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Reactions of $GeMe_2$-bridged dicyclopentadienes with molybdenum carbonyl: formation of germylidyne trimolybdenum clusters

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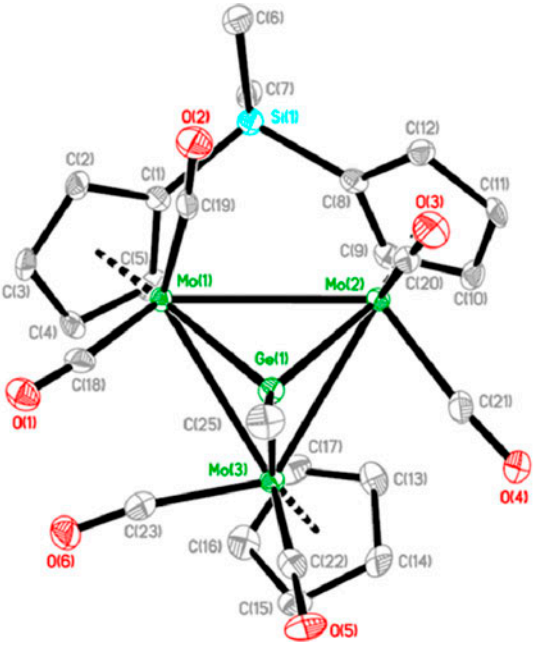

The $GeMe_2$-bridged dicyclopentadienes, including the doubly bridged dicyclopentadienes $(C_5H_3R(SiMe_2))(C_5H_3R(GeMe_2))$ (R=H (**1**), ^{t}Bu (**5**)) and the singly bridged one $(C_5H_5)_2GeMe_2$ (**9**), react with $Mo(CO)_6$ to produce the germylidyne trimolybdenum clusters $[(\eta^5\text{-}C_5H_3R)_2(SiMe_2)](\eta^5\text{-}C_5H_4R)[Mo(CO)_2]_3(\mu_3\text{-}GeMe)$ (**4**, **8**) and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_3(\mu_3\text{-}GeMe)$ (**10**), respectively.

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In thermal reactions of the doubly bridged dicyclopentadienes $(C_5H_3R(SiMe_2))(C_5H_3R(GeMe_2))$ (R=H (**1**), ^{t}Bu (**5**)) with $Mo(CO)_6$, the bridging $GeMe_2$ is cleaved to give the corresponding degermylated products $[(\eta^5\text{-}C_5H_3R)_2(SiMe_2)]Mo_2(CO)_6$ (**3**, *rac*-**7**), or both $GeMe_2$ and $SiMe_2$ are cleaved to afford the nonbridged products $[(\eta^5\text{-}C_5H_4R)Mo(CO)_3]_2$ (**2**, **6**). The reactions also produce germylidyne trimolybdenum clusters $[(\eta^5\text{-}C_5H_3R)_2(SiMe_2)](\eta^5\text{-}C_5H_4R)[Mo(CO)_2]_3(\mu_3\text{-}GeMe)$ (**4**, *rac-*/*meso*-**7**) containing the $Mo_3(\mu_3\text{-}GeMe)$ units. Similarly, reaction of the single $GeMe_2$-bridged dicyclopentadienes $(C_5H_5)_2GeMe_2$ (**9**) with $Mo(CO)_6$ also results in the degermylated **2**, as well as the similar trimolybdenum cluster $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_3(\mu_3\text{-}GeMe)$ (**10**). The molecular structures of **4** and *trans*-**5** were determined by X-ray diffraction.

Keywords: $GeMe_2$-bridged dicyclopentadienes; $Mo(CO)_6$; Germylidyne; Trimolybdenum clusters; X-ray diffraction

1. Introduction

The reactions of doubly bridged dicyclopentadienes $(C_5H_4(X))(C_5H_4(Y))$ (X, Y = CH_2, CMe_2, CH_2CH_2, $SiMe_2$, $SiMe_2SiMe_2$, $GeMe_2$, etc.) with transition metal carbonyls have attracted attention [1–7]. This research group reported a series of thermal reactions of the doubly bridged dicyclopentadienes $(C_5H_4(X))(C_5H_4(Y))$ (X, Y = CMe_2, $SiMe_2$, $GeMe_2$, or $SnMe_2$) with $M(CO)_6$ (M = Mo, W), $Fe(CO)_5$, and $Ru_3(CO)_{12}$ [8–16]. The bridging groups in the ligands could migrate to metal in the reaction to afford different types of products. For example, in the reaction of $(C_5H_4(SiMe_2))(C_5H_4(GeMe_2))$ (**1**) with $Fe(CO)_5$ (or $W(CO)_6$), the bridging group $GeMe_2$ generally migrates from the ligand to Fe (or W) atom to give $(SiMe_2)(\eta^5\text{-}C_5H_3)(\eta^5\text{:}\eta^1\text{-}C_5H_3)[(GeMe_2)M(CO)_n][M(CO)_n]$ (M = Fe, $n = 2$; or M = W, $n = 3$) containing a Ge–Fe(W) bond; the bridging $SiMe_2$ does not migrate (Chart 1) [14]. However, as a continuous part of this program, the reaction of **1** with $Mo(CO)_6$ did not afford the similar product containing a Ge–Mo bond, but a germylidyne trimolybdenum cluster. Recently, several mononuclear germylidyne complexes have been reported [17–20]; however, to the best of our knowledge, the type of cluster described in this work is the first structurally characterized trinuclear germylidyne complex featuring a $Mo_3(\mu_3\text{-}GeMe)$ unit.

2. Experimental

2.1. *General considerations*

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under nitrogen prior to use. ^1H NMR spectra were recorded on a Bruker AV400 instrument. IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Compounds **1** and **9** were prepared by literature methods [21, 22].

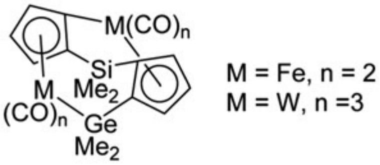


Chart 1. Complexes $(SiMe_2)(\eta^5\text{-}C_5H_3)(\eta^5\text{:}\eta^1\text{-}C_5H_3)[(GeMe_2)M(CO)_n][M(CO)_n]$.

2.2. *Reaction of ($C_5H_4(SiMe_2)$)($C_5H_4(GeMe_2)$) (1) with $Mo(CO)_6$*

A solution of 0.29 g (1.0 mM) of **1** and 0.92 g (3.5 mM) of $Mo(CO)_6$ in 30 mL of xylene was refluxed for 20 h. After removal of solvent, the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (red) afforded **2** (103 mg, 21% yield) as dark red crystals. The second band (red) gave **3** (98 mg, 18% yield) as red crystals. The third band (green) gave **4** (61 mg, 7% yield) as dark green crystals. All spectroscopic data for **2** and **3** are in agreement with literature data [23, 24].

For **4**, Anal. Calcd for $C_{24}H_{22}GeMo_3O_6Si{\bullet}CH_2Cl_2$ (%): C, 34.12; H, 2.75. Found: C, 33.94; H, 2.69. ^1H NMR (400 MHz, $CDCl_3$) δ 5.36 (m, 2H, C_5H_4), 5.14 (m, 2H, C_5H_4), 5.10 (m, 2H, C_5H_4), 5.06 (s, 5H, C_5H_5), 4.72 (m, 2H, C_5H_4), 2.01 (s, 3H, Ge(CH_3)), 0.49 (s, 3H, Si(CH_3)), 0.36 (s, 3H, Si(CH_3)) ppm. IR (KBr, ν_{CO}, cm^{-1}): 1944 (s), 1899 (br), 1855 (w), 1845 (w), 1833 (w), 1818 (w).

2.3. *Syntheses of ($C_5H_3{}^tBu(SiMe_2)$)($C_5H_3{}^tBu(GeMe_2)$) (5)*

To a solution of the dilithium salt of ($SiMe_2$)($C_5H_4{}^tBu$)$_2$, prepared from 2.1 g (7.0 mM) of (CMe_2)($C_5H_4{}^tBu$)$_2$ and 14.0 mM of an *n*-BuLi hexane solution in 50 mL of THF, was added slowly 1.2 g (6.8 mM) of $GeMe_2Cl_2$ in 20 mL of THF. After the mixture was stirred at room temperature for 16 h, the solvents were removed under reduced pressure. The residue was extracted with *n*-hexane. Upon concentration and cooling at –10 °C, 1.8 g (67%) of *trans*-**5** was obtained as colorless crystals.

For *trans*-**5**, Anal. Calcd for $C_{22}H_{36}GeSi$ (%): C, 65.86; H, 9.04. Found: C, 65.75; H, 9.22. ^1H NMR (400 MHz, $CDCl_3$): δ 6.95 (m, 1H, C_5H_3), 6.88 (m, 1H, C_5H_3), 6.35 (m, 1H, C_5H_3), 6.33 (m, 1H, C_5H_3), 3.54 (m, 1H, C_5H_3), 3.33 (m, 1H, C_5H_3), 1.24 (s, 3H, C(CH_3)$_3$), 1.23 (s, 3H, C(CH_3)$_3$), 0.68 (s, 3H, CH_3), 0.51 (s, 3H, CH_3), −0.35 (s, 3H, CH_3), −0.48 (s, 3H, CH_3) ppm.

2.4. *Reaction of trans-5 with $Mo(CO)_6$*

A solution of 0.48 g (1.2 mM) of *trans*-**5** and 0.80 g (3.0 mM) of $Mo(CO)_6$ in 30 mL of xylene was refluxed for 20 h. After removal of the solvent, the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (red) afforded **6** (123 mg, 17% yield) as dark red crystals. The second band (red) gave *rac*-**7** (110 mg, 14% yield) as dark red crystals. The third band (green) afforded *meso*-**8** (58 mg, 5% yield) as dark green crystals. The last band (green) gave *rac*-**8** (46 mg, 4% yield) as dark green crystals. All spectroscopic data for **6** are in agreement with literature data [25].

For *rac*-**7**, Anal. Calcd for $C_{26}H_{30}Mo_2O_6Si$ (%): C, 47.42; H, 4.59. Found: C, 47.55; H, 4.36. ^1H NMR (400 MHz, $CDCl_3$): δ 5.52 (m, 2H, C_5H_3), 5.47 (m, 2H, C_5H_3), 4.82 (m, 2H, C_5H_3), 1.25 (s, 18H, C(CH_3)$_3$), 0.41 (m, 6H, Si(CH_3)) ppm. IR (KBr, ν_{CO}, cm^{-1}): 2005 (s), 1948 (s), 1898 (s), 1870 (s).

For *meso*-**8**, Anal. Calcd for $C_{36}H_{46}GeMo_3O_6Si$ (%): C, 44.88; H, 4.81. Found: C, 44.75; H, 4.99. ^1H NMR (400 MHz, $CDCl_3$): δ 5.19 (m, 1H, Cp–*H*), 5.01 (m, 4H, Cp–*H*), 4.86 (m, 1H, Cp–*H*), 4.72 (m, 1H, Cp–*H*), 4.59 (m, 1H, Cp–*H*), 4.28 (m, 2H, Cp–*H*), 1.93 (s, 3H, Ge (CH_3)), 1.27 (s, 9H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$), 0.57 (s, 3H, Si (CH_3)), 0.34 (s, 3H, Si(CH_3)) ppm. IR (KBr, ν_{CO}, cm^{-1}): 2010 (s), 1954 (s), 1910 (s).

For *rac*-**8**, Anal. Calcd for $C_{36}H_{46}GeMo_3O_6Si$ (%): C, 44.88; H, 4.81. Found: C, 44.82; H, 5.04. ^1H NMR (400 MHz, $CDCl_3$): δ 5.00 (m, 2H, Cp–*H*), 4.95 (m, 2H, Cp–*H*), 4.92

(m, 2H, Cp–*H*), 4.84 (m, 2H, Cp–*H*), 4.61 (m, 2H, Cp–*H*), 1.97 (s, 3H, Ge(C*H*$_3$)), 1.27 (s, 9H, C(C*H*$_3$)), 1.25 (s, 18H, C(C*H*$_3$)$_3$), 0.44 (s, 3H, Si(C*H*$_3$)), 0.28 (s, 3H, Si(C*H*$_3$)) ppm. IR (KBr, ν_{CO}, cm^{-1}): 2026 (s), 1956 (s), 1918 (s).

2.5. *Reaction of $(C_5H_5)_2GeMe_2$ (9) with $Mo(CO)_6$*

A solution of 0.23 g (1.0 mM) of **9** and 0.70 g (2.7 mM) of $Mo(CO)_6$ in 20 mL of xylene was refluxed for 20 h. After removal of the solvent, the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (red) gave **2** (157 mg, 32% yield) as dark red crystals. The second band (green) gave **10** (81 mg, 11% yield) as dark green solid.

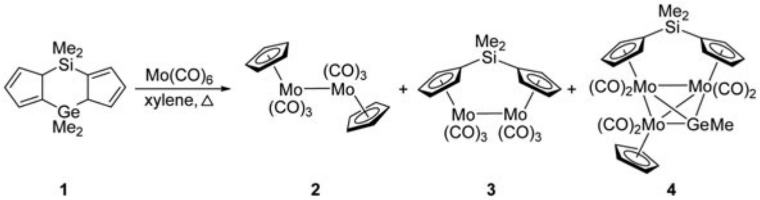
For **10**, Anal. Calcd for $C_{22}H_{18}GeMo_3O_6$ (%): C, 35.76; H, 2.46. Found: C, 34.63; H, 2.55. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.04 (s, 15H, C$_5$*H*$_5$), 2.04 (s, 3H, Ge(C*H*$_3$)) ppm. IR (KBr, ν_{CO}, cm^{-1}): 2026 (s), 1957 (w), 1908 (br), 1830 (w).

2.6. *X-ray crystallographic studies*

Single crystals of **4** suitable for X-ray diffraction were obtained by crystallization from *n*-hexane/CH_2Cl_2 (1 : 1), and the single crystal of *trans*-**5** was obtained by crystallization from pure *n*-hexane. Data collection was performed on a Bruker SMART 1000 X-ray diffractometer using graphite-monochromated Mo Kα radiation (ω–2θ scans, $\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using SHELXTL-97. The crystal data and summary of X-ray data collection are presented in table 1.

Table 1. Crystal data and summary of X-ray data collection for **4** and *trans*-**5**.

Complex	**4**·CH_2Cl_2	*trans*-**5**
Empirical formula	$C_{25}H_{24}Cl_2GeMo_3O_6Si$	$C_{22}H_{36}GeSi$
Molecular weight	879.84	401.19
T (K)	173(2)	173(2)
Crystal system	Orthorhombic	Triclinic
Space group	Fdd2	P–1
Unit cell dimensions (Å, °)		
a	27.903(3)	10.072(3)
b	42.503(4)	18.328(6)
c	9.5514(9)	12.362(4)
α	90	90
β	90	107.629(5)
γ	90	90
Volume (Å^3)	11327.5(19)	2174.9(12)
Z	16	4
Calculated density (g cm^{-3})	2.064	1.225
Absorption coefficient (mm^{-1})	2.619	1.465
F(000)	6848	856
Crystal size (mm)	0.18 × 0.17 × 0.16	0.18 × 0.17 × 0.16
Max. 2θ (deg)	50.00	50.02
Reflections collected	14,260	10,473
Independent reflections/R_{int}	4733/0.0529	3802/0.0348
Parameters	346	241
Goodness-of-fit on F^2	1.049	1.026
R_1, wR_2 [$I > 2\sigma$(I)]	0.0354, 0.0803	0.0333, 0.0723
R_1, wR_2 (all data)	0.0388, 0.0823	0.0448, 0.0772
Largest diff peak and hole (e Å^{-3})	0.588 and −0.530	0.319 and −0.408



Scheme 1. Reaction of $(C_5H_4(SiMe_2))(C_5H_4(GeMe_2))$ (**1**) with $Mo(CO)_6$.

3. Results and discussion

3.1. *Reaction of $(C_5H_4(SiMe_2))(C_5H_4(GeMe_2))$ (1) with $Mo(CO)_6$*

The doubly bridged dicyclopentadiene **1** reacts with $Mo(CO)_6$ in refluxing xylene to afford two red solids **2** and **3**, and a dark green crystalline solid **4** (scheme 1). Through comparing the spectroscopic data of **2** and **3** with those of known complexes, **3** is the singly bridged dicyclopentadienyl bimetallic Mo complex $[(\eta^5\text{-}C_5H_4)_2(SiMe_2)]Mo_2(CO)_6$ [23], **2** is the nonbridged dicyclopentadienyl dinuclear Mo complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ [24]. Formation of **2** and **3** indicates that both the bridging $GeMe_2$ and $SiMe_2$ groups in the ligand could be cleaved in the reaction of **1** with $Mo(CO)_6$. For **4**, the ^1H NMR spectrum shows four multiplets at δ 5.36, 5.14, 5.10, and 4.72 for the protons in two bridged cyclopentadienyl rings, one singlet at δ 5.06 for the protons in the third cyclopentadienyl ring, two singlets at δ 0.49 and 0.36 for the different CH_3 protons in $SiMe_2$, and one singlet at δ 2.01 which corresponds to the Ge–Me group. Comparing with the signal (1.35 ppm) for $GeMe_2$ methyl on $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2GeMe_2$ [26], the signal of Ge–Me group on **4** is significantly shifted to low field, indicating the electron withdrawing ability of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$. The IR spectrum exhibits two distinct ν(CO) bands at 1944 and 1899 cm^{-1} and four weak bands at 1855–1818 cm^{-1}. A single-crystal X-ray structural determination (figure 1, table 1) of **4** shows that three Mo and one Ge are bonded to form a tetrahedron, in which two Mo ions coordinate to the $SiMe_2$-bridged dicyclopentadienyl, the third Mo coordinates to a simple cyclopentadienyl ring, and Ge is bonded to a methyl. Each Mo carries two terminal carbonyl ligands and three Mo ions are bridged by a GeMe unit in μ_3-mode. The mean distance of three Mo–Mo bonds is 3.1502 Å, which compares very well with the data (3.1406 Å) for the singly bridged dicyclopentadienyl dinuclear Mo complex $[(\eta^5\text{-}C_5H_4)_2(CH_2)]Mo_2(CO)_6$ [27], but slightly longer than those reported for trinuclear μ_3-methylidyne analogs $(\mu_3\text{-}CR)[(\eta^5\text{-}C_5H_4R')Mo(CO)_2]_3$ (R, R′=H, Me) (2.985–3.062 Å) [28]. The mean distance of three Mo–Ge bonds is 2.521 Å, shorter than normal Mo–Ge single bond distances in $(\eta^5\text{-}C_5H_5)(CO)_2Mo(GePh_3)\{C(OEt)Ph\}$ (2.658(2) Å) [29], $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_6H_{11})(NO)MoGePh_3$ (2.604(2) Å) [30], $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2GeCl_2$ (2.6668(6) and 2.6536(7) Å) [31], and $(CMe_2)(\eta^5\text{-}C_5H_3)(\eta^5,\eta^1\text{-}C_5H_3)[(GeMe_2)Mo(CO)_3][Mo(CO)_3]$ (2.667(1) Å) [16], as well as the calculated Ge–Mo bond distance of 2.695 Å for $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(GeMe)]$ [18]. The shortening seen in **4** may arise from the tetrahedral $Mo_3(\mu_3\text{-}GeMe)$ unit. The formation of germylidyne cluster **4** involves cleavage of a Ge–Me bond. While there are some thermal reactions involving a cleavage of a Ge–Cp bond and formation of **2** and **3** reported previously [10, 12–16], there are no examples of $Mo_3(\mu_3\text{-}GeMe)$ cluster formation.

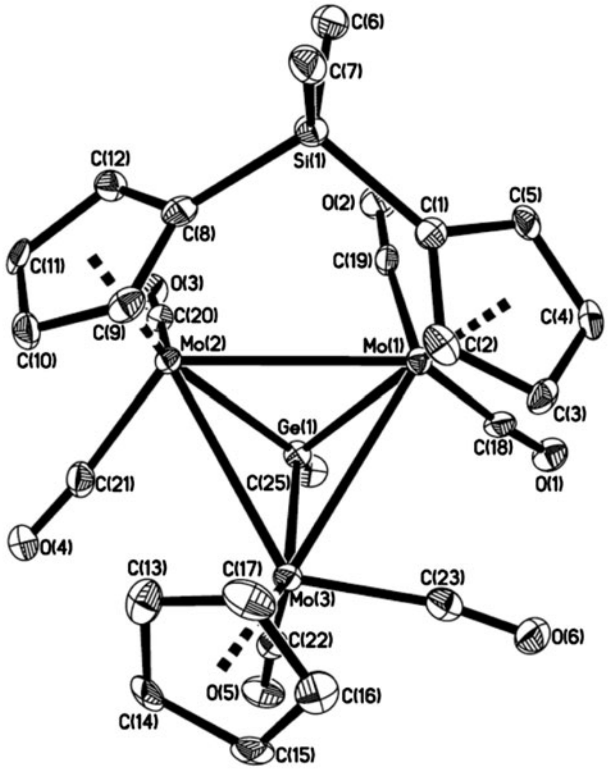
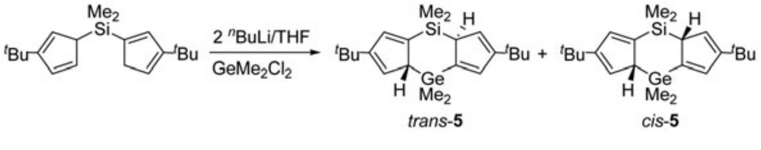


Figure 1. Thermal ellipsoid drawing of $[(\eta^5\text{-}C_5H_4)_2(SiMe_2)](\eta^5\text{-}C_5H_5)[Mo(CO)_2]_3(\mu_3\text{-}GeMe)$ (**4**) showing the labeling scheme and 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°) are: Mo(1)–Mo(2) 3.1444(8), Mo(2)–Mo(3) 3.1334(8), Mo(1)–Mo(3) 3.1728(8), Mo(1)–Ge(1) 2.5231(8), Mo(2)–Ge(1) 2.514(1), Mo(3)–Ge(1) 2.5259(8), Ge(1)–C(25) 1.954(7), Mo(1)–Cp(centroid) 2.013, Mo(2)–Cp(centroid) 2.027, Mo(3)–Cp(centroid) 2.026, Mo(1)–C(18) 1.961(8), Mo(1)–C(19) 1.973(7), C(18)–O(1) 1.162(9), C(19)–O(2) 1.159(8), ∠Mo(1)–Mo(2)–Mo(3) 60.72(2), ∠Mo(2)–Mo(1)–Mo(3) 59.47(2), ∠Mo(1)–Ge(1)–Mo(2) 77.26(3), ∠Mo(1)–Ge(1)–C(25) 130.2(2), C(1)–Si(1)–C(8) 107.1(3), ∠Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 18.2, ∠Cp–Cp 120.3.



Scheme 2. Syntheses of **5**.

3.2. *Syntheses of* $(C_5H_3{}^tBu(SiMe_2))(C_5H_3{}^tBu(GeMe_2))$ *(5)*

To develop a wider generality of formation of clusters of type **4**, the *tert*-butyl substituted doubly bridged **5** was prepared according to a similar method synthesizing its analog $(C_5H_3{}^tBu(CMe_2))(C_5H_3{}^tBu(SiMe_2))$ [15]. Reaction of the dilithium salts of the $SiMe_2$-bridged dicyclopentadiene, $SiMe_2(C_5H_3{}^tBu^- \, Li^+)_2$, with 1 equiv of $GeMe_2Cl_2$ in THF at room temperature for 16 h yields **5** (scheme 2). In theory, **5** should exist as a mixture of

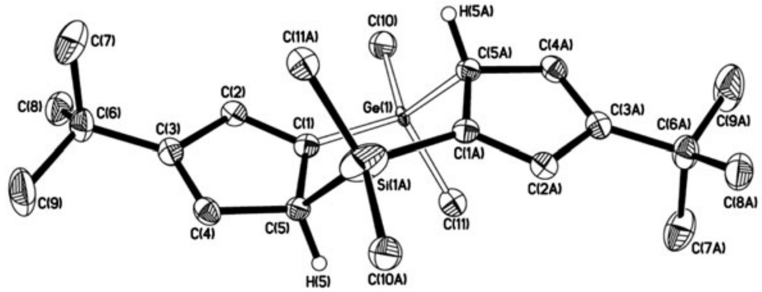


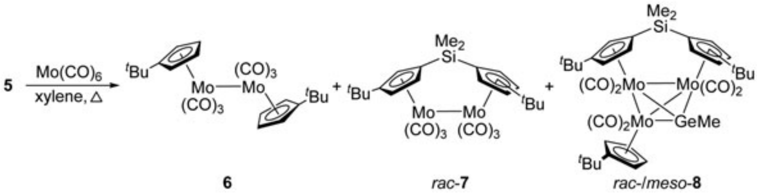
Figure 2. Thermal ellipsoid drawing of $(C_5H_3{}^tBu(SiMe_2))(C_5H_3{}^tBu(GeMe_2))$ (*trans*-**5**) showing the labeling scheme and 30% probability level. Hydrogens are partly omitted for clarity. Selected bond lengths (Å) and angles (°) are: C(1)–C(2) 1.344(3), C(2)–C(3) 1.451(3), C(3)–C(4) 1.344(3), C(4)–C(5) 1.469(3), C(1)–C(5) 1.494(3), Si (1A)–C(5) 1.953(6), ∠C(1)–Ge(1)–C(5A) 103.1(1), ∠Si(1A)–C(5)–C(1) 104.4(2), ∠C(5)–C(1)–Ge(1) 124.4(2), ∠C(10)–Ge(1)–C(11) 112.0(1).

trans and *cis* isomers, and the interconversion may occur between them by 1,5-sigma tropic shift [32]. However, only the *trans* isomer (*trans*-**5**) was isolated by crystallization from *n*-hexane in 67% yield in the form of colorless crystals, which may be attributed to the lower solubility or higher yield of *trans*-**5**. We have not isolated pure *cis*-**5**, so in the reaction mentioned below, we used a single isomer *trans*-**5** as the starting material.

The molecular structure of *trans*-**5** is presented in figure 2. It is different with C_s symmetry from some doubly bridged analogs ($(C_5H_3{}^tBu(CMe_2))(C_5H_3{}^tBu(SnMe_2))$ [9] and $(C_5H_3{}^tBu(SiMe_2))(C_5H_3{}^tBu(SnMe_2))$ [33]), which possess a symmetry plane in their respective molecular structures. *Trans*-**5** does not show the preference that other doubly bridged cyclopentadienes of this type show for sp^3 geometry at the more electropositive element since the difference in this case in going from Si to Ge is smaller than in going from C or Si to Sn where the preference is shown. In *trans*-**5**, H(5) and H(5A) on the bridgehead carbons are *trans* to each other. The six-membered ring C(1)–C(5)–Si(1A)–C(1A)–C(5A)–Ge (1) constituting the molecular framework adopts a stable chair conformation. The bridging groups ($SiMe_2$ and $GeMe_2$) are connected to one sp^2-hybridized carbon and one sp^3-hybridized carbon, reflected by C–C bond distances on the two cyclopentadiene rings. Two *tert*-butyl groups occupy the position at each cyclopentadienyl ring that is farthest away from the bridging $SiMe_2$ and $GeMe_2$ groups.

3.3. *Reaction of 5 with $Mo(CO)_6$*

Like its parent **1**, **5** reacts with $Mo(CO)_6$ in refluxing xylene to afford three products (**6–8**) (scheme 3). The only difference is that **7** and **8** exist as a mixture of *rac* and *meso* isomers arising from the introduction of two *t*-butyl groups on **5**. Complexes *rac* and *meso*-**8** were separated by column chromatography and isolated as pure dark green solids. For *rac*-**8**, its ^1H NMR spectrum shows five groups of peaks at δ 5.00, 4.95, 4.92, 4.84, and 4.61 for the 10 protons in three cyclopentadienyl rings, one singlet at δ 1.25 for the protons in two ^{t}Bu groups on the bridged ligand $(\eta^5\text{-}C_5H_3{}^tBu)_2SiMe_2]_2$, and one singlet at δ 1.27 for the protons in ^{t}Bu group on $(\eta^5\text{-}C_5H_4{}^tBu)$, which is consistent with its *rac* configuration. For *meso*-**8**, its ^1H NMR spectrum shows six unequal peaks at δ 5.19, 5.01, 4.86, 4.72, 4.59, and 4.28 for all protons in three cyclopentadienyl rings, two singlets at δ 1.25 and 1.24 for the protons in two ^{t}Bu groups on the bridged ligand $(\eta^5\text{-}C_5H_3{}^tBu)_2SiMe_2]_2$, which indicates



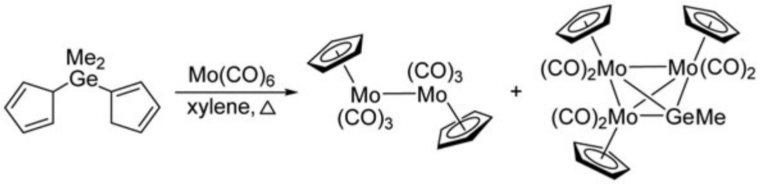
6 *rac*-**7** *rac*-/*meso*-**8**

Scheme 3. Reaction of $(C_5H_3{}^t Bu(SiMe_2))(C_5H_3{}^t Bu\ (GeMe_2))$ (**5**) with $Mo(CO)_6$.

its *meso* configuration. However, *rac* and *meso* isomers of **7** could not be separated by normal column chromatography owing to their almost equal R_f values. Only pure *rac*-**7** was isolated by crystallization from *n*-hexane/CH_2Cl_2 (1 : 1).

3.4. *Reaction of $(C_5H_5)_2GeMe_2$ (9) with $Mo(CO)_6$*

Based on the two reactions described above, the germylidyne trimolybdenum clusters (**4** and **8**) can be synthesized from reactions of $(SiMe_2)(GeMe_2)$ doubly bridged dicyclopentadienes (**1** and **5**) with $Mo(CO)_6$. In order to find out whether the bridging $SiMe_2$ group in the doubly bridged ligand is necessary for formation of the cluster, the reaction of the single $GeMe_2$-bridged dicyclopentadienes $(C_5H_5)_2GeMe_2$ (**9**) with $Mo(CO)_6$ was studied. Reaction of **9** with $Mo(CO)_6$ in refluxing xylene gives red **2** and dark green **10** (scheme 4). For **10**, the ^1H NMR spectrum shows one singlet at δ 5.04 for protons in the cyclopentadienyl rings and one singlet at δ 2.04 for the CH_3 protons in GeMe, which compares very well with the data (2.01 ppm) in **4**. The IR spectrum exhibits several $\nu(CO)$ bands at 2026–1830 cm^{-1}. All these spectroscopic data support that **10** is the germylidyne trimolybdenum cluster $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_3(\mu_3\text{-}GeMe)$ similar to **4** and **8**. It is apparent that the $SiMe_2$ bridge in the doubly bridged ligand is not necessary for formation of the cluster. Generally, the $GeMe_2$-bridged dicyclopentadienes (including the doubly and singly bridged dicyclopentadienes) would react with $Mo(CO)_6$ in refluxing xylene to produce the germylidyne trimolybdenum clusters. This type of cluster is only generated with $Mo(CO)_6$. Based on our previous report, no similar cluster is produced from reactions of $GeMe_2$-bridged dicyclopentadienes with other transition metal carbonyls, like $W(CO)_6$ or $Fe(CO)_5$ [14]. In a series of reactions of doubly bridged dicyclopentadienes with transition metal carbonyls, the bridging group in the ligands generally does ring-to-metal migration. For example, in the reaction of $(C_5H_4(SiMe_2))(C_5H_4(SnMe_2))$ with $Mo(CO)_6$, the $SnMe_2$ bridge migrates from the ring to metal to give $SiMe_2[(\eta^5\text{-}C_5H_4)Mo(CO)_3]_2SnMe_2$, which contains a Mo–Sn–Mo unit [10].



9 **2** **10**

Scheme 4. Reaction of $(C_5H_5)_2GeMe_2$ (**9**) with $Mo(CO)_6$.

We consider that clusters like **10** could be generated from further reaction of the GeMe$_2$-migrated compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2\text{GeMe}_2$ with the degermylated product $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$, or the active species $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3$, because $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2\text{GeMe}_2$ is thermally unstable, decomposing at room temperature to the corresponding metal carbonyl dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ and some unknown products [26].

4. Conclusion

The GeMe$_2$-bridged dicyclopentadienes, including the doubly bridged dicyclopentadienes $(\text{C}_5\text{H}_3\text{R}(\text{SiMe}_2))(\text{C}_5\text{H}_3\text{R}(\text{GeMe}_2))$ (R=H (**1**), ^{t}Bu (**5**)) and the singly bridged one $(\text{C}_5\text{H}_5)_2\text{GeMe}_2$ (**9**), react with Mo(CO)$_6$ to produce germylidyne trimolybdenum clusters $[(\eta^5\text{-C}_5\text{H}_3\text{R})_2(\text{SiMe}_2)](\eta^5\text{-C}_5\text{H}_4\text{R})[\text{Mo(CO)}_2]_3(\mu_3\text{-GeMe})$ (**4**, **8**) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2]_3(\mu_3\text{-GeMe})$ (**10**), respectively. This class of cluster is only generated when the reactant, transition metal carbonyl is Mo(CO)$_6$. A plausible pathway for formation of the germylidyne trimolybdenum clusters is discussed, although the exact mechanism still remains unclear under our current experimental conditions.

Supplementary material

CCDC 1017415 and 1017416 contain the supplementary crystallographic data for **4** and *trans*-**5**. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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