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MOLECULAR REARRANGEMENT OF $Me_5C_5(Cl)Ge \rightarrow W(CO)_5$

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Summary

The complex $Me_5C_5(Cl)Ge \rightarrow W(CO)_5$ (I), which has a fairly low thermal stability, was prepared by treatment of the ylide complex $(THF)Cl_2Ge \rightarrow W(CO)_5$ with a Me_5C_5 donor, and has been found to undergo a molecular rearrangement. The complex cannot be prepared directly by irradiation of $W(CO)_6$ in the presence of Me_5C_5GeCl in an inert solvent, and attempts to prepare it in this way yield the ionic species $Me_5C_5Ge^+\ Cl_3Ge \rightarrow W(CO)_5]^-$ (III), as does its thermal decomposition. Studies of the formation of III and independent syntheses are described.

Introduction

The synthesis of carbene-analogous complexes of heavier IVB elements such as $R_2El \rightarrow M(CO)_5$ ($R = (Me_3Si)_2CH$, $(Me_3Si)_2N$; El = Ge, Sn; M = Cr, Mo, W) has been carried out by Lappert and co-workers by irradiation of hexacarbonyl-chromium, -molybdenum and -tungsten in the presence of the appropriate free carbene-homologue [1–4]. In contrast, attempts to bring about the complexation of cyclopentadienyl-substituted subvalent Group IVB species were unsuccessful [5]. The identities of the adducts from $(C_5H_5)_2Sn$ and $(MeC_5H_4)_2Sn$ with transition metal Lewis acids described in the literature [6,7] must be questioned.

The first cyclopentadienyl substituted carbene-analogous Group IVB complexes, whose identities were established beyond doubt were those of the type $Me_5C_5(Cl)$-$El \rightarrow M(CO)_5$ (El = Ge, Sn; M = Cr, W) [5]. The complexes, however, are only accessible by a synthetic detour, by treatment of the ylide complexes $(THF)Cl_2$-$El \rightarrow M(CO)_5$ [8,9] with Me_5C_5 donors. Of such complexes the structure of the title compound, $Me_5C_5(Cl)Ge \rightarrow W(CO)_5$ (I), and that of a substituted derivative $Me_5C_5[(Me_3Si)_2CH]Ge \rightarrow W(CO)_5$ [10] have been determined by X-ray crystallography. The chloro(pentamethylcyclopentadienyl)-substituted complexes of the heavier Group IVB elements are not very stable thermally, decomposing extensively within a short time at room temperature. The NMR spectra of $Me_5C_5(Cl)Ge \rightarrow W(CO)_5$ (I), which is the least sensitive complex, show additional peaks after a few hours;

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TABLE 1

NMR DATA[a] OF $\mathrm{Me_5C_5}$ SUBSTITUTED GERMANIUM(II) COMPOUNDS

(The NMR pattern described for the decomposition of I was observed previously in attempts to prepare the complex I directly by irradiation of $\mathrm{W(CO)_6}$ in the presence of $\mathrm{Me_5C_5GeCl}$ [15].)

	$\mathrm{(Me_5C_5)_2Ge}$ [b]	$\mathrm{Me_5C_5GeCl}$ [c]	$\mathrm{Me_5C_5GeCl \downarrow W(CO)_5}$ (I)	$\mathrm{Me_5C_5Ge^+}$ $\mathrm{AlCl_4^-}$ [14]	Decomposed I
^{1}H NMR (δ, ppm)	1.96	2.00	2.10	2.18	2.19
^{13}C NMR (δ, ppm)					
$\mathit{Me}_5\mathrm{C}_5$	9.84	9.59	11.28	9.36	9.40
$\mathrm{Me}_5\mathit{C}_5$	118.16	120.31	127.05	122.16	121.71

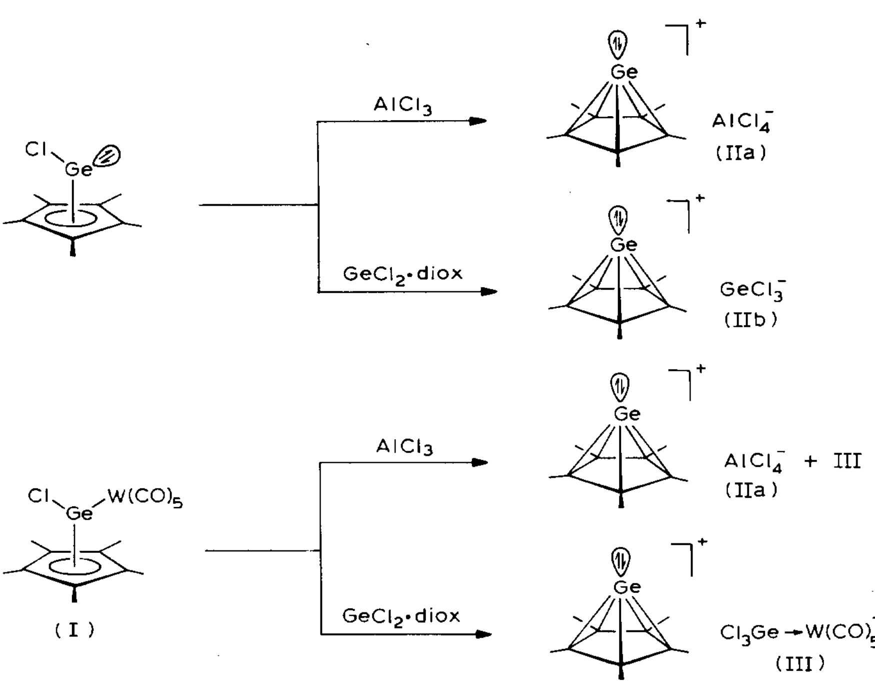
[a] Conditions are given in the experimental section. [b] Prepared as described in ref. 12. [c] Prepared as described in ref. 13.

however only four new signals were observed, and as they were very sharp the decomposition was concluded to involve only thermal rearrangement of the molecule. From comparison of ^{1}H and ^{13}C NMR data we considered the possibility of the presence of the cluster cation $\mathrm{Me_5C_5Ge^+}$ [5] (Table 1). The ^{13}C NMR spectra in the CO region show a peak for $\mathrm{W(CO)_6}$ at δ 191.16 ppm (cf. 191.0 ppm [11]), but also a peak at 196.78 ppm which did not correspond with either of those for $\mathrm{[ClW(CO)_5]^-}$ (δ 198.7 and 201.6 ppm [11]).

Results and discussion

Halogen abstraction from $\mathrm{Me_5C_5GeCl}$ with aluminum trichloride and also with germanium dichloride · dioxane gave rise to the ionic species $\mathrm{Me_5C_5Ge^+}$ $\mathrm{AlCl_4^-}$ (IIa) and $\mathrm{Me_5C_5Ge^+}$ $\mathrm{GeCl_3^-}$ (IIb), respectively [14] (Scheme 1). Upon treatment of the $\mathrm{W(CO)_5}$ complex of $\mathrm{Me_5C_5GeCl}$ with aluminum trichloride the Ge–Cl bond of the complex was broken, to yield mainly the tetrachloroaluminate species IIa; the pentacarbonyl tungsten complex III was isolated as a by-product, indicating the occurrence of ligand exchange between aluminum and germanium. The action of germanium dichloride dioxane on I, however, is not accompanied by loss of tungsten carbonyl, and gives only compound III, in which the anion $\mathrm{GeCl_3^-}$ acts as a ligand towards the $\mathrm{W(CO)_5}$ fragment [16].

The pentacarbonyl(trichlorogermyl)tungstate species III was also obtained directly by irradiation of hexacarbonyltungsten in the presence of (pentamethylcyclopentadienyl)germanium trichlorogermanate in dichloromethane, while treatment of the tetrafluoroborate or the tetrachloroaluminate complex resulted in decomposition; it should be noted, however, that in the case of the tetrachloroaluminate species the formation of small amounts of the complex III was detected spectroscopically. Compound III was prepared efficiently from the ylide complex $\mathrm{(THF)Cl_2Ge{\rightarrow}W(CO)_5}$ and (pentamethylcyclopentadienyl)germanium chloride. Finally we found that III can also be obtained by irradiation of hexacarbonyltungsten in the presence of



SCHEME 1

(pentamethylcyclopentadienyl)germanium chloride:

$$Me_5C_5Ge^+GeCl_3^- + W(CO)_6 \xrightarrow[-CO]{h\nu \text{ in } CH_2Cl_2} III$$

$$(THF)Cl_2Ge \rightarrow W(CO)_5 + Me_5C_5GeCl \xrightarrow[-THF]{} III$$

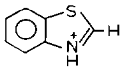
$$Me_5C_5GeCl + W(CO)_6 \xrightarrow[-CO]{h\nu \text{ in } (H)} III + \cdots$$

Compound III was obtained as pale yellow cubes, m.p. 109°C, soluble in polar solvents such as dichloromethane, trichloromethane and acetonitrile and also in benzene. In all cases the composition of the product was confirmed by elemental analyses and spectroscopic data (see Experimental). To confirm that it is not the $Me_5C_5Ge^+$ cation but the $GeCl_3^-$ anion which is complexed by $W(CO)_5$, the NMR data for III were compared with those for the separate components in (pentamethylcyclopentadienyl)germanium tetrafluoroborate, tetrachloroaluminate and trichlorogermanate, respectively, in tetramethylammonium and benzothiazolium pentacarbonyl(trichlorogermyl)tungstate (Table 2). Also the IR spectra of free $GeCl_3^-$ and the complexed species $Cl_3Ge \rightarrow W(CO)_5]^-$ differ significantly in the range of the ν(GeCl) vibrations. The ^{13}C NMR spectra (in $CDCl_3$) of the complexed anion show a strong signal at δ 197.0 ppm and an additional weak one at 201.0 ppm corresponding to the *trans* CO group (see Experimental).

Though III could not be isolated from the thermal decomposition of the complex

TABLE 2

NMR DATA FOR COMPARISON

	$Me_5C_5Ge^+$ BF_4^- [14]	$Me_5C_5Ge^+$ $AlCl_4^-$ [14]	$Me_5C_5Ge^+$ $GeCl_3^-$ [14]	Me_4N^+ $Cl_3Ge \rightarrow W(CO)_5^-$ (in CD_3CN) [a]	 [b] $Cl_3Ge \rightarrow W(CO)_5^-$
^1H NMR (δ, ppm) Me_5C_5	2.15	2.18	2.12	–	–
^{13}C NMR (δ, ppm)					
Me_5C_5	8.90	9.36	9.48	–	–
$Me_5\mathit{C}_5$	121.56	122.16	121.29	–	–
$W(CO)_5$	–	–	–	198.59 202.96	197.05 201.05

[a] Prepared as described in ref. 9. [b] Prepared as given in ref. 18.

$Me_5C_5(Cl)Ge \rightarrow W(CO)_5$ (I), its presence was confirmed by spectroscopy. Thus the basic reaction involved in the decomposition of I must be formulated as follows:

$$Me_5C_5(Cl)Ge \rightarrow W(CO)_5 \xrightarrow{O} Me_5C_5Ge^+\left[Cl_3Ge \rightarrow W(CO)_5\right]^- + W(CO)_6 + \cdots\cdot\cdot$$

No direct evidence for the formation of decamethylgermanocene $(Me_5C_5)_2Ge$ as a by-product was obtained, but the presence of small amounts of it would not be inconsistent with the NMR data, since decamethylgermanocene was shown to undergo exchange reactions with the cluster cation $Me_5C_5Ge^+$ and therefore not to give separate NMR signals [17]. A rearrangement of I into $Me_5C_5Ge^+$ $[ClW(CO)_5]^-$, however, can be ruled out, since NMR spectra did not show the corresponding CO peaks but did show the presence of $W(CO)_6$, which is not consistent with such a simple rearrangement. Finally the nature of the reactions indicates that the cluster cation $Me_5C_5Ge^+$ possesses no nucleophilic activity towards the $W(CO)_5$ fragment.

Experimental

All reactions were performed under dried, oxygen-free argon using Schlenk type flasks. Solvents and reagents were dried and purified by standard methods. Melting-points were measured using a Büchi 510 capillary melting point apparatus. ^1H NMR spectra were recorded on a Bruker AM 300 (300 MHz); ^{13}C NMR spectra with a Bruker AM 300 (75 MHz), ^1H decoupled , spectra were recorded in $CDCl_3$ unless otherwise stated. IR spectra were recorded on a Perkin-Elmer 598 infrared spectrometer; ν(CO) (CH_2Cl_2), KBr windows; ν(GeCl): Nujol mull, TlBr windows. Elemental analyses were performed by "Mikroanalytisches Laboratorium Beller" (Göttingen) and the analytical laboratory of the Universität Bielefeld. Cl analyses were obtained by use of the Schöninger method.

Preparation of pentamethylcyclopentadienylgermanium tetrachloroaluminate (IIa) and pentamethylcyclopentadienylgermanium pentacarbonyl(trichlorogermyl)tungstate (III) from pentacarbonyl[chloro(pentamethylcyclopentadienyl)germylene]tungsten(0) (I) and aluminum trichloride

Freshly sublimed $AlCl_3$ (0.33 g, 2.47 mmol) was added to a cooled solution of

1.40 g of I (2.47 mmol) in 30 ml of benzene. The mixture was stirred for 30 min, during which the yellow color deepened to orange and a red oil separated. The oil was extracted with 5 ml of dichloromethane and the solution was covered with a layer of 20 ml of hexane. Cooling to 4°C yielded 450 mg (48%) yellow rhombic crystals of IIa, m.p. 154°C (dec.). ^{1}H NMR: δ 2.18 (s) ppm. ^{13}C NMR: δ 9.38 ($\mathit{Me}_5\mathrm{C}_5$), 122.05 ($\mathrm{Me}_5\mathit{C}_5$) ppm. Anal. Found: C, 30.92; H, 4.21; Cl, 36.3. $C_{10}H_{15}AlCl_4Ge$ (376.62) calcd.: C, 31.89; H, 4.01; Cl, 37.65%.

Evaporation of the benzene layer in vacuo, extraction of the residue with 5 ml of dichloromethane, followed by concentration and cooling to -80°C yielded 370 mg (21%) of pale yellow crystals of III, m.p. 109°C. ^{1}H NMR: δ 2.18 (s) ppm; ^{13}C NMR: δ 9.36 ($\mathit{Me}_5\mathrm{C}_5$), 122.02 ($\mathrm{Me}_5\mathit{C}_5$), 196.88 ($\mathrm{CO}_{cis}$), 200.97 ($\mathrm{CO}_{trans}$) ppm. IR ν(CO): 2063 (m), 1970 (m), 1930 (vs) cm^{-1}; IR ν(Ge–Cl): 385 (m), 352 (m), 332 (m) cm^{-1}. Anal. Found: C, 24.85; H, 2.07; Cl, 14.2. $C_{15}H_{15}Cl_3Ge_2O_5W$ (710.67) calcd.: C, 25.35; H, 2.13; Cl, 14.97%.

Preparation of III from pentacarbonyl[chloro(pentamethylcyclopentadienyl)germylene]-tungsten(0) (I) and germanium dichloride · dioxane

0.46 g of crystalline $GeCl_2 \cdot C_4H_8O_2$ (1.99 mmol) were added to a solution of 1.12 g of I (1.97 mmol) in 20 ml of benzene. The mixture was stirred for 3 h at room temperature and the crystals of $GeCl_2 \cdot C_4H_8O_2$ slowly dissolved. After evaporation of the solvent in vacuo the orange residue was extracted with dichloromethane. Concentration of the solution in vacuo and cooling to -80°C yielded 1.14 g (81%) of pale yellow crystals, m.p. 109°C. ^{1}H NMR: δ 2.19 (s) ppm; ^{13}C NMR: δ 9.35 ($\mathit{Me}_5\mathrm{C}_5$), 122.03 ($\mathrm{Me}_5\mathit{C}_5$), 196.92 ($\mathrm{CO}_{cis}$), 200.93 ($\mathrm{CO}_{trans}$) ppm. IR ν(CO): 2063 (m), 1970 (m), 1930 (vs) cm^{-1}; IR ν(Ge–Cl): 385 (m), 352 (m), 332 (m) cm^{-1}. Anal. Found: C, 24.93; H, 2.45; Cl, 15.0%.

Preparation of III from irradiation of hexacarbonyltungsten in the presence of (pentamethylcyclopentadienyl)germanium trichlorogermanate

A solution of 1.84 g (pentamethylcyclopentadienyl)germanium trichlorogermanate (6.42 mmol) and 2.26 g hexacarbonyltungsten (6.42 mmol) in 150 ml of dichloromethane was irradiated for 45 min, during which the pale yellow color of the solution deepened to orange. Concentration of the solution in vacuo and cooling to -20°C yielded 3.21 g (70%) of pale yellow crystals, m.p. 109°C. ^{1}H NMR: δ 2.19 (s) ppm; ^{13}C NMR: δ 9.37 ($\mathit{Me}_5\mathrm{C}_5$), 122.07 ($\mathrm{Me}_5\mathit{C}_5$), 196.94 ($\mathrm{CO}_{cis}$), 200.97 ($\mathrm{CO}_{trans}$) ppm. IR ν(CO): 2063 (m), 1970 (m), 1930 (vs) cm^{-1}; IR ν(Ge–Cl): 385 (m), 352 (m), 332 (m) cm^{-1}. Anal. Found: C, 25.16; H, 2.25; Cl, 14.9%.

Preparation of III from pentacarbonyl[dichloro(tetrahydrofuran)germyl]tungsten(0) with (pentamethylcyclopentadienyl)germanium chloride

A solution of 1.33 g Me_5C_5GeCl (5.47 mmol) in 20 ml of dichloromethane was slowly added to a solution of 2.95 g $Cl_2(THF)Ge \rightarrow W(CO)_5$ (5.47 mmol) in 20 ml of dichloromethane. The mixture was stirred for 2 h at room temperature, during which the light yellow color deepened to orange. Concentration of the solution in vacuo and cooling to -80°C yielded 3.45 g (89%) of pale yellow crystals. ^{1}H NMR: δ 2.19 (s) ppm; ^{13}C NMR: δ 9.35 ($\mathit{Me}_5\mathrm{C}_5$), 122.00 ($\mathrm{Me}_5\mathit{C}_5$), 196.73 ($\mathrm{CO}_{cis}$), 200.80 ($\mathrm{CO}_{trans}$) ppm; ^{13}C NMR ($CD_3CN$): δ 9.31 ($\mathit{Me}_5\mathrm{C}_5$), 118.22 ($\mathrm{Me}_5\mathit{C}_5$), 198.56 ($\mathrm{CO}_{cis}$), 202.95 ($\mathrm{CO}_{trans}$) ppm. IR ν(CO): 2063 (m), 1970 (m), 1930 (vs) cm^{-1}; IR

ν(Ge–Cl): 385 (m), 352 (m), 332 (m) cm^{-1}. Anal. Found: C, 25.26; H, 2.03; Cl, 14.7%.

Preparation of III from irradiation of hexacarbonyltungsten in the presence of (pentamethylcyclopentadienyl)germanium chloride

A solution of 1.47 g (pentamethylcyclopentadienyl)germanium chloride (6.04 mmol) and 2.12 g hexacarbonyltungsten (6.04 mmol) in 150 ml of methylcyclohexane was irradiated for 45 min, during which a pale yellow material crystallized out. Recrystallisation from dichloromethane yielded 1.13 g (79%, basing on chlorine) of pale yellow crystals, m.p. 109°C. ^{1}H NMR: δ 2.19 (s) ppm; ^{13}C NMR: δ 9.36 (Me_5C_5), 121.99 ($Me_5\mathit{C}_5$), 196.90 (CO_{cis}), 200.95 (CO_{trans}) ppm. IR ν(CO): 2063 (m), 1970 (m), 1930 (vs) cm^{-1}; IR ν(Ge–Cl): 385 (m), 352 (m), 332 (m) cm^{-1}. Anal. Found: C, 25.68; H, 2.60; Cl, 14.7%.

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