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Triple Bonding to Germanium: Characterization of the Transition Metal Germylynes ($(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge\text{-}C_6H_3\text{-}2,6\text{-}Mes_2$ ($M = Mo$, W; Mes = $-C_6H_2\text{-}2,4,6\text{-}Me_3$) and $(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge\text{-}C_6H_3\text{-}2,6\text{-}Trip_2$ (M = Cr, Mo, W; Trip = $-C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3$) and the Related Single Bonded Metallogermylenes $(\eta^5\text{-}C_5H_5)(CO)_3M\text{-}\ddot{G}e\text{-}C_6H_3\text{-}2,6\text{-}Trip_2$ (M = Cr, W)

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Abstract: The synthesis and characterization of several m-terphenyl stabilized germylyne transition metal complexes and related metallogermylenes are reported. The reaction of $Na[M(\eta^5\text{-}C_5H_5)(CO)_3]$ (M = Cr, or W) with $Ge(Cl)C_6H_3\text{-}2,6\text{-}Trip_2$ (Trip = $-C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3$) below room temperature affords the metallogermylenes $(\eta^5\text{-}C_5H_5)(CO)_3M\text{-}\ddot{G}e\text{-}C_6H_3\text{-}2,6\text{-}Trip_2$ (M = Cr, **1**; W, **5**). However, for the analogous reaction with $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$, the metallogermylene was not isolated. Instead, the germylyne complex $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Trip_2$ (**3**) was obtained directly with elimination of carbon monoxide. The corresponding chromium and tungsten compounds $(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Trip_2$ (M = Cr, **2**; W, **6**) could be obtained by refluxing **1** or **5** in toluene or by photolysis. The related germylyne $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Mes_2$ (**7**), as well as the recently reported molybdenum analogue $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Mes_2$ (**4**), which was the first example of a triply bonded germanium species, are also described. All compounds were characterized by ^1H and ^{13}C NMR, UV−vis, and IR spectroscopy, and by C, H analysis. The X-ray crystal structures of **1**−**3**, **5**, and **7** have also been determined. The M≡Ge (M = Cr, Mo, W) triple bonds in the germylynes are typically ca. 0.4 Å shorter than the M−Ge single bonds in the metallogermylenes. In addition, angles at germanium in the germylynes are nearly linear (range 170.9(3)−175.99(6)°) whereas in the metallogermylenes the corresponding angles are 114.7(6) and 117.8(2)°, consistent with the presence of a lone pair at germanium. The synthesis of the series of compounds **1**−**7** has enabled, for the first time, a comparison of single and triple bond lengths between closely related species involving the same coordination number and substituents at the heavier group 14 element.

Introduction

The reaction between $[Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$[1] and $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$[2] in THF solution, as shown in eq 1, was recently reported to afford the unique compound $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Mes_2$ (**4**) as red crystals.[3]

$$Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3] + {}^1/_2[Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2 \xrightarrow[-CO]{THF,\ 50\ ^\circ C} \underset{\mathbf{4}}{(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge\text{-}C_6H_3\text{-}2,6\text{-}Mes_2} + NaCl \quad (1)$$

Its X-ray crystal structure showed that it had a very short Ge−Mo bond length of 2.271(1) Å, and an almost linear coordination at germanium (Mo−Ge−C = 172.2(2)°), which are consistent with the presence of a Mo≡Ge triple bond. This compound was the first stable species to feature a triple bond to a heavier group 14 element (Si, Ge, Sn, or Pb).[4] The triple bonding description was justified on the basis that the GeMo bond is formed from a 3-fold interaction between the three frontier orbitals (of a and e symmetry)[5] from the 15-electron moiety $Mo(\eta^5\text{-}C_5H_5)(CO)_2$ and the three valence orbitals of the 3-electron fragment GeR which combine to generate a stable 18-electron complex. Although the formulation of the compound as the first transition metal germylyne complex appeared to be fully consistent with the structural data and widely accepted bonding models,[5] there are surprisingly few complexes closely related enough in either stoichiometry or structure to corroborate this bonding picture. For example, there are no structurally characterized compounds of the type $(\eta^5\text{-}C_5H_5)(CO)_3M{-}\ddot{G}e{-}R$ (M = Cr, Mo, or W), which should have M−Ge single bonds and bent geometries at germanium.[6] These compounds are probably produced as intermediates in synthetic routes exemplified by eq 1 prior to

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[1] Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.

[2] Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031.

[3] Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 11966.

[4] The previously known compound $[(\eta^5\text{-}C_5Me_5)(Me_3P)_2RuSi\{(bipy)\text{-}(SC_6H_4\text{-}4\text{-}Me)\}][OTf]_2$, can be formally described as a silylyne complex, but it has four-coordinate silicon. See: Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518.

[5] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

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the elimination of carbon monoxide. Also, further examples of germylynes involving triple bonds to the congeneric transition metals chromium and tungsten would be extremely desirable to compare their structural and spectroscopic parameters. In this paper the synthesis and characterization of several new compounds from these classes are now presented.

Experimental Section

General Procedures All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed twice before use. The compounds $[Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$,[1] $Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$,[7] and $Na[M(\eta^5\text{-}C_5H_5)(CO)_3]\cdot 2DME$ (M= Cr, Mo, W; DME = 1,2-dimethoxyethane)[8] were prepared according to literature procedures. ^1H and ^{13}C NMR data were recorded on a Bruker QE-300 spectrometer and referenced to the deuterated solvent. Infrared data were recorded on a Perkin PE-1430 instrument. UV−vis data were recorded on a Hitachi-1200 instrument. Compounds **1**−**7** afforded satisfactory C, H analyses.

$(\eta^5\text{-}C_5H_5)(CO)_3CrGeC_6H_3\text{-}2,6\text{-}Trip_2$ (1). $Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ (1.30 g, 2.2 mmol) in toluene (30 mL) was added dropwise to a suspension of $Na[Cr(\eta^5\text{-}C_5H_5)(CO)_3]\cdot 2DME$ (0.89 g, 2.2 mmol) in toluene (10 mL) at ca. −78 °C with constant stirring. The reaction mixture, which assumed a green color, was stirred for a further 30 min after which time it was allowed to come to room temperature and stirred for a further 4 h. The toluene was removed under reduced pressure, and the green residue was extracted with hexane (30 mL). After filtering through Celite, the volume of the green solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer to give the product **1** as green crystals. Yield 1.10 g, 66%, decomposes to **2** with CO evolution at 140 °C. ^1H NMR (C_6D_6): δ 1.20 (br, 24H, o-CH(CH_3), J_{HH} = 6.9 Hz), 1.49 (d, 12H, *p*-CH(CH_3), J_{HH} = 6.6 Hz), 2.77 (sept, 2H, *p*-C*H*(CH_3), J_{HH} = 6.6 Hz), 3.55 (broad, 4H, o-C*H*(CH_3)), 3.87 (s, 5H, η^5-C_5H_5), 7.20 (s, 4H, *m*-Trip), 7.40 (mult, 3H, m, *p*-C_6H_3, $J_{AB}/\Delta\nu$ = 0.42). $^{13}C\{^1H\}(C_6D_6)$: δ 23.16 (*o*-CH($CH_3)_2$), 24.09 (*o*-CH($CH_3)_2$), 27.24 (*p*-CH($CH_3)_2$), 31.16 (*o*-*C*H($CH_3)_2$), 34.80 (*p*-*C*H($CH_3)_2$), 89.97 (η^5-C_5H_5), 122.01 (*m*-Trip), 128.29 (*m*-C_6H_3), 129.60 (*p*-C_6H_3), 133.03 (i-Trip), 142.33 (*p*-Trip), 147 (*o*-Trip), 149.76 (*o*-C_6H_3), 173.47 (*i*-C_6H_3), 242.41 (br, CO). IR (Nujol mull): 2018(s), 1970(s,sh), 1950(s), 1935(s), 1898(m,sh), 1878(s) cm^{-1}. UV−vis (hexane): 396 (1980), 609 nm (400).

$(\eta^5\text{-}C_5H_5)(CO)_2CrGeC_6H_3\text{-}2,6\text{-}Trip_2$ (2). A solution of **1** (0.81 g, 1.07 mmol) in toluene (30 mL) was refluxed for 15 min, after which time CO evolution had ceased. The toluene was removed under reduced pressure and the red residue was extracted with pentane (25 mL). After filtration, the red solution was reduced to incipient crystallization and was stored in a ca. −20 °C freezer for 20 h to give the product **2** as red crystals. Yield 0.46 g, 59%, mp 240−242 °C. ^1H NMR (C_6D_6): δ 1.15 (d, 12H, *o*-CH (CH_3), J_{HH} = 6.9 Hz), 1.33 (d, 12H, *o*-CH(CH_3), J_{HH} = 6.9 Hz), 1.53 (d, 12H, *p*-CH(CH_3), J_{HH} = 6.9 Hz), 2.88 (sept, 2H, *p*-C*H*(CH_3), J_{HH} = 6.9 Hz), 2.98 (sept, 4H, *o*-C*H*(CH_3), J_{HH} = 6.9 Hz), 4.15 (s, 5H, η^5-C_5H_5), 7.08 (s, 2H, *m*-C_6H_3), 7.15 (s, 4H, *m*-Trip), 7.29 (s, 2H, *m*-C_6H_3). $^{13}C\{^1H\}(C_6D_6)$: δ 23.86 (*o*-CH($CH_3)_2$), 24.16 (*o*-CH($CH_3)_2$), 25.44 (*p*-CH($CH_3)_2$), 31.43 (*o*-*C*H($CH_3)_2$), 35.03 (*p*-*C*H($CH_3)_2$), 82.88 (η^5-C_5H_5), 122.05 (*m*-Trip), 128.77 (*m*-C_6H_3), 129.83 (*p*-C_6H_3), 133.47 (i-Trip), 142.80 (*p*-Trip), 148.21 (*o*-Trip), 150.08 (*o*-C_6H_3), 168.54 (*i*-C_6H_3), 242.48 (CO). IR (Nujol mull): 1932(s), 1922(s), 1870(s), 1840(sh) cm^{-1}. UV−vis (hexane): 458 nm (2780).

$(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3\text{-}2,6\text{-}Trip_2$ (3). $Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ (0.52 g, 0.88 mmol) in toluene (5 mL) and hexane (30 mL) was added to a suspension of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]\cdot 2DME$ (0.59 g, 1.32 mmol) in toluene (10 mL) at ca. −78 °C with constant stirring. The reaction mixture, which turned green, was allowed to warm to ca. 0 °C and stirred for 30 min. The ice bath was then removed, and stirring was continued for 2 h at room temperature by which time the solution had become red. The toluene was removed under reduced pressure, and the orange residue was extracted with hexane (30 mL). After filtration, the red solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer to give the product **3** as orange-red crystals. Yield 0.41 g, 60%, mp 233−235 °C. ^1H NMR (C_6D_6): δ 1.15 (d, 12H, *o*-CH(CH_3), J_{HH} = 6.9 Hz), 1.34 (d, 12H, *o*-CH(CH_3), J_{HH} = 6.9 Hz), 1.53 (d, 12H, *p*-CH(CH_3), J_{HH} = 6.9 Hz), 2.97 (mult, 6H, *p*-C*H*(CH_3), *o*-C*H*(CH_3), J_{HH} = 6.9 Hz), 4.65 (s, 5H, η^5-C_5H_5), 7.09 (mult, 3H, m, *p*-C_6H_3, $J_{AB}/\Delta\nu$ > 2.0), 7.28 (s, 4H, *m*-Trip). $^{13}C\{^1H\}(C_6D_6)$: δ 23.83 (o-CH($CH_3)_2$), 24.15 (*o*-CH($CH_3)_2$), 25.41 (*p*-CH($CH_3)_2$), 31.40 (*o*-*C*H($CH_3)_2$), 34.97 (*p*-*C*H($CH_3)_2$), 86.06 (η^5-C_5H_5), 121.91 (*m*-Trip), 128.85 (*m*-C_6H_3), 130.12 (*p*-C_6H_3), 133.33 (i-Trip), 143.39 (*p*-Trip), 148.15 (*o*-Trip), 150.07 (*o*-C_6H_3), 167.15 (*i*-C_6H_3), 231.37 (CO). IR (Nujol mull): 1960(w,sh), 1940(s), 1930(s), 1875(s), 1840(w,sh) cm^{-1}. UV−vis (hexane): 417 nm (1700).

$(\eta^5\text{-}C_5H_5)(CO)_3WGeC_6H_3\text{-}2,6\text{-}Trip_2$ (5). $Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ (0.54 g, 0.91 mmol) in toluene (25 mL) was added to $Na[W(\eta^5\text{-}C_5H_5)(CO)_3]\cdot 2DME$ (0.58 g, 1.08 mmol) in toluene (10 mmol) at ca. −78 °C with constant stirring. The green reaction mixture was stirred at ca. −78 °C for 30 min, and then was warmed to room temperature and stirred for a further 4 h. The toluene was removed under reduced pressure, and the green residue was extracted with hexane (30 mL). After filtering through Celite, the green solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer to give the product **5** as green crystals. Yield 0.44 g, 55%, mp 159−160 °C (CO evolution). ^1H NMR (C_6D_6): δ 1.20 (d, 6H, *o*-CH(CH_3), J_{HH} = 5.4 Hz), 1.32 (d, 12H, *o*-CH(CH_3), J_{HH} = 6.6 Hz), 1.37 (d, 6H, *o*-CH(CH_3), J_{HH} = 5.4 Hz), 1.57 (d, 12H, *p*-CH(CH_3), J_{HH} = 6.3 Hz), 2.87 (sept, 2H, *p*-C*H*(CH_3), J_{HH} = 6.9 Hz), 3.60 (broad mult, 2H, *o*-C*H*(CH_3)), 3.75 (broad mult, 2H, *o*-C*H*(CH_3)), 4.51 (s, 5H, η^5-C_5H_5), 7.28 (s, 4H, *m*-Trip), 7.46 (mult, 3H, m, *p*-C_6H_3, $J_{AB}/\Delta\nu$ = 0.48). $^{13}C\{^1H\}(C_6D_6)$: δ 23.12 (*o*-CH($CH_3)_2$), 23.56 (*o*-CH($CH_3)_2$), 24.14 (o-CH($CH_3)_2$), 26.58 (o-CH($CH_3)_2$), 27.79 (*o*-CH($CH_3)_2$), 30.14 (*o*-*C*H($CH_3)_2$), 31.47 (*o*-*C*H($CH_3)_2$), 34.97 (*p*-*C*H($CH_3)_2$), 92.77 (η^5-C_5H_5), 92.82 (η^5-C_5H_5), 121.28 (m-Trip), 122.69 (*p*-Trip), 128.32 (*m*-C_6H_3), 129.59 (*m*-C_6H_3), 133.10 (i-Trip), 141.96 (*p*-Trip), 146.41 (*o*-Trip), 148.10 (*o*-Trip), 149.45 (*o*-C_6H_3), 170.98 (*i*-C_6H_3), 217.39 (br, CO). IR (Nujol mull): 2022(m), 1974(s), 1950(m,sh), 1935(w), 1902(w), 1885(s) cm^{-1}. UV−vis (hexane): 420(sh) (2270), 611 nm (870).

$(\eta^5\text{-}C_5H_5)(CO)_2WGeC_6H_3\text{-}2,6\text{-}Trip_2$ (6). A green solution of **5** (0.44 g, 0.50 mmol) in hexane (35 mL) was irradiated with UV light in a quartz Schlenk tube for 2 h. The hexane was removed under reduced pressure and the red residue was extracted with pentane (20 mL). After filtering, the red solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer to give the product **6**, as orange-red crystals. Yield 0.23 g, 53.5%, mp 214−216 °C. ^1H NMR (C_6D_6): δ 1.46 (d, 12H, *o*-CH(CH_3), J_{HH} = 6.9 Hz), 1.34 (d, 12H, *o*-CH(CH_3), J_{HH} = 6.9 Hz), 1.53 (d, 12H, *p*-CH(CH_3), J_{HH} = 6.9 Hz), 2.96 (mult, 6H, *p*-C*H*(CH_3), *o*-C*H*(CH_3), J_{HH} = 6.9 Hz), 4.60 (s, 5H η^5-C_5H_5), 7.09 (mult, 3H, m, *p*-C_6H_3, $J_{AB}/\Delta\nu$ > 2.0), 7.28 (s, 4H, m-Trip). $^{13}C\{^1H\}(C_6D_6)$: δ 23.65 (*o*-CH($CH_3)_2$), 24.15 (*p*-CH($CH_3)_2$), 25.44 (*o*-CH($CH_3)_2$), 31.43 (*o*-*C*H($CH_3)_2$), 34.40 (*p*-*C*H($CH_3)_2$), 84.30 (η^5-C_5H_5), 121.89 (*m*-Trip), 129.44 (*m*-C_6H_3), 129.88 (*p*-C_6H_3), 133.68 (i-Trip), 143.74 (*p*-Trip), 148.13 (*o*-Trip), 150.07 (*o*-C_6H_3), 168.99 (*i*-C_6H_3) (J_{cw} = $^{13}C-^{183}W$ = 48 Hz), 219.90 (CO, J_{cw} = $^{13}C-^{183}W$ = 93 Hz). IR (Nujol mull): 1952(m), 1932(s), 1922(s), 1890(w), 1863(s), 1840(sh) cm^{-1}. UV−vis (hexane): 407 (3760), 517(sh) nm (430).

$(\eta^5\text{-}C_5H_5)(CO)_2WGeC_6H_3\text{-}2,6\text{-}Mes_2$ (7). $[Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$ (0.27 g, 0.32 mmol) in toluene (20 mL) was added to $Na[W(\eta^5\text{-}C_5H_5)(CO)_3]\cdot 2DME$ (0.34 g, 0.64 mmol) in toluene (10 mL) at ca. −78 °C with constant stirring. The green reaction mixture was allowed to warm to room temperature and was stirred for a further 1 h. The toluene was removed under reduced pressure, and the green residue was extracted with hexane (30 mL). After filtering through Celite, the greenish red solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer to give the product **7**, as red crystals. Yield 0.18 g, 40.9%, mp 158−160 °C. ^1H NMR (C_6D_6): δ 2.15 (s, 12H, *o*-CH_3), 2.22 (s, 6H, *p*-CH_3), 4.65 (s, 5H, η^5-C_5H_5), 6.93 (s, 4H, *m*-Mes), 6.89 (d, 2H, *m*-C_6H_3, J_{HH} = 7.5 Hz), 7.22 (t, 1H, *p*-C_6H_3, J_{HH} = 7.5 Hz).

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[6] Metallogermylene derivatives of iron have been synthesized but no structures have been published. See: Jutzi, P.; Leue, C. *Organometallics* **1994**, *13*, 2898.

[7] Pu, L.; Olmstead, M. M.; Power, P. P.; Schiemenz, B. *Organometallics* **1998**, *17*, 5602.

[8] Braunstein, P.; Bender, R.; Jud, J. *Inorg. Synth.* **1989**, *26*, 341.

Table 1. Selected Crystallographic Data for Compounds **1**, **2**, **3**·0.5 Methylcyclopentane, **5**, and **7**

	1	**2**	**3**·0.5 methylcyclopentane	**5**	**7**
formula	$C_{44}H_{54}GeCrO_3$	$C_{43}H_{54}GeCrO_2$	$C_{46}H_{60}GeMoO_2$	$C_{44}H_{54}GeWO_3$	$C_{31}H_{30}GeWO_2$
fw	755.46	727.45	813.47	887.31	690.99
crystal color/habit	green, plate	red, block	red, parallelepiped	green, parallelepiped	red, parallelepiped
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
space group	*Pnma*	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$I2/a$
a (Å)	15.611(3)	9.5217(5)	9.529(2)	8.651(2)	17.2849(14)
b (Å)	23.872(5)	9.5594(5)	17.936(4)	21.323(4)	16.5583(13)
c (Å)	10.654(2)	21.368(1)	27.064(5)	21.941(4)	19.8218(15)
a (deg)		80.859(1)			
b (deg)		85.880(1)	98.36(3)	97.31(3)	103.864(7)
γ (deg)		88.574(1)			
V (Å^3)	3970.2(14)	1915.1(2)	4576.4(16)	4014.5(14)	5507.9(7)
Z	4	2	4	4	8
cryst dims, mm	0.34 × 0.20 × 0.1	0.46 × 0.18 × 0.08	0.40 × 0.36 × 0.34	0.26 × 0.12 × 0.04	0.2 × 0.1 × 0.06
d_{calc} (Mg/m^3)	1.264	1.261	1.181	1.416	1.667
μ (mm^{-1})	3.465	1.102	0.962	6.416	9.137
no. of data	2698	11548	10512	5101	3647
obsd data $I > 2(\sigma)I$	1829	7882	6733	2301	2830
no. of params.	256	424	440	454	322
$R1$(obsd)	0.0677	0.0406	0.0613	0.0873	0.0551
$wR2$(all data)	0.1874	0.0929	0.1791	0.2899	0.1528

$^{13}C\{^1H\}(C_6D_6)$: δ 20.89 (o-CH_3), 21.17 (p-CH_3), 84.44 (η^5-C_5H_5), 128.76 (m-Mes), 129.16 (p-C_6H_3), 131.22 (m-C_6H_3), 135.80 (p-Mes), 136.94 (o-Mes), 138.43 (i-Mes), 144.60 (o-C_6H_3), 166.92 (i-C_6H_3), (J_{cw} = $^{13}C-^{183}W$ = 46 Hz), 219.48 (CO, J_{cw} = $^{13}C-^{183}W$ = 94 Hz). IR (Nujol mull): 2008(w), 1935(s,sh), 1875(s,sh), 1920(s), 1850(s) cm^{-1}. UV−vis (hexane): 407 (2660), 517(sh) nm (460).

X-ray Crystallography. Sample preparation consisted of coating the crystal with hydrocarbon oil, mounting it on a glass fiber, and placing it under a cold stream of N_2 on the diffractometer.[9] All data were collected using the following instruments: compounds **1**, **5**, and **7**, Siemens P4RA (Cu Kα radiation); compound **2**, Bruker SMART 1000 (Mo Kα radiation and a CCD area detector); and compound **3**, Siemens R3 (Mo Kα radiation). The SHELXTL program suite[10] was used for structure solution and refinement. Absorption corrections for compounds **1**, **3**, **5**, and **7** were applied using the program XABS2.[11] The SADABS program[12] was used for compound **2**. The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. The structure of **1** was subject to disorder of the peripheral organic groups which could be modeled successfully using partial occupancies for the disordered atoms as described in the Supporting Information. Some details of the data collection and refinement are given in Table 1. Compound **3** crystallized from hexane as the solvate **3**·0.5 methylcyclopentane. The latter comprises a significant fraction (ca. 10%) of the “hexanes” employed as solvent in these experiments.

Results and Discussion

Synthesis. The reaction of the bulky terphenylgermanium(II) halide Ge(Cl){C_6H_3-2,6-Trip$_2$} with Na[M(η^5-C_5H_5)(CO)$_3$]·2DME (M = Cr or W) in toluene produces the metallogermylene products **1** and **5** as shown by eq 2.

$$\mathrm{Na[M(\eta^5\text{-}C_5H_5)(CO)_3]\cdot 2DME} + \mathrm{Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}} \xrightarrow{\text{PhMe, }-78\text{ to }25\,°\text{C}} \underset{\mathbf{1},\ \mathrm{M = Cr};\ \mathbf{5},\ \mathrm{M = W}}{\mathrm{(\eta^5\text{-}C_5H_5)(CO)_3M{-}\ddot{G}e{-}C_6H_3\text{-}2,6\text{-}Trip_2}} + \mathrm{NaCl} \quad (2)$$

The simultaneous elimination of carbon monoxide previously reported in eq 1 is avoided in this reaction (eq 2) by maintaining the reaction mixture at or below room temperature. The attempted synthesis of a molybdenum analogue of **1** and **5** by performing the reaction of Ge(Cl){C_6H_3-2,6-Trip$_2$}[7] with Na[Mo(η^5-C_5H_5)(CO)$_3$]·2DME[8] under identical conditions led directly to the product **3** as illustrated by eq 3.

$$\mathrm{Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]\cdot 2DME} + \mathrm{Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}} \xrightarrow[-\mathrm{CO}]{\text{PhMe, }-78\text{ to }25\,°\text{C}} \underset{\mathbf{3}}{\mathrm{(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Trip_2}} + \mathrm{NaCl} \quad (3)$$

Compound **3** is isolated even if the temperature of the solution is maintained below 0 °C throughout the synthesis. It appears therefore that the putative, intermediate tricarbonyl species (η^5-C_5H_5)(CO)$_3$M−G̈e−C_6H_3-2,6-Trip$_2$ spontaneously undergoes elimination of carbon monoxide at temperatures ≤0 °C. This germylene complex also seems to be unstable at lower temperatures where the color of the reaction mixture changes from green to red at ca. −20 °C. Compound **3** differs from **4** only in that it bears the larger terphenyl substituent −C_6H_3-2,6-Trip$_2$ instead of −C_6H_3-2,6-Mes$_2$.

In contrast to the apparent instability of the molybdenum tricarbonyl derivatives, which readily eliminate carbon monoxide to give **3** or **4**, the chromium and tungsten tricarbonyl compounds **1** and **5** only undergo a similar reaction under more forcing conditions as shown in eq 4.

$$\underset{\mathbf{1},\ \mathrm{M = Cr};\ \mathbf{5},\ \mathrm{M = W}}{\mathrm{(\eta^5\text{-}C_5H_5)(CO)_3M{-}\ddot{G}e{-}C_6H_3\text{-}2,6\text{-}Trip_2}} \xrightarrow[-\mathrm{CO}]{\text{reflux PhMe or }h\nu} \underset{\mathbf{2},\ \mathrm{M = Cr};\ \mathbf{6},\ \mathrm{M = W}}{\mathrm{(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge{-}C_6H_3\text{-}2,6\text{-}Trip_2}} \quad (4)$$

The difference in reactivity between the chromium, molybdenum, and chromium or tungsten species is not easy to explain although it is known that carbonyls of molybdenum are usually more reactive than those of tungsten or chromium.[13] However, this difference should not obscure the fact that CO elimination

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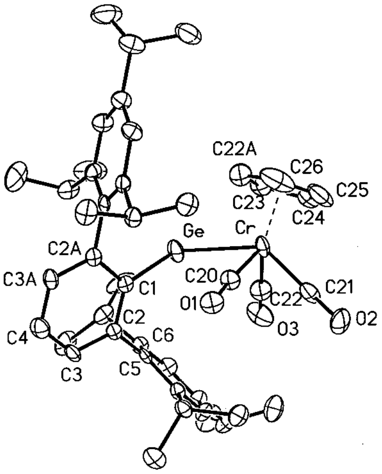

Figure 1. Drawing of the germylene **1**. H atoms are not shown. Important structural parameters are in Table 1.

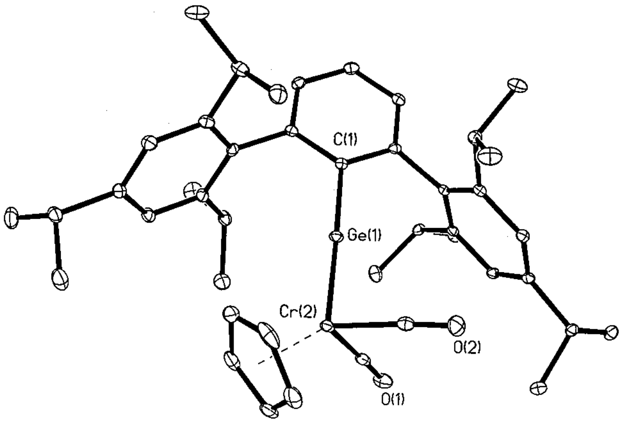

Figure 2. Drawing of germylyne **2**. H atoms are not shown. Important structural parameters are in Table 1.

takes place under relatively mild conditions in all complexes. This can be attributed to large sizes of the terphenyl substituents which tend to promote the elimination of CO to reduce steric crowding.

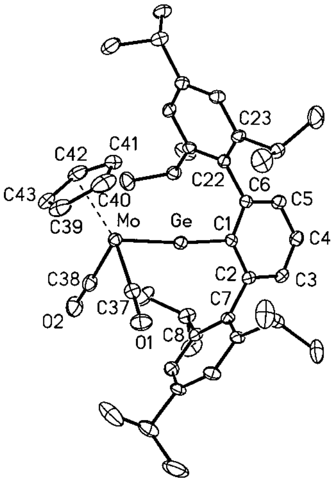

Figure 3. Drawing of germylyne **3**. H atoms are not shown. Important structural parameters are in Table 1.

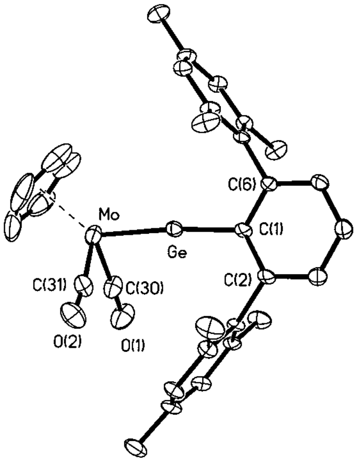

Figure 4. Drawing of germylyne **4**. H atoms are not shown. Important structural parameters are in Table 1.

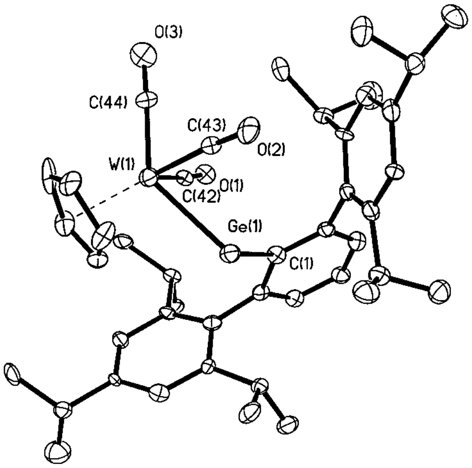

Figure 5. Drawing of germylene **5**. H atoms are not shown. Important structural parameters are in Table 1.

Structural Data and Bonding. The structures of **1** and **5** are illustrated in Figures 1 and 5 and some important structural data are listed in Table 2. Although the crystals of the two compounds are not isomorphous, their structures are quite similar. The most important parameters are the Cr−Ge (2.590(2) Å) and W−Ge (2.681(3) Å) bond lengths and the angles C−Ge−Cr = 117.9(3)° and C−Ge−W = 114.7(6)°. The bent geometries at germanium in both compounds are consistent with the presence of a stereochemically active lone pair and a divalent germanium(II) center which is singly bonded to carbon and either chromium or tungsten. The metal−germanium bond distances may be compared with the values 2.50 and 2.61 Å which are predicted from the sum of the transition metal radii and germanium covalent radius (Cr, 1.28 Å; W, 1.39 Å; Ge, 1.22 Å).[14] There do not appear to exist any structurally characterized molecules with single bonds between germanium and chromium. However, the formally double-bonded germylene (germanediyl) complexes $(CO)_5CrGe\{CH(SiMe_3)_2\}_2$[15] (Cr−Ge = 2.378(4) Å), $(OC)_5CrGe(SMes)_2$[16] (Cr−Ge = 2.367(2) Å), and $(CO)_5CrGe(tmtaa)$[17] (Cr−Ge = 2.500(2) Å, tmtaa = dibenzotetramethyltetraaza[14]annulene) all show considerably shorter Cr−Ge distances than that in **1**. This is especially true

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds **1**−**5**, and **7**

	1				**2**		
Ge−C(1)	1.989(8)	C(1)−Ge-Cr	117.8(2)	Ge−C(1)	1.9512(18)	C(1)−Ge-Cr(2)	175.99(6)
Ge−Cr(2)	2.590(2)	C(2)−C(1)-Ge	119.3(4)	Ge−Cr	2.1666(4)	Ge−C(1)−C(2)	120.25(14)
Cr−C(20)	1.833(10)			Cr(2)−C(42)	1.850(2)	Ge−C(1)−C(6)	117.86(13)
Cr−C(22)	1.889(16)			Cr(2)−C(43)	1.846(2)		
Cr−C(η^5-C_5H_5) (av.)	2.13(2)			Cr(2)−C(η^5-C_5H_5) (av.)	2.190(5)		
C−O (av.)	1.15(1)			C−O (av.)	1.151(6)		
	3				**4**		
Ge−C(1)	1.936(5)	C(1)−Ge-Mo	174.25(14)	Ge−C(1)	1.933(7)	C(1)−Ge-Mo	172.2(2)
Ge−Mo	2.272(8)	C(2)−C(1)-Ge	117.8(4)	Ge−Mo	2.271(1)	C(2)−C(1)-Ge	120.6(5)
Mo−C(37)	1.959(5)	C(6)−C(1)-Ge	119.9(4)	Mo−C(30)	1.950(9)	C(6)−C(1)-Ge	117.9(6)
Mo−C(38)	1.974(6)			Mo−C(31)	1.960(13)		
Mo−C(η^5-C_5H_5) (av.)	2.335(7)			Mo−C(η^5-C_5H_5) (av.)	2.33(3)		
C−O (av.)	1.149(6)						
	5				**7**		
Ge−C(1)	1.99(2)	C(1)−Ge(1)-W(1)	114.7(6)	Ge−C(1)	1.916(11)	C(1)−Ge-W	170.9(3)
Ge−W	2.681(3)	C(2)−C(1)-Ge(1)	115.4(2)	Ge−W	2.2767(14)	C(2)−C(1)-Ge	117.8(8)
W−C(42)	2.00(2)	C(6)−C(1)-Ge(1)	121.4(2)	W−C(25)	1.92(2)	C(6)−C(1)-Ge	121.8(8)
W−C(43)	1.99(2)			W−C(26)	1.946(15)		
W−C(44)	1.98(2)			W−C(η^5-C_5H_5) (av.)	2.32(2)		
W−C(η^5-C_5H_5) (av.)	2.35(2)			C−O (av.)	1.18(2)		
C−O (av.)	1.16(3)						

for the first two complexes[15,16] that have three-coordinate germanium where some multiple character in the Cr−Ge bond is quite probable. The Cr−C(CO) distances in **1** are essentially identical with the average value, 1.86(1) Å, observed in the dimer $\{Cr(\eta^5\text{-}C_5H_5)(CO)_3\}_2$[18] although the average Cr−C (η^5-C_5H_5) bond length, 2.13 Å, is slightly shorter than the 2.20 Å in $\{Cr(\eta^5\text{-}C_5H_5)(CO)_3\}_2$. The CO bonds in **1** (1.15(1) Å) are slightly longer (within two standard deviations however) than the 1.143(2) Å observed in the dimer $\{Cr(\eta^5\text{-}C_5H_5)(CO)_3\}_2$. The structure of the Cr−Cr dimer is notable for its long Cr−Cr distance of 3.281(1) Å[18] which, if extrapolated to **1**, would suggest that the Cr−Ge distance should be 2.86 Å. However, it seems probable that, in the structure of **1**, the effects causing the elongation of the Cr−Cr bond are not present.

The W−Ge distance, 2.681(3) Å, in **5** is ca. 0.09 Å longer than the Cr−Ge distance in **1**. This is approximately equal to the difference 0.11 Å in their metallic radii (1.28 vs 1.39 Å).[14] Several complexes featuring W−Ge single bonds have been characterized. These include the species η^5-$C_5H_5(CO)_3WGeCo_2(CO)_3Mo(\eta^5\text{-}C_5H_5)(CO)_2$[19] (W−Ge = 2.589(4) Å), $(\eta^5\text{-}C_5H_5)_2W(H)(\mu^2\text{-}GeMe_2)(\mu\text{-}GeMe)(\mu{-}\eta^5\text{-}C_5H_4)W(\eta^5\text{-}C_5H_5)$[20] (W−Ge = 2.605(2) Å), $W_2(GePh_3)_2(NMe_2)_4$[21] (W−Ge = 2.625(1) Å), and $(\eta^5\text{-}C_5H_5)_2W(SiMe_3)Ge(Me_2Cl)$[22] (W−Ge = 2.542(1) Å), which have W−Ge single bonds, and the formally double-bonded germylene (germanediyl) complexes, $(CO)_5WGe(Cl)(\eta^2\text{-}C_5Me_5)$[23] (W−Ge = 2.571(1) Å), $(CO)_5WGe(\eta^2\text{-}C_5H_5)\{CH(SiMe_3)_2\}$[24] (W−Ge = 2.632(4) Å), $(OC)_5WGe(SeMes^*)_2$[25] (W−Ge = 2.528(1) Å, Mes* = C_6H_2-2,4,6-*t*-Bu_3), $(CO)_5WGe(Tbt)Trip$[26] (W−Ge = 2.5934(8) Å, Trip = −C_6H_2-2,4,6-*i*-Pr_3, Tbt = C_6H_2-2,4,6-$\{CH(SiMe_3)_2\}_3$). In addition, there is the ion $[W(CO)_5(GeH_3)]^-$ which was reported[27] to have an unusually short W−Ge distance of 2.39 Å. Like the Cr−Ge distance in **1**, the W−Ge bond in **5** is the longest bonding distance reported for this pair of atoms. While the generally shorter Cr−Ge and W−Ge distances in the germylene complexes can be accounted for in terms of the multiple character of the M−Ge bond, it is difficult to explain why the W−Ge bond in **5** is ca. 0.1 Å longer than the formally single W−Ge bonds as well. It is possible that the apparent lengthening in **5** (and **1**) is due to the large size of the −C_6H_3-2,6-$Trip_2$ substituent. However, it may be noted that if the estimation of the W−Ge bond distance were to be based on the tungsten radius given by the structure of $\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2$ (W−W = 3.222(1) Å),[28] i.e., 1.61 Å, then a W−Ge bond length of 2.83 Å would be calculated. Although the number of available structures is not large, the known variation in W−Ge single bond lengths is 0.14 Å, i.e., the range 2.542(1)−2.681(3) Å is quite significant. The W−C (CO) and W−C (η^5-C_5H_5) distances in **5** (1.99(2) and 2.35(2) Å) are essentially the same as those observed in the structure of the dimer $\{W(\eta^5\text{-}C_5H_5)(CO)_2\}_2$.

Compounds **1** and **5** are also notable in the sense that they are the first structurally characterized metallogermylenes. Previous, spectroscopically characterized examples[6] include the compounds $(\eta^5\text{-}C_5R_5)(CO)_2FeGeMes^*$ (R = H or Me) and the closely related species $(\eta^5\text{-}C_5H_5)(CO)_2FeGeCH(SiMe_3)_2$.

The complexes **1** and **5** are converted into **2** (Figure 2) and **6** with elimination of CO by refluxing them in toluene. Compound **7** (Figure 6), which could be obtained by photolysis or refluxing in PhMe, differs from **6** only in the smaller size of its terphenyl group. The mechanism of this elimination reaction is currently unknown, but it is probable that CO is dissociated from the more crowded tricarbonyl molecule under the influence of the availability of the germanium lone pair and the large germanium substituents which compensate for the loss of CO by generating a triple bond between the group 6 metal and germanium. Apparently, the strength of the germanium metal π-bonds is more than sufficient to conpensate for the linearization barrier at germanium. The generation of a triple bond, with concomitant ligand elimination, is in some respects related to the rearrangement of vinyl complexes to give carbynes[29] such

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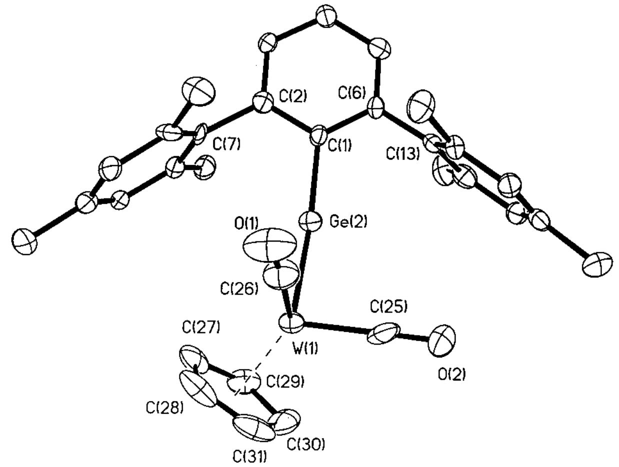

Figure 6. Drawing of germylyne **7**. H atoms are not shown. Important structural parameters are in Table 1.

as that shown in eq 5.

$$(\eta^5\text{-C}_5\text{H}_5)(\text{L})_3\text{Mo}{-}\text{C(H)}{=}\text{C(H)}(t\text{-Bu}) \xrightarrow[25\ ^\circ\text{C}]{-\text{L}} (\eta^5\text{-C}_5\text{H}_5)(\text{L})_2\text{Mo}{\equiv}\text{C}{-}\text{CH}_2(t\text{-Bu}) \qquad \text{L} = \text{P(OMe)}_3 \tag{5}$$

In the germylyne molecule **2**, the Cr−Ge distance (2.166(4) Å) is shortened by ca. 0.42 Å with respect to the Cr−Ge distance in **1**. Moreover, the Cr−Ge−C angle has widened to the almost linear value of 175.99(6)°. The Ge−C bond in **2** is also 0.047 Å shorter than the corresponding distance in **1**. This suggests that some of the shortening in the Cr−Ge bond is due to rehybridization of the valence orbitals at germanium, owing to the change in its geometry from bent to linear. Even so, it can be assumed that the major part, ca. 0.35 Å, of the shortening in this bond is due to the extra two bonding interactions as suggested in the Introduction. In other words, the structural data fully support the characterization of the bond as a triple one. The Cr−C (CO) bonds in **2** (av 1.848(2) Å) are almost the same length as those in **1** and in the $\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2$ dimer.[18] The CO bond lengths in **1**, **2**, and the dimer are also very similar.

Unfortunately, a satisfactory X-ray data set was not obtained for compound **6**. This was, most probably, a result of the inclusion of disordered solvent molecules and possibly some singly bonded **5** in the crystalline sample employed. Instead, the structural data for **5** may be compared with those of compound **7** which is closely related to **6**. As already mentioned, the only difference between **6** and **7** concerns the terphenyl substituent which in the case of **7** is the less bulky $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$. The change of substituent is not expected to have a large effect on the important structural parameters, however, and this is borne out by the two molybdenum compounds **3** and **4** which differ only in their terphenyl substituents but (as will be seen) have very similar structures. The W−Ge distance in **7** is 2.277(1) Å which, like the Cr−Ge distance in **2**, is more than 0.4 Å shorter than the single W−Ge bond in **5**. The W−Ge−C angle has widened to 170.9(3)° and the Ge−C distance is 1.92(1) Å, which is ca. 0.07 Å shorter than the Ge−C bond in **5** and is at the shorter end of the range of Ge−C bond lengths.[30] Clearly, the structural pattern in **7** is very similar to that seen in **2**. The major difference between the structures is in the lengths of the Cr−Ge and W−Ge bonds which now differ by ca. 0.11 Å. This is slightly greater than the ca. 0.09 Å difference between **1** and **5** but is in exact agreement with the difference in metallic radii between chromium and tungsten.[14] The W−C (CO) distances in **7** (av 1.93(2) Å) are significantly shorter than the corresponding ones in **5** although the W−C (η^5-C_5H_5) and CO bond lengths in the complexes are within two standard deviations of each other.

The previously reported[3] molybdenum compound **4** has a Mo−Ge bond length of 2.271(1) Å and an interligand angle of 172.2(2)° at germanium. These two parameters are very close to the 2.272(8) Å and 174.25(14)° observed in the structure of **3**. The structural data also show that, provided both ligands are large enough to stabilize the monomeric structure, there is little change in the length of the Mo≡Ge triple bond. Comparison of the other structural parameters of **3** and **4** also underlines their similarity. The average Mo−C (CO) distances differ by only 0.01 Å and the Mo−C(η^5-C_5H_5) bond lengths are essentially identical. Even the almost linear angles at germanium differ by only ca. 2°. The Mo≡Ge triple bond lengths in **3** and **4** are ca. 0.35 to 0.4 Å shorter than Mo−Ge single bond lengths in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo(GePh}_3)\{\text{C(OEt)Ph}\}$[31] (Mo−Ge = 2.658(2) Å) or $(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_6\text{H}_{11})(\text{NO})\text{MoGePh}_3$[32] (Mo−Ge = 2.604(2) Å).

The drawings in Figures 1−6 illustrate the steric protection afforded the germanium centers in the cavity formed by the *o*-aryl groups of the terphenyl ligands. However, the structural data do not provide evidence of severe distortion in the structural parameters. For example, the two Ge−C−C angles at the ipso-carbon of the terphenyl ligands differ by only a few degrees in **1**−**7**. In general these angles might have been expected to show greater differences if there were excessive steric congestion or interactions involving the *o*-aryl groups.[1] It is true that the M−C (η^5-C_5H_5) distances to carbons closest to the terphenyl ligand are slightly longer than those further away but the differences are generally not great. In addition, the M−C−O moieties in **1**−**7** do not deviate greatly from linearity.

Spectroscopic Studies. The infrared spectra of the metallogermylenes **1** and **5** bear a relatively close resemblance to each other in the carbonyl region. Each compound features a medium to strong intensity band near 2020 cm^{-1} and a series of bands between ca. 1975 and 1875 cm^{-1} that are either well-resolved or appear as shoulder features with maxima that differ in frequency by no more than 2−7 cm^{-1}. This pattern is similar to that observed for the parent dimeric complexes $\{\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2$. For example, the infrared spectrum[8] of $\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2$ in chloroform solution displays peaks at 2012, 1948, 1925, 1913, and 1880 cm^{-1} (cf. 2018, 1950, 1935, 1898, and 1878 cm^{-1} in **1**). These data suggest that electronic properties of the $\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}$ and $\{\text{GeC}_6\text{H}_3\text{-2,6-Trip}_2\}$ moieties are similar to each other in these molecules. The GeC_6H_3-2,6-Trip_2 moiety formally has an empty p-orbital when attached to the transition metal fragment $\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}$ and does not seem to engage in any strong interaction with the transition metal centered d-orbitals. In the infrared spectra of the germylyne complexes **2**−**4**, **6**, and **7**, the main features consist of two moderately broad bands centered near 1930 and 1875 cm^{-1}. These values may be contrasted with those of the related aryl-

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substituted carbyne complexes[33] which, for the series (η^5-C_5H_5)-$(CO)_2M\equiv C-C_6H_3$-2,6-Me_2 (M = Cr, Mo, or W), are observed at 1992 and at 1919−1924 cm^{-1}. The significantly higher frequencies (ca. 60 and 45 cm^{-1}) seen for the bands of the carbyne molecules suggest that the germylyne ligand is probably a weaker p-acceptor than the carbyne ligand. This property of the germylyne ligand may be due to the more electropositive character of germanium and possibly the relatively low energy of the germanium s-orbital which may be close enough in energy to the frontier orbitals of the $\{M(\eta^5\text{-}C_5H_5)(CO)_3\}$ fragment to permit a relatively strong interaction. On the other hand, the germanium p-orbitals are expected to be at significantly higher energy which would afford a less efficient interaction with the frontier orbitals of the transition metal moiety.

The UV−vis spectra of the metallogermylenes **1** and **5** are characterized by two bands. The higher energy band, centered at 396 nm in **1** and at 420 nm in **5**, can be attributed to the n → p transition since they have similar energies to bands for other two-coordinate aryl germanium species; e.g. 393 and 430 nm for the germylenes Ge(Cl)C_6H_3-2,6-$Trip_2$[7] and $GeMes^*_2$.[34] The other less intense band in the spectra of **1** and **5** appears at 609 and 611 nm, respectively. These are tentatively asigned to interorbital transitions located mostly on the chromium or tungsten moiety. The UV−vis spectra of **2**−**4** and **6** and **7** all feature a single prominent band, in the range 407−458 nm, with a weak shoulder (possibly due to d−π^* transitions) being observed for both **6** and **7** at 517 nm. For the series of complexes (η^5-C_5H_5)$(CO)_2M\equiv Ge-C_6H_3$-2,6-$Trip_2$ (M = Cr, Mo or W) the major band appears at 458 (Cr), 417 (Mo), and 407 nm (W). Since the energy of this absorption increases with increasing atomic number it is a possibility that it may be associated with the M≡Ge bond and involve transitions from π to π^* orbitals since bond strengths usually increase in the sequence first < second < third row for transition metal complexes.[13]

The ^1H and ^{13}C NMR spectra of **1**−**7** are of use in their characterization and establishing purity. In the ^1H NMR spectra, the η^5-C_5H_5 resonance appears in the range δ 4.51−4.70 for the molybdenum and tungsten derivatives but at higher field, δ 3.87 and 4.15, for the chromium derivatives **1** and **2**. The chemical shifts of the terphenyl protons do not permit a similar distinction although some of these resonances show evidence of broadening, probably as a result of restricted rotation of the terphenyl group caused by steric congestion. Attempted measurement of the energy barriers associated with this process was unsuccessful owing to decomposition of **1** and **2** into **5** and **6** during heating of the solutions. The ^{13}C NMR spectra, having greater dispersion, could in principle be more readily used as a diagnostic tool. The usually distinctive C(ipso) resonance appears at δ 173.5 and 170.98 for the germylene complexes **1** and **5** whereas for the germylyne complexes **2**−**4** and **6** and **7** it appears more upfield in the range δ 165.03−168.99. Although no ^{183}W NMR signals have been detected so far, coupling of this nucleus to the C(ipso) signal in the ^{13}C NMR spectra of **6** (48 Hz) and **7** (46 Hz) is detectable. Significantly perhaps, these values are similar to the couplings observed in related tungsten−carbyne complexes, e.g. 38 Hz in (η^5-C_5H_5)(CO)$W\equiv C-C_6H_3$-2,6-Me_2.[33]

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Supporting Information Available: Tables of data-collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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