

TRANSITION METAL COMPLEXES OF CYCLOPENTADIENYLGERMYLENES; THE X-RAY STRUCTURE OF $(\text{Me}_5\text{C}_5)[(\text{Me}_3\text{Si})_2\text{CH}]\text{Ge}\rightarrow\text{W}(\text{CO})_5$

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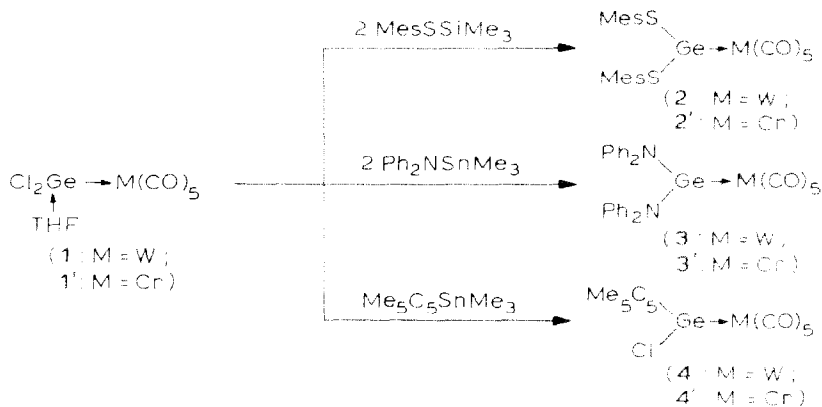
Summary

Pentacarbonyl[chloro(pentamethylcyclopentadienyl)germylene]tungsten, $\text{Me}_5\text{C}_5\text{-(Cl)Ge}\rightarrow\text{W}(\text{CO})_5$ (**4**), the first germylene complex containing a cyclopentadienyl ligand bound to germanium, has been shown to react with nucleophiles. On treatment with lithium mesitylthiolate or mesitylthiotrimethylsilane displacements of both the chlorine and the cyclopentadienyl ligand occur and selective replacement of the chlorine alone could not be achieved. In contrast, treatment of **4** with lithium bistrimethylsilylamide, bis(trimethylsilyl)methyl lithium and methyl lithium yields the cyclopentadienyl containing germylene complexes $\text{Me}_5\text{C}_5(\text{R})\text{Ge}\rightarrow\text{W}(\text{CO})_5$ (**5**: $\text{R} = (\text{Me}_3\text{Si})_2\text{N}$; **6**: $\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$; **7**: $\text{R} = \text{Me}$) as extremely air-sensitive orange crystals. An X-ray crystal structural investigation of **6** reveals the same dihapto bonding of the cyclopentadienyl ring as was found for **4**, suggesting that the electron deficiency at the Ge-center is mainly satisfied by acceptance of π -electron density from the cyclopentadienyl system. Crystals of **6** are orthorhombic, space group *Pnam* with *a* 19.211(5), *b* 9.782(1), *c* 14.938(5) Å, *Z* = 4, and the structure has been refined to *R* and *R_w* values of 0.040 and 0.042, respectively, for 2021 observed/2571 measured reflections. The Ge–W bond length is 2.632(4) Å, 0.06 Å longer than in the analogous chloride, **4**.

Introduction

Although analogous carbene complexes of the type $\text{R}_2\text{Ge}\rightarrow\text{M}(\text{CO})_5$ ($\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$, $(\text{Me}_3\text{Si})_2\text{N}$; $\text{M} = \text{Cr}$, W) are directly available [1] from irradiation of hexacarbonylchromium and -tungsten in the presence of the germylene, attempts to make related complexes from cyclopentadienyl-substituted germylenes failed [2]. An

alternative synthetic approach makes use of an existing germanium-transition element bond in ylide complexes, $\text{Cl}_2(\text{THF})\text{Ge} \rightarrow \text{M}(\text{CO})_5$ (**1**: M = W; **1'**: M = Cr) [3]. Previous investigations have indicated that in nucleophilic substitutions of such complexes loss of the additional coordinated THF can occur, so that gerymlene complexes are obtained [4,5]. While treatment of the ylides **1**, **1'** with mesitylthiotrimethylsilane and diphenylaminotrimethylstannane leads to disubstituted gerymlene species (**2**, **2'**, **3**, **3'**), reaction with pentamethylcyclopentadienyl-trimethylstannane yields monoalkylated compounds [2].

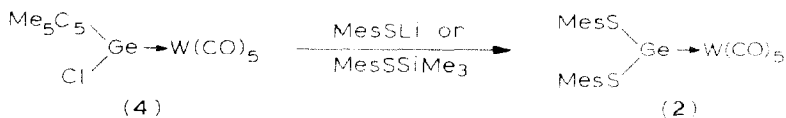


(Mes = 2,4,6-Me₃C₆H₂, Ph = C₆H₅)

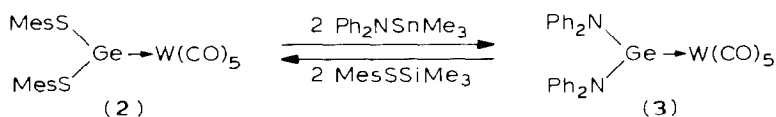
Pentacarbonyl[chloro(pentamethylcyclopentadienyl)germylene]tungsten (**4**) and -chromium (**4'**) are the first gerymlene complexes containing a cyclopentadienyl ligand. The cyclopentadienyl ligands in **4** and **4'** affect the nature of the transition metal-germanium bond, presumably because they can remove the electronic deficiency at the germanium and thus reduce the back donation by the transition metal. This assumption is confirmed by X-ray structural studies on compound **4** [2], which reveal the dihapto character of the cyclopentadienyl-germanium bonding.

Results

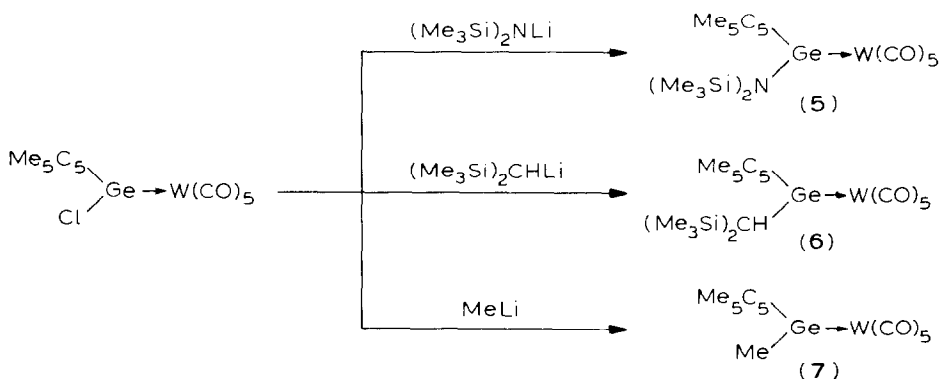
Attempts to prepare a transition metal complex of a germylene species by further alkylation of **4** with pentamethylcyclopentadienyl or cyclopentadienyl alkali metal compounds (Li, Na, K) were unsuccessful. Nevertheless, complex **4** is reactive towards other nucleophiles. Reactions with lithium mesitylthiolate or mesitylthiotrimethylsilane yielded the known dimesitylthio-germylene-complex **2** even when stoichiometric amounts of the reagents were used. The reaction with mesitylthiotrimethylsilane required about 90 h.



The replacement of both ligands in gerymlene complexes has already been studied, and the exchange reactions shown below involving the mesitylthio and the diphenyl-amino substituents have been described [4].



In contrast, selective substitution of only the chlorine takes place on reaction of the chloro(pentamethylcyclopentadienyl)germylene-complex **4** with lithium bistrimethylsilylamide. Alkylation reactions using bis(trimethylsilyl)methyl lithium and methyl lithium also proceed as expected, so that chlorine substitution appears to offer a suitable approach to complexes containing a cyclopentadienyl group and another substituent.



The silylated compounds **5** and **6** readily crystallize from diethyl ether as bright yellow to orange prisms, while **7** separates from methylcyclohexane as orange

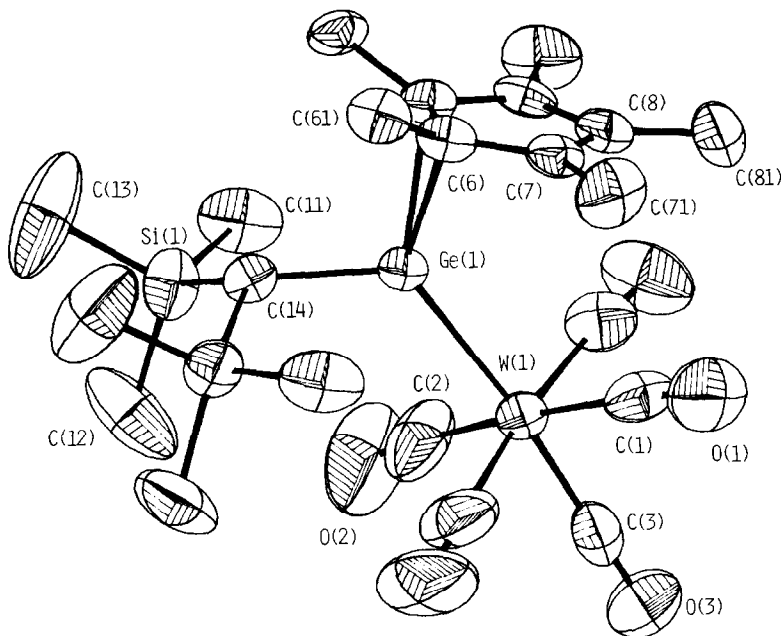


Fig. 1. Molecular structure of compound **6**.

TABLE 1

BOND LENGTHS (Å) FOR $(\text{Me}_3\text{C}_2)(\text{Me}_3\text{Si})_2\text{CH}[\text{Ge} \rightarrow \text{W}(\text{CO})_6]$

Ge(1)-W(1)	2.632(4)	C(1)-W(1)	2.019(13)
C(2)-W(1)	2.010(14)	C(3)-W(1)	1.956(17)
C(14)-Ge(1)	1.987(13)	C(6)-Ge(1)	2.194(9)
C(11)-Si(1)	1.858(13)	C(12)-Si(1)	1.867(15)
C(13)-Si(1)	1.873(13)	C(14)-Si(1)	1.890(8)
O(1)-C(1)	1.128(12)	O(2)-C(2)	1.166(14)
O(3)-C(3)	1.168(18)	C(6)-C(6)	1.513(12)
C(7)-C(6)	1.410(12)	C(6)-C(6a)	1.473(15)
C(7)-C(7)	1.535(13)	C(8)-C(7)	1.426(11)
C(8)-C(8)	1.520(19)		

Key to symmetry operations relating designated atoms to reference atoms

a) $(-x, y, z)$ b) $(x, y, 0.5 - z)$

needles. The extremely air-sensitive compounds are soluble in benzene, ether, di- and trichloromethane. The identities of the compounds were confirmed by analytical and spectroscopic data. Interestingly, the NMR spectra reveal the presence of equivalent methyl groups and ring carbon atoms for the pentamethylcyclopentadienyl systems even at -60°C .

The structure of **6** was investigated by X-ray crystallography. The structure is shown in Fig. 1 and bond lengths and angles are given in Tables 1 and 2. The structure is analogous to that found for **4**, and has crystallographic mirror symmetry (through W, Ge and the bonded carbon of the alkyl, and bisecting pairs of "equatorial" CO bonds), with the dihapto Me_3C_2 ligand oriented so that the unbonded C_3 fragment is distal to the alkyl carbon (or the chlorine in complex **4**). This presumably avoids steric repulsions involving the C or Cl atoms.

The structural parameters for this alkyl complex show some small but significant differences from those for the chloro complex **4**, and these probably reflect changes

TABLE 2

BOND ANGLES (deg.) FOR $(\text{Me}_3\text{C}_2)(\text{Me}_3\text{Si})_2\text{CH}[\text{Ge} \rightarrow \text{W}(\text{CO})_6]$

C(1)-W(1)-Ge(1)	95.4(4)	C(2)-W(1)-Ge(1)	90.4(4)
C(2)-W(1)-C(1)	173.3(4)	C(3)-W(1)-Ge(1)	174.2(4)
C(3)-W(1)-C(1)	88.8(5)	C(3)-W(1)-C(2)	85.6(5)
C(14)-Ge(1)-W(1)	126.1(4)	C(6)-Ge(1)-W(1)	128.4(3)
C(6)-Ge(1)-C(14)	101.8(5)	C(12)-Si(1)-C(11)	106.2(6)
C(13)-Si(1)-C(11)	108.2(8)	C(13)-Si(1)-C(12)	106.3(9)
C(14)-Si(1)-C(11)	111.6(5)	C(14)-Si(1)-C(12)	117.8(7)
C(14)-Si(1)-C(13)	106.6(6)	Si(1)-C(14)-Si(1a)	117.1(7)
O(1)-C(1)-W(1)	173.7(8)	C(1)-W(1)-C(1a)	86.8(7)
O(2)-C(2)-W(1)	176.2(10)	C(2)-W(1)-C(2a)	93.9(9)
O(3)-C(3)-W(1)	177.9(12)	Si(1)-C(14)-Ge(1)	113.8(4)
C(6)-C(6)-Ge(1)	118.3(6)	C(7)-C(6)-Ge(1)	100.9(6)
C(7)-C(6)-C(6)	122.8(8)	C(6)-Ge(1)-C(6a)	39.2(4)
C(7)-C(7)-C(6)	123.7(9)	C(8)-C(7)-C(6)	109.7(8)
C(8)-C(7)-C(7)	126.8(9)	C(7)-C(8)-C(7a)	106.9(11)
C(8)-C(8)-C(7)	126.5(6)	C(7)-C(6)-C(6a)	106.9(11)

arising from the replacement of the electron-withdrawing chlorine by the electron-releasing and bulky alkyl ligand. Thus, the W–Ge bond is 0.06 Å longer in the alkyl derivative, suggesting a weakening due to reduction in W \rightarrow Ge π -back-bonding. Similarly the W–C(carbonyl) distances in the alkyl complex are shorter than in the chloride, indicating enhanced W \rightarrow CO back-bonding. Otherwise, related parameters show very similar features, including an indication that the dihapto bonding of Me₅C₅ produces a lengthening of the ring C–C bond (C(6)–C(6a) in this case) involving the bonded carbons.

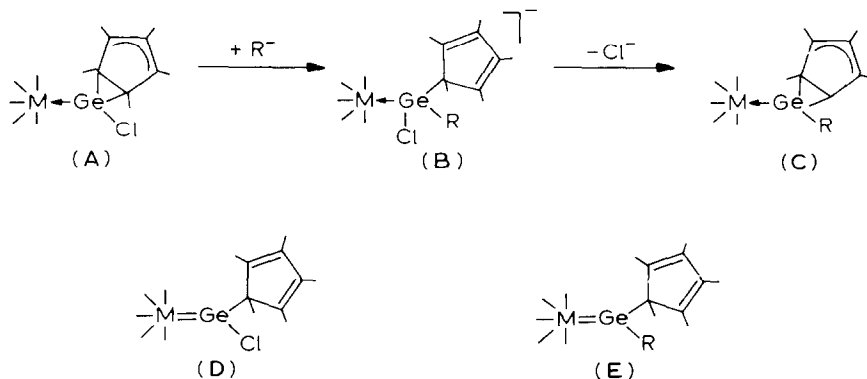
Discussion

The solid state structures of **4** and **6** suggest that electron donation resulting from cyclopentadienyl ligation in germylene complexes weakens the transition metal–germanium interaction. The involvement of π -electron density of the cyclopentadienyl system leads to an increase of the hapticity, resulting in a η^2 -coordination, as portrayed in **A** and **C**.

The ¹H and ¹³C NMR spectra show that complexes **4–7** are highly fluxional in solution. The structure **D** and **E** may represent the monohapto-transition states in the rearrangement process.

The substitution reaction in cyclopentadienylgermylene complexes appears to have a similar mechanism to that generally accepted for carbene ligand modification in Fischer-type carbene complexes [6]. If the double bond is assumed to be localized mainly between germanium and the cyclopentadienyl system, the substitution mechanism can be represented as in Scheme 1. The additional coordination of a nucleophile results in an ylide-type [3] complex **B**; the subsequent dissociation of chloride leads to a reorganization of the dihapto cyclopentadienyl ligation.

As there is no other synthetic approach to cyclopentadienyl-containing germylene complexes [2], the replacement of chlorine from pentacarbonyl[chloro(pentamethylcyclopentadienyl)germylene]tungsten provides a useful route, which will permit further investigations of the bonding in other germylene complexes.



SCHEME 1

Experimental

All reactions were carried out under dry oxygen-free argon using Schlenk-type flasks. Solvents and reagents were appropriately dried and purified.

Melting points: Büchi 510 capillary melting point apparatus. ^1H NMR spectra: Varian EM 360 L (60 MHz), Bruker AM 300 (300 MHz). ^{13}C NMR spectra: Bruker AM 300 (75 MHz), ^1H -decoupled, ^{29}Si NMR spectra: Bruker AM 300 (60 MHz), ^1H -decoupled. Infrared spectra: Perkin-Elmer 598, compounds in Nujol mull. FTIR windows. Mass spectra: Varian 311 A (70 eV, 300 μA emission), only characteristic fragments are listed. Elemental analysis: Perkin-Elmer 240 elemental analyzer.

Pentacarbonyl[chlorotpentamethylcyclopentadienyl]germylene]tungsten (4)

This was prepared from pentacarbonyl[dichloro(tetrahydrofuran)germylene]tungsten (**1**) and pentamethylcyclopentadienyltrimethylstannane as previously described [2], but with methylcyclohexane as solvent.

Pentacarbonyl(dimesitylthiogermylene)tungsten (2) [5], via reaction of 4 with lithium mesitylthiolate

A suspension of lithium mesitylthiolate [prepared from 118 mg of mesitylthiol (0.78 mmol) in 5 ml of diethyl ether, and 0.53 ml of a 1.47 *M* solution of butyllithium in hexane (0.78 mmol)] was added to a suspension of 440 mg of **4** (0.78 mmol) in 20 ml of diethyl ether cooled to -80°C . As the resulting clear solution was allowed to warm up to room temperature, a colorless powder separated. After filtration the solution was concentrated and cooled to -80°C , to give dark yellow prisms of **2**.

2 via reaction of 4 with mesitylthiotrimethylsilane

169 mg of MesSSiMe_3 (0.88 mmol) was added to a solution of 500 mg of **4** (0.88 mmol) in 10 ml of benzene. During about 90 h the yellow color of the solution deepened to orange. After removal of the solvent in vacuo, the oily residue was extracted with 10 ml of petroleum ether b.p. $50-70^\circ\text{C}$. Cooling of the extract to -80°C yielded dark yellow prisms of **2**, which decompose above 142°C . ^1H NMR (CH_2Cl_2) δ 7.01(s, 2H), 2.41(s, 6H, *o*-Me), 2.32(s, 3H, *p*-Me); MS, m/e 698 (M^+ , 13.9), 614 ($M^+ - 3\text{CO}$, 3.3), 558 ($M^+ - 5\text{CO}$, 7.9), 547 ($M^+ - \text{SMes}$, 1.4), 491 ($M^+ - \text{SMes} - 2\text{CO}$, 23.6), 463 ($M^+ - \text{SMes} - 3\text{CO}$, 4.0), 435 ($M^+ - \text{SMes} - 4\text{CO}$, 13.6), 407 (MesSGeW^+ , 9.4), 223 (MesSGe^+ , 23.3), 152 (MesS^+ , 40.8), 119 (Mes^+ , 100); Anal. Found: C, 37.92 [7]; H, 3.38, $\text{C}_{23}\text{H}_{22}\text{GeO}_5\text{S}_2\text{W}$ (698.98) calcd.: C, 39.52; H, 3.17%.

Pentacarbonyl(bistrimethylsilylamino)(pentamethylcyclopentadienyl)germylene]tungsten (5)

Crystalline lithium bistrimethylsilylamide (283 mg, 1.69 mmol) was added to a cooled solution of 960 mg of **4** (1.69 mmol) in 20 ml of benzene to give a red orange mixture. After removal of the solvent in vacuo, the residue was extracted with diethyl ether. Concentration of the solution and cooling to -80°C yielded 670 mg (67%) of small orange crystals, m.p. $122-124^\circ\text{C}$ with decomposition.

^1H NMR (C_6D_6) δ 1.90(s, 15H, Me_3C_3), 0.41(s, 18H, Me_3Si); ^{13}C NMR (C_6D_6) δ 197.55 (CO), 127.66 (Me_3C_3), 12.29 (Me_3C_3), 4.98 (Me_3Si); IR $\nu(\text{CO})$ 2061m, 1980s, 1940vs cm^{-1} ; MS, m/e 556 ($M^+ - \text{Me}_3\text{C}_3$, 58.9), 528 ($M^+ - \text{Me}_3\text{C}_3 - \text{CO}$, 20.5),

500 ($M^+ - \text{Me}_5\text{C}_5 - 2\text{CO}$, 24.1), 472 ($M^+ - \text{Me}_5\text{C}_5 - 3\text{CO}$, 48.7), 444 ($M^+ - \text{Me}_5\text{C}_5 - 4\text{CO}$, 7.2), 416 ($(\text{Me}_3\text{Si})_2\text{NGeW}^+$, 19.3), 398 ($\text{GeW}(\text{CO})_5^+$, 10.4), 370 ($\text{GeW}(\text{CO})_4^+$, 1.9), 234 ($(\text{Me}_3\text{Si})_2\text{NGe}^+$, 16.3), 209 ($\text{Me}_5\text{C}_5\text{Ge}^+$, 26.7), 146 (Me_6Si_2^+ (?), 100), 135 (Me_5C_5^+ , 79.3); Anal. Found: C, 34.46 [7]; H, 4.41; N, 1.82. $\text{C}_{21}\text{H}_{33}\text{GeNO}_5\text{Si}_2\text{W}$ (692.11) calcd.: C, 36.44; H, 4.81; N, 2.02%.

Pentacarbonyl[(pentamethylcyclopentadienyl)(bistrimethylsilylmethyl)germylene]tungsten (6)

When 3.59 ml of a 0.53 *M* solution of bis(trimethylsilyl)methyl lithium in diethyl ether (1.90 mmol) was added dropwise to a cooled solution of 1.09 g of **4** (1.92 mmol) in 5 ml of benzene a bright yellow mixture was obtained. Work-up as described above yielded 830 mg (63%) of yellow-orange prisms, m.p. 113–115°C with decomposition.

^1H NMR [8] (CDCl_3) δ 1.98(s, 15H, Me_5C_5), 0.15(s, 18H, Me_3Si); ^{13}C NMR [8] (CDCl_3) δ 197.83 (CO), 127.43 (Me_5C_5), 12.82 (Me_5C_5), 3.11 (Me_3Si); ^{29}Si NMR (CDCl_3) δ -40.60; IR $\nu(\text{CO})$ 2060s, 1979s, 1935vs cm^{-1} ; MS, *m/e* 555 ($M^+ - \text{Me}_5\text{C}_5$, 4.1), 527 ($M^+ - \text{Me}_5\text{C}_5 - \text{CO}$, 4.6) 499 ($M^+ - \text{Me}_5\text{C}_5 - 2\text{CO}$, 3.2), 471 ($M^+ - \text{Me}_5\text{C}_5 - 3\text{CO}$, 2.5), 415 ($(\text{Me}_3\text{Si})_2\text{CHGeW}^+$, 1.4). Anal. Found: C, 37.44 [7]; H, 5.01. $\text{C}_{22}\text{H}_{34}\text{GeO}_5\text{Si}_2\text{W}$ (691.12) calcd.: C, 38.23; H, 4.96%.

Pentacarbonyl[(pentamethylcyclopentadienyl)methylgermylene]tungsten (7)

A 1.39 *M* solution of methyl lithium in diethyl ether (2.36 ml, 3.28 mmol) was added dropwise to a mixture of 1.86 g of **4** (3.28 mmol) in 20 ml of diethyl ether cooled to -80°C. The mixture was allowed to warm to room temperature and 50 ml of methylcyclohexane was added. After evaporation of the diethyl ether in vacuo and filtration to remove the pale yellow precipitate, the solution was cooled to -80°C, yielding 860 mg (48%) of orange needles, m.p. 89–90°C with decomposition.

^1H NMR (CDCl_3) δ 2.02 (s, 15H, Me_5C_5), 1.01 (s, 3H, MeGe); ^{13}C NMR (CDCl_3) δ 196.94 (CO), 126.90 (Me_5C_5), 11.62 (Me_5C_5), 11.16 (MeGe); IR $\nu(\text{CO})$ 2061m, 1978s, 1930vs cm^{-1} ; MS, *m/e* 546 (M^+ , 5.2), 531 ($M^+ - \text{Me}$, 14.8), 411 ($M^+ - \text{Me}_5\text{C}_5$, 11.6) 396 ($\text{GeW}(\text{CO})_5^+$, 3.3), 383 ($M^+ - \text{Me}_5\text{C}_5 - \text{CO}$, 51.2), 355 ($M^+ - \text{Me}_5\text{C}_5 - 2\text{CO}$, 15.3), 327 ($M^+ - \text{Me}_5\text{C}_5 - 3\text{CO}$, 9.3) 299 ($M^+ - \text{Me}_5\text{C}_5 - 4\text{CO}$, 5.7), 271 (MeGeW $^+$, 4.0), 209 ($\text{Me}_5\text{C}_5\text{Ge}^+$, 100). Anal. Found: C, 34.76; H, 3.09. $\text{C}_{16}\text{H}_{18}\text{GeO}_5\text{W}$ (546.76) calcd.: C, 35.15; H, 3.32%.

X-Ray crystallography

A crystal of **6** was sealed under argon in a thin walled glass capillary. All measurements were made on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo- K_α radiation (λK_{α_1} , K_{α_2} 0.70930, 0.71359 Å) at room temperature (295 ± 2 K); for details of the procedure see ref. 9. Data were recorded for a crystal of dimensions $0.6 \times 0.5 \times 0.3$ mm³ using an $\omega/2\theta$ scan mode (ω scan width = $0.8 + 0.35 \tan \theta$) for $1.5 \leq \theta \leq 25^\circ$ within the octant $+h$, $+k$, $+l$, giving 2820 measured, 2571 unique and 2021 observed [$I > 1.5\sigma(I)$] reflections. An empirical absorption correction was made using φ scan data for the reflections 710, 411, 510, with x values of 88.23, 82.63 and 89.68°, respectively.

Crystal data. $\text{C}_{22}\text{H}_{34}\text{Si}_2\text{GeO}_5\text{W}$, $M = 691.12$, Orthorhombic, space group *Pnam*, a 19.211(5), b 9.782(1), c 14.938(5) Å, V 2801 Å³, $Z = 4$, D_c 1.635 g cm⁻³,

TABLE 3
 FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $(\text{Me}_3\text{C}_3)_3(\text{Me}_3\text{Si})_2\text{CHGe}-\text{W}(\text{CO})_6$.

Atom	x	y	z
W(1)	5279(1)	4457(1)	2500
Ge(1)	3981(1)	3596(1)	2500
Si(1)	2999(1)	5740(3)	3579(2)
C(1)	5615(5)	3110(10)	1571(7)
O(1)	5848(5)	2444(9)	1033(6)
C(2)	5058(6)	5791(12)	3485(10)
O(2)	4966(6)	6598(12)	4045(8)
C(3)	6206(8)	5286(14)	2500
O(3)	6768(6)	5741(13)	2500
C(11)	3398(6)	4842(11)	454(6)
C(12)	3322(10)	7539(11)	3628(9)
C(13)	2936(6)	5825(21)	3766(9)
C(14)	3136(6)	4768(11)	2500
C(6)	3567(4)	1646(8)	2007(5)
C(61)	2914(4)	1672(9)	1446(6)
C(7)	4184(5)	990(8)	1733(5)
C(71)	4373(6)	721(11)	386(7)
C(8)	4574(6)	579(10)	2500
C(81)	5269(8)	165(17)	2500

$\mu(\text{Mo}-\text{K}\alpha)$ 50.6 cm^{-1} . The structure was solved by the heavy-atom method and refined using full matrix least-squares. All atoms were refined with anisotropic thermal parameters; hydrogen atoms could not be located in difference maps and so were not included. The function minimized was $\omega(\Delta F)^2$, and weights were calculated as $\omega = 1/[\sigma^2(F_o) + g(F_o)]$, with $g = 0.0004$ giving acceptable agreement analyses. The final R ($= |\Delta F|/\Sigma |F_o|$) and R' ($= \Sigma \omega^{1/2} |\Delta F|/\Sigma \omega^{1/2} |F_o|$) values were 0.040 and 0.042, respectively, for a total of 2021 reflections. Final atomic coordinates are given in Table 3. Neutral atom scattering factors, including corrections for anomalous scattering were based on data from Ref. 10, and all computations were made using the SHELX program [11] on a VAX II/750 computer. Tables of observed and calculated structure factor amplitudes and thermal parameters are available from the authors.

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