph*Me). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, RT): δ 43.9 (s, ^1J(W,P) = 262.3 Hz).$^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, RT): δ 45.9 (s, ^1J(W,P) = 262.6 Hz).$^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, 220K): δ 12.7 (s, C_5Me_5), 21.6 (s, Ph*Me*), 37.4 (m, 4 × CH_2), 126.2 (s, *p-C*, *Ph*Me), 127.1 (s, C_5Me_5), 128.1 (m, *m-C*, 4 × Ph_APPh_B), 128.5 and 129.3 (s, *p-C*, 4 × Ph_APPh_B), 129.1 (s, *m-C*, *Ph*Me), 129.8 (s, *o-C*, *Ph*Me), 134.6 and 135.5 (m, *o-C*, 4 × Ph_APPh_B), 138.4 (s, *ipso-C*, *Ph*Me), 138.7 and 148.7 (m, *ipso-C*, 4 × Ph_APPh_B).

6. Preparation of *trans*-[I(dppe)$_2$W≡Ge(η^1-Cp*)]·toluene (7c·toluene). A Schlenk tube was charged with **6** (214 mg, 0.206 mmol) and Cp*GeI (**1c**) (77 mg, 0.23 mmol), and the mixture was suspended in 30 mL of toluene. The suspension was heated in a preheated oil bath (120 °C), so that the solvent boiled gently. On heating the reaction mixture all starting material dissolved to give an orange solution, which turned gradually to red. IR monitoring of the reaction revealed a continuous decrease in intensity of the $\nu(N_2)$ absorptions of **5** at 2010 and 1949 cm^{-1}. After approximately 20 min the color of the solution had changed to dark red and complex **5** had been completely consumed (IR detection). The reaction mixture was allowed to cool to ambient temperature and filtered from some dark brown insoluble material, and the filtrate was concentrated in vacuo to approximately 4 mL and cooled to −78 °C. The supernatant solution was decanted and the precipitate was washed with 10 mL of pentane at −78 °C and dried under high vacuum at room temperature overnight to afford **7c·**toluene as a red-brown powder: yield 189 mg (65%), mp 221 °C (dec). Anal. Calcd for $C_{69}H_{71}GeIP_4W$ (1407.58): C, 58.88; H, 5.08; N, 0; I, 9.02. Found: C, 58.79; H, 5.20; N, 0.00; I, 9.23. ^{1}H NMR (300 MHz, THF-d_8, RT): δ 1.31 (s, 15H, C_5Me_5), 2.31 (s, 3H, Ph*Me*), 2.54 (m, 4H, 4 × H_ACH_B), 3.09 (m, 4H, 4 × H_ACH_B), 6.89−7.72 (m, 45H, 4 × P*Ph*$_2$ and *Ph*Me). ^{1}H NMR (300 MHz, C_6D_6, RT): δ 1.40 (s, 15H, C_5Me_5), 2.10 (s, Ph*Me*), 2.46 (m, 4H, 4 × H_ACH_B), 3.07 (m, 4H, 4 × H_ACH_B), 6.98−7.84 (m, 45H, 4 × P*Ph*$_2$ and *Ph*Me). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, RT): δ 38.7 (s, ^1J(W,P) = 258.8 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, RT): δ 40.6 (s, ^1J(W,P) = 258.0 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, RT): 12.6 (s, C_5Me_5), 21.5 (s, Ph*Me*), 38.4 (m, 4 × CH_2), 126.0 (s, *p-C*, *Ph*Me), 127.0 (s, C_5Me_5), 126.8 and 128.4 (m, *m-C*, 4 × Ph_APPh_B), 128.0 and 129.1 (s, *p-C*, 4 × Ph_APPh_B), 128.9 (s, *m-C*, *Ph*Me), 129.6 (s, *o-C*, *Ph*Me), 134.6 and 135.6 (m, *o-C*, 4 × Ph_APPh_B), 138.4 (s, *ipso-C*, *Ph*Me), 140.7 and 149.9 (m, *ipso-C*, 4 × Ph_APPh_B).

7. Crystal Structure Determination of 4a·0.5pentane, 4b·0.5pentane, 7b·0.5pentane, 7c·toluene, 8, and 9. A summary of the crystal data, data collection, and refinement is given in Table 4.

The data collection of **8** and of the solvates of **4a**, **4b**, and **7c** was performed on a STOE IPDS diffractometer (area

Table 4. Summary of Crystallographic Data of the Compounds 4a·0.5pentane, 4b·0.5pentane, 7b·0.5pentane, 7c·toluene, 8, and 9

	4a·0.5pentane	**4b**·0.5pentane	**7b**·0.5pentane	**7c**·toluene	**8**	**9**
empirical formula	$C_{64.5}H_{69}ClGeMoP_4$	$C_{64.5}H_{69}BrGeMoP_4$	$C_{64.5}H_{69}BrGeP_4W$	$C_{69}H_{71}GeIP_4W$	$C_{10}H_{15}GeI_3$	$C_{20}H_{30}Cl_2Ge$
M_t	1172.06	1216.52	1304.43	1407.48	588.51	413.93
cryst color	dark red	dark red	dark red	red-brown	red	pale yellow
cryst size (mm)	0.24 × 0.20 × 0.16	0.52 × 0.30 × 0.20	0.36 × 0.32 × 0.20	0.24 × 0.16 × 0.08	0.64 × 0.44 × 0.24	0.34 × 0.23 × 0.02
temp (K)	180(2)	180(2)	180(2)	180(2)	180(2)	183(2)
cryst syst	monoclinic	monclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$I2/a$ (no. 15)	$I2/a$ (no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a (Å)	24.664(4)	24.715(5)	39.57(3)	10.592(2)	8.376(2)	14.986(3)
b (Å)	13.3460(16)	13.2501(19)	13.225(8)	16.287(3)	13.524(4)	8.9304(12)
c (Å)	34.453(5)	34.527(7)	34.48(4)	17.928(3)	13.774(3)	16.878(4)
α (deg)	90	90	90	97.24(2)	89.35(3)	90
β (deg)	97.322(18)	97.68(2)	141.95(4)	96.58(2)	82.45(3)	112.20(2)
γ (deg)	90	90	90	103.31(2)	89.67(3)	90
V (Å^3)	11248(3)	11205(3)	11121(16)	2952.8(10)	1546.7(7)	2091.4(7)
Z	8	8	8	2	4	4
ρ_{calcd} (g·cm^{-3})	1.384	1.442	1.558	1.583	2.527	1.315
$\mu_{MoK\alpha}$ (mm^{-1})	0.959	1.628	3.482	3.128	7.938	1.718
F(000)	4856	5000	5256	1408	1064	864
2θ min/max (deg)	4.3/50.5	4.3/49.8	3.3/52.0	4.6/50.5	5.4/50.5	5.2/52.0
hkl range	−29, 29/−16, 16/−41, 41	−29, 28/−15, 15/−40, 40	−48, 48/0, 16/−42, 42	−12, 12/−19, 19/−21, 21	−10, 10/−16, 16/−16, 16	−18, 17/−10, 10/0, 20
total no. of data	36 274	96 78	18 487	19 795	13 610	2048
no. of unique data ($I > 2\sigma I$)	10 154	9678	10 919	10 062	5191	2048
R(int)	0.0875	0.1226	0.0695	0.0528	0.0420	0.0867
abs corr	none	numerical	empirical	numerical	refdelf	empirical
min./max. density (e·Å^{-3})	0.932/−0.759	0.787/−0.822	1.187/−0.899	1.541/−2.004	0.923/−0.723	0.768/−0.688
no. of params refined	651	650	632	686	254	106
$R_1{}^a$ ($I > 2\sigma I$)	0.0405	0.0403	0.0491	0.0413	0.0255	0.0624
$wR_2{}^b$ (all data)	0.0983	0.0872	0.1107	0.0936	0.0651	0.1754
GOF^c	0.929	0.819	1.089	0.947	1.024	0.785

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$. [c] $GOF = S = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(n - p)\}^{1/2}$.

detector), whereas data of **7b**·0.5pentane[43] and **9** were collected on a STOE STADI-4 diffractometer (scintillation counter) with Mo Kα radiation ($\lambda = 0.71073$ Å). Both diffractometers were equipped with a low-temperature device. An absorption correction was applied in all cases instead of **4a**·0.5pentane.[44] The data of **4b**·0.5pentane and **7c**·toluene were treated by a numerical absorption correction. The crystal of **4b**·0.5pentane was optimized by the program XSHAPE1.02, whereas in **7c**·toluene the crystal faces were indexed with a microscope on the diffractometer before the numerical absorption correction was applied that is based on a Gaussian algorithm and implemented in XRED1.08.[45] The data of **7b**·pentane, **8** (ψ-scan each),[46] and **9** ("refdelf")[47] were corrected empirically. The structure solution and refinement was carried out following standard methods (SHELXS97 and SHELXL97).[48] Hydrogen atoms were calculated at idealized positions ("AFIX", $D(C_{aliph}-H) = 98$ pm, $D(C_{ar}-H) = 95$ pm). All non-hydrogen atoms were refined anisotropically except the n-pentane carbon atoms in **7b**·0.5pentane. In the structure of **7b**·0.5pentane the pentane molecule could be localized only after absorption correction. A split atom model could not be applied successfully for **9** (C(3), C(4), C(8), and C(9) atoms were split, $wR_2 = 0.1957$). Geometrical calculations were performed with PLATON[49] and illustrations with DIAMOND.[50]

Acknowledgment. We thank the Humboldt Universität zu Berlin and the Fonds der Chemischen Industrie for financial support of this work, Dr. B. Ziemer, Dr. G. Kociok-Köhn, and P. Neubauer for the single-crystal X-ray diffraction studies, Dr. U. Hartmann, U. Kursawe, and U. Kätel for the elemental analyses, and Dr. J. G. Winter for a sample of **9**.

Supporting Information Available: Further details of the crystal structure determinations including tables of crystal data and structure refinement, atomic coordinates, bond lengths, bond angles, and thermal parameters for **4a**·0.5pentane, **4b**·0.5pentane, **7b**·0.5pentane, **7c**·toluene, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010785X

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(43) A mixture of pentane isomers was used for the crystallizations. Only n-pentane was found in all hemipentane solvates.

(44) Programs for data collection, cell refinement, and data reduction and correction: IPDS-2.87, STADI4-1.06, XRED-1.08, and XSHAPE-1.02, Stoe&Cie: Darmstadt, Germany, 1997.

(45) More than 200 strong reflections with 4 symmetry equivalents in each case were used for the optimization of **4b**·0.5pentane. XSHAPE is based on the program HABITUS (Herrendorf, W. PhD Thesis, Universität Karlsruhe, Germany, 1993).

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