(Supermesityl)chlorogermylene (Supermesityl = ${}^tBu_3C_6H_2$): Synthesis and Derivatization to (Supermesityl)ferriogermylenes

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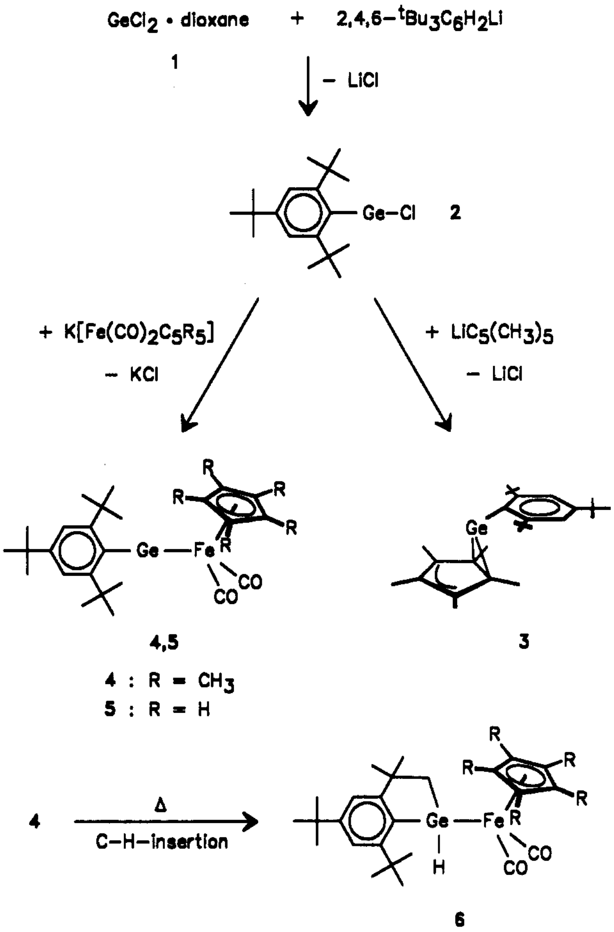
*Summary: $GeCl_2$·(dioxane) (1) reacts at low temperatures with stoichiometric amounts of (2,4,6-tri-tert-butylphenyl)lithium to give the unsymmetrically substituted (supermesityl)chlorogermylene (2), which is stable at ambient temperature. The monomeric structure of 2 has been proven both in solution and in the solid state. 2 is a suitable substrate for the synthesis of mixed germylenes. Thus, reaction of 2 with Cp*Li leads to the germylene Mes*GeCp* (3), whereas the reaction with the corresponding alkali-metal metalates yields the first organometallogermylenes, Mes*GeFe(CO)$_2$R (4, R = Cp*; 5, R = Cp).*

Organohalogermylenes, RGeHal, constitute an interesting class of compounds in germanium(II) chemistry with regard to structure and bonding. Furthermore, species of this class are important substrates for the synthesis of new low-valent germanium compounds by nucleophilic substitution or reductive dehalogenation processes.[1] The only stable, well-characterized organohalogermylene that has been reported so far is the π-complex (pentamethylcyclopentadienyl)chlorogermylene, Me_5C_5GeCl.[2] As expected, this compound allows the nucleophilic substitution of the chloro ligand,[3] but the synthetic utility of this strategy is restricted by the fact that the Me_5C_5 ligand also is a good leaving group.[4] All other germylenes of the type RGeHal known so far are described as reactive intermediates[5] and thus are difficult, if not impossible, to characterize; they must be transient species in the synthesis of diorganogermylenes starting from germanium(II) halides.[6] Here we report the synthesis of a stable and well-characterized arylchlorogermylene and also some substitution reactions.

Treatment of $GeCl_2$·diox (diox = dioxane) with 1 equiv of (2,4,6-tri-*tert*-butylphenyl)lithium ((supermesityl)lithium, Mes Li) yielded (supermesityl)chlorogermylene (2), which was obtained in satisfactory yields as a pale yellow solid (Scheme 1); 2 is air-stable for short times of exposure and soluble in common aprotic organic solvents.

Scheme 1



The high thermal stability of 2 is noteworthy. Whereas the deep red bis(supermesityl)-substituted germylene Mes*$_2$Ge undergoes oxidative addition of a C–H unit of one of the *tert*-butyl groups to the germanium(II) center at temperatures of about −10 °C,[6d] 2 is stable in benzene solution up to 80 °C. At higher temperatures, decomposition to give 1,3,5-tri-*tert*-butylbenzene takes place. The formation of Mes*$_2$Ge as a byproduct in the synthesis of 2 can be minimized by performing a slow addition of the aryllithium compound at low temperatures.

Cryoscopic molecular mass determinations showed that 2 is monomeric in benzene solution. That 2 is a monomer also in the solid state was proved by an X-ray crystal structure analysis, which showed rather long *inter*molecular Ge–Cl distances to be present.[7] Thus, association by *inter*molecular donor–acceptor interactions is excluded. The stability of 2 can be explained in terms of the

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[1] The latter reactions can lead to germynes (GeR) or to germyne derivatives ((GeR)$_n$).

[2] Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 31.

[3] (a) Jutzi, P.; Hampel, B. *Organometallics* **1986**, *5*, 1944. (b) Jutzi, P.; Becker, A.; Leue, C.; Stammler, H. G.; Neumann, B.; Hursthouse, M. B.; Karaulov, A. *Organometallics* **1991**, *10*, 3838.

[4] (a) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1. (b) Jutzi, P.; Becker, A.; Stammler, H. G.; Neumann, B. *Organometallics* **1991**, *10*, 1647.

[5] The coordination polymers RGeCl (R = Ph, Et) have been synthesized and characterized by oxidative-addition reactions. The structure assignment has been supported by IR data obtained in the germanium–chlorine absorption region: Satgé, J.; Massol, M.; Rivière, P. *J. Organomet. Chem.* **1973**, *56*, 1 and literature cited therein.

[6] (a) Scibelli, J. V.; Curtis, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 924. (b) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480. (c) Schumann, H.; Janiak, C.; Hahn, E.; Löbel, J.; Zuckerman, J. J. *Angew. Chem.* **1985**, *97*, 765. (d) Lange, L.; Du Mont, W.-W. *J. Organomet. Chem.* **1987**, *239*, C17. (e) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167.

[7] Due to the unsatisfactory quality of the crystals the structure could not be solved exactly. Thus, bond lengths and angles are not discussed in detail.

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pronounced steric hindrance of the supermesityl ligand. Furthermore, thermodynamic stabilization due to an *intra*molecular Cl→Ge back-bonding seems possible.

Nucleophilic substitution of the chloro ligand in 2 is a useful route for the synthesis of mixed germylenes. Thus, reaction of 2 with (pentamethylcyclopentadienyl)lithium yielded the π-complex $\mathrm{Mes^*GeC_5Me_5}$ (3).[3b] Treatment of 2 with potassium metalates allowed the synthesis of (supermesityl)metallogermylenes; reaction of 2 with potassium (pentamethylcyclopentadienyl)dicarbonylferrate or potassium (cyclopentadienyl)dicarbonylferrate in pentane gave the (supermesityl)ferriogermylenes 4 and 5, respectively (Scheme 1). These compounds were obtained as dark red (4) or green (5) air-sensitive solids, which are soluble in common organic solvents. They were characterized by ^{1}H and ^{13}C NMR, IR, and MS data (see Experimental Section). The germylenes 4 and 5 are the first well-characterized members of a novel class of germanium compounds.[8]

In analogy to the bis(supermesityl)-substituted germylene of Du Mont,[6d] germylene 5 undergoes oxidative addition of a C–H unit of one of the *tert*-butyl groups to the germanium(II) center, forming the insertion product 6, but only at temperatures above 80 °C[9] (Scheme 1).

Experiments concerning the synthesis of other RGeHal compounds, further derivatizations of 2, and the chemistry of 4 and 5 are in progress.

Experimental Section

All reactions and preparations were performed under an atmosphere of dried, oxygen-free argon using Schlenk techniques. Solvents and reagents were appropriately dried and purified.

Melting points were determined with a Büchi 510 capillary melting point apparatus. ^{1}H NMR spectra were recorded on a Bruker AM 300 (300 MHz) spectrometer; ^{13}C NMR spectra (75 MHz, ^{1}H-decoupled) were also recorded on the Bruker AM 300 spectrometer. Mass spectra were obtained with a Varian 311 A spectrometer (70 eV, 300-μA emission); only characteristic fragments are listed. Elemental analyses were carried out by "Mikroanalytisches Laboratorium der Fakultät für Chemie, Universität Bielefeld" (Bielefeld, Germany). (2,4,6-Tri-*tert*-butylphenyl)lithium,[10] potassium (pentamethylcyclopentadienyl)dicarbonylferrate, and potassium (cyclopentadienyl)dicarbonylferrate were prepared in analogy to literature procedures.[11]

(2,4,6-Tri-*tert*-butylphenyl)chlorogermylene (2). A solution of (2,4,6-tri-*tert*-butylphenyl)lithium (6.17 g, 24.4 mmol) in 30 mL of THF, freshly prepared at −80 °C, was added very slowly to a solution of 1 (5.66 g, 24.4 mmol) in 50 mL of THF at −80 °C. The reaction mixture was warmed to −10 °C. At this temperature the solvents were removed in vacuo, followed by extraction of the orange residue with 60 mL of hexane. Filtering and cooling the hexane solution to −70 °C yielded 3.69 g (43%) of pale yellow crystals, mp 56 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.36 (s, 2 H, $\mathrm{C_6}\mathit{H}_2{}^t\mathrm{Bu_3}$), 1.34 (s, 18 H, 2,6-$\mathrm{C(C}\mathit{H}_3)_3$), 1.27 (s, 9 H, 4-$\mathrm{C(C}\mathit{H}_3)_3$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 157.5 (s, 1-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 156.1 (s, 2,6-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 150.8 (s, 4-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 122.3 (s, 3,5-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 39.9 (s, 2,6-$\mathit{C}\mathrm{(CH_3)_3}$), 34.8 (s, 4-$\mathit{C}\mathrm{(CH_3)_3}$), 34.6 (s, 2,6-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 31.3 (s, 4-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$). Anal. Calcd for $\mathrm{C_{18}H_{29}GeCl}$: C, 61.16; H, 8.27; Cl, 10.03. Found: C, 61.10; H, 8.18; Cl, 10.4.

[(Pentamethylcyclopentadienyl)dicarbonylferrio](2,4,6-tri-*tert*-butylphenyl)germylene (4). A solution of 2 (1.42 g, 4.02 mmol) in 30 mL of pentane was added quickly to a suspension of potassium (pentamethylcyclopentadienyl)dicarbonylferrate (1.15 g, 4.02 mmol) in 30 mL of pentane at −60 °C. The reaction mixture was warmed to room temperature and was stirred overnight. Removal of KCl by filtration and cooling to −70 °C yielded 0.91 g (40%) of dark red crystals mp 161 °C.[12] ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.50 (s, 2 H, $\mathrm{C_6}\mathit{H}_2{}^t\mathrm{Bu_3}$), 1.54 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.40 (s, 18 H, 2,6-$\mathrm{C(C}\mathit{H}_3)_3$), 1.37 (s, 9 H, 4-$\mathrm{C(C}\mathit{H}_3)_3$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 218.0 (s, CO), 164.0 (s, 1-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 153.2 (s, 2,6-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 148.8 (s, 4-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 122.1 (s, 3,5-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 95.9 (s, $\mathit{C}_5\mathrm{(CH_3)_5}$), 40.4 (s, 2,6-$\mathit{C}\mathrm{(CH_3)_3}$), 34.7 (s, 4-$\mathit{C}\mathrm{(CH_3)_3}$), 31.6 (s, 2,6-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 31.5 (s, 4-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 9.3 (s, $\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$). MS (*m/z* (relative intensity)): 566 ($\mathrm{M^+}$, 4), 538 ($\mathrm{M^+ - CO}$, 49), 319 ($^t\mathrm{Bu_3C_6H_2Ge^+}$, 53), 247 ($\mathrm{Cp^*Fe(CO)_2{}^+}$, 21), 219 ($\mathrm{Cp^*Fe(CO)^+}$, 30), 191 ($\mathrm{Cp^*Fe^+}$, 65), 57 ($\mathrm{Me_3C^+}$, 100). IR (hexane): ν 1969, 1920 cm^{-1} (CO). Anal. Calcd for $\mathrm{C_{30}H_{44}O_2GeFe}$: C, 63.76; H, 7.85. Found: C, 63.84; H, 7.85.

[(Cyclopentadienyl)dicarbonylferrio](2,4,6-tri-*tert*-butylphenyl)germylene (5). A solution of 2 (0.67 g, 1.90 mmol in 20 mL of pentane was added quickly to a suspension of potassium (cyclopentadienyl)dicarbonylferrate (0.41 g, 1.90 mmol) in 30 mL of pentane at −60 °C. The reaction mixture was warmed to room temperature and was stirred overnight. After the solvent was removed in vacuo, the green residue was extracted with 30 mL of toluene. Filtering and cooling to −70 °C yielded 0.18 g (19%) of a dark green powder.[13] ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.46 (s, 2 H, $\mathrm{C_6}\mathit{H}_2{}^t\mathrm{Bu_3}$), 4.15 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 1.38 (s, 9 H, 4-$\mathrm{C(C}\mathit{H}_3)_3$), 1.27 (s, 18 H, 2,6-$\mathrm{C(C}\mathit{H}_3)_3$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 216.2 (s, CO), 165.4 (s, 1-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 153.3 (s, 2,6-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 149.2 (s, 4-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 122.4 (s, 3,5-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_3}$), 85.9 (s, $\mathit{C}_5\mathrm{H_5}$), 40.0 (s, 2,6-$\mathit{C}\mathrm{(CH_3)_3}$), 34.7 (s, 4-$\mathit{C}\mathrm{(CH_3)_3}$), 34.1 (s, 4-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 31.5 (s, 2,6-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$). IR (THF): ν 2004, 1950 cm^{-1} (CO).

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(8) (a) Species of the type $[\mathrm{(CO)_4Co]GeY}$ (Y = F, $\mathrm{Co(CO)_4}$) were shown to be reactive intermediates and thus have been characterized only by trapping reactions: Castel, A.; Rivière, P.; Satgé, J.; Moreau, J. J. E.; Corriu, R. J. P. *Organometallics* **1983**, *2*, 1498. (b) $\mathrm{Cp(CO)_2Fe{-}GeCH(SiMe_3)_2}$ has been synthesized according to $\mathrm{Cp^*GeCH(SiMe_3)_2 + Cp(CO)_2FeNa \rightarrow Cp(CO)_2Fe{-}GeCH(SiMe_3)_2 + Cp^*Na}$ and was isolated in the form of deep blue crystals, mp 80–85 °C dec. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 4.46 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 2.53 (s, 1 H, $\mathrm{C}\mathit{H}\mathrm{(Si(CH_3)_3)_2}$), 0.45 (s, 18 H, $\mathrm{CH(Si(C}\mathit{H}_3)_3)_2$). ^{13}C NMR (THF-$d_8$): δ 217.5 (s, CO), 86.0 (s, $\mathit{C}_5\mathrm{H_5}$), 30.8 (s, $\mathit{C}\mathrm{H(Si(CH_3)_3)_2}$), 3.7 (s, $\mathrm{CH(Si(}\mathit{C}\mathrm{H_3)_3)_2}$. IR (hexane): ν 2010, 1989 cm^{-1} (CO). Anal. Calcd for $\mathrm{C_{14}H_{24}O_2Si_2FeGe}$: C, 41.12; H, 5.92. Found: C, 41.23; H, 5.74. Becker, A. Thesis, Universität Bielefeld, 1990.

(9) The insertion product was obtained by heating a solution of 4 in toluene to 100 °C for 1 h. ^{1}H NMR (toluene-d_8): δ 7.56, 7.39 (2 d, 2 × 1H, $^4J_{\mathrm{HH}} = 1.9$ Hz, $\mathrm{C_6}\mathit{H}_2{}^t\mathrm{Bu_2R}$), 5.06 (pseudo t, 1H, Ge–*H*), 1.89–1.74 (AB part of an ABX spin system, 2H, 2-$\mathrm{C(CH_3)_2C}\mathit{H}_2$), 1.66 (s, 9H, 6-$\mathrm{C(C}\mathit{H}_3)_3$), 1.60, 1.56 (2 s, 2 × 3H, 2-$\mathrm{C(C}\mathit{H}_3)_2\mathrm{CH_2}$), 1.52 (s, 15H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.36 (s, 9H, 4-$\mathrm{C(C}\mathit{H}_3)_3$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 218.80, 218.16 (2 s, CO), 159.96, 155.18, 150.77 (3 s, 2,4,6-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2R}$), 137.91 (s, 1-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2R}$), 121.30, 118.72 (2 s, 3,5-$\mathit{C}_6\mathrm{H_2}{}^t\mathrm{Bu_2R}$), 94.68 (s, $\mathit{C}_5\mathrm{(CH_3)_5}$), 44.95 (s, 2-$\mathit{C}\mathrm{(CH_3)_2CH_2}$), 37.90 (s, 6-$\mathit{C}\mathrm{(CH_3)_3}$), 34.91 (s, 4-$\mathit{C}\mathrm{(CH_3)_3}$), 34.63, 34.03 (2 s, 2-$\mathrm{C(}\mathit{C}\mathrm{H_3)_2CH_2}$), 33.38 (s, 2-$\mathrm{C(CH_3)_2}\mathit{C}\mathrm{H_2}$), 33.09, 31.67 (2 s, 4,6-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 9.53 (s, $\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$). IR (hexane): ν 1991, 1942 (CO), 1930 cm^{-1} (Ge–H).

(10) (a) Yoshifuji, M.; Shima, I.; Inamoto, N. *Tetrahedron Lett.* **1979**, 3963. (b) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.

(11) Cathelyne, D.; Astruc, D. *J. Organomet. Chem.* **1982**, *226*, C52.

(12) Melting point of the C–H insertion product.[9]

(13) Due to the unsatisfactory crystallization behavior, 5 could not be obtained free from traces of impurities.