

(η^5 -C₅H₅)(CO)₂MoGeC₆H₃-2,6-Mes₂: A Transition-Metal Germlyne Complex

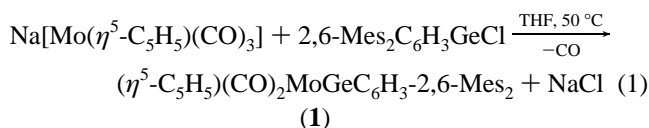
Richard S. Simons and Philip P. Power*

Department of Chemistry, University of California
Davis, California 95616

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Triple bonding between transition elements is a feature commonly encountered in several classes of dimetal complexes.¹ For the most part such bonding is homonuclear, whereas heteronuclear triple bonding is generally confined to species with bonds to first row main group elements, as exemplified in carbyne² or nitrido complexes.³ Rare exceptions to this generalization are the recently reported phosphido derivatives Mo(P)(NRAr)₃⁴ (R = -C(CD₃)₂CH₃, Ar = 3,5-(CH₃)₂C₆H₃-) and W(P)(NN₃)⁵ (NN₃ = {(Me₃SiNCH₂CH₂)₃N}³⁻) which feature formal triple bonds between phosphorus and molybdenum or tungsten. Despite the existence of the donor stabilized silylyne complex [(η^5 -C₅Me₅)(Me₃P)₂RuSi{(bipy)(SC₆H₄-4-Me)}][OTf]₂,⁶ in which the silicon is four-coordinate, no transition complexes featuring triple bonds to the heavier elements of the carbon group (i.e., Si, Ge, Sn, or Pb) have been isolated as stable molecules. In this paper the synthesis and characterization of (η^5 -C₅H₅)(CO)₂MoGeC₆H₃-2,6-Mes₂ (**1**), which contains a molybdenum–germanium triple bond, is now described.

The compound (**1**) was synthesized⁷ in THF solution by treatment of Na[Mo(η^5 -C₅H₅)(CO)₃] with 2,6-Mes₂C₆H₃GeCl (generated in situ) as shown in eq 1



The formula of **1** was established by spectroscopic and structural

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(7) (a) All manipulations were carried out under anaerobic and anhydrous conditions. Na[Mo(η^5 -C₅H₅)(CO)₃] (2 mmol), prepared in THF solution (20 mL) by a literature procedure,^{7b} was added by cannula to a rapidly stirred THF solution (20 mL) of 2,6-Mes₂C₆H₃GeCl, prepared in situ from 2,6-Mes₂C₆H₃Li^{7c} (0.64 g, 2.0 mmol) and GeCl₂dioxane^{7d} (0.46 g, 2.0 mmol), at room temperature. The solution was heated to ca. 50 °C and stirred for 2 h. The volatile materials were then removed under reduced pressure. The dark red residue was extracted with hexane (50 mL) and filtered through Celite. The filtrate was concentrated to incipient crystallization and stored in a -20 °C freezer for 1 day to give (η^5 -C₅H₅)(CO)₂MoGeC₆H₃-2,6-Mes₂ (**1**) as red crystals. Yield: 0.41 g, 0.68 mmol, 34%; mp 165 °C. IR (Nujol, cm⁻¹): 1930, 1872 (CO). UV (λ_{max} , ϵ): 353 nm, 6400. ¹H NMR (C₆D₆): δ 2.17 (s, 12H, *o*-CH₃), 2.22 (s, 6H, *p*-CH₃), 4.70 (s, 5H, η^5 -C₅H₅), 6.86 (d, 2H, $J_{\text{HH}} = 7.5$ Hz, *m*-C₆H₃), 6.92 (s, 4H, *m*-Mes), 7.14 (tr, 1H, $J_{\text{HH}} = 7.2$ Hz, *p*-C₆H₃). ¹³C NMR (C₆D₆): δ 20.94 (*o*-CH₃), 21.16 (*p*-CH₃), 86.27 (η^5 -C₅H₅), 128.13 (*m*-Mes), 129.26 (*m*-C₆H₃), 131.35 (*p*-C₆H₃), 135.81 (*p*-Mes), 137.02 (*o*-Mes), 138.48 (*o*-C₆H₃), 144.35 (*i*-Mes), 165.03 (*i*-C₆H₃), 231.02 (CO). Anal. Calcd for C₃₁H₃₀GeMoO₂: C, 61.73, H, 5.01. Found C, 61.48, H, 4.98. (b) Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031. (c) Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353. (d) Fjellberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

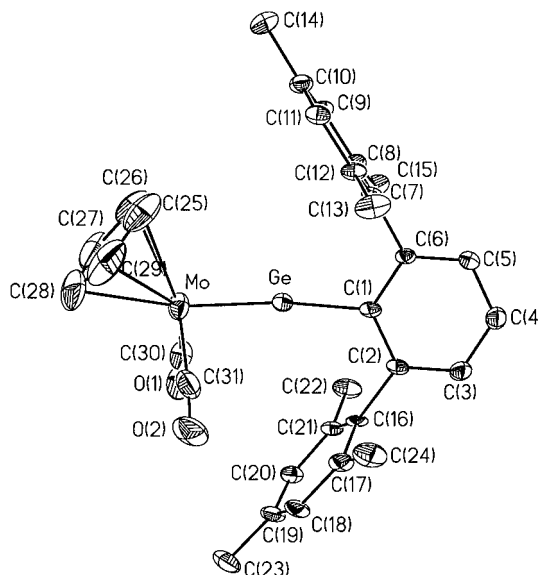


Figure 1. Thermal ellipsoid plot (30%) of **1** with hydrogen atoms not shown. Selected bond distances (Å) and angles (deg) are as follows: Mo–Ge = 2.271(1), Mo–C(25) = 2.379(12), Mo–C(26) = 2.34(1), Mo–C(27) = 2.31(1), Mo–C(28) = 2.30(1), Mo–C(29) = 2.34(1), Mo–C(30) = 1.950(9), Mo–C(31) = 1.960(13), Ge–C(1) = 1.933(7), C(30)–O(1) = 1.165(10), C(31)–O(2) = 1.174(13), Mo–Ge–C(1) = 172.2(2)°, Ge–Mo–C(30) = 88.2(2), Ge–Mo–C(31) = 86.6(3), Mo–C(30)–O(1) = 177.2(7), Mo–C(31)–O(2) = 173.8(9), Ge–C(1)–C(2) = 120.6(5), Ge–C(1)–C(6) = 117.9(6).

characterization. The X-ray crystal structure⁸ (Figure 1) reveals an almost linear coordination (Mo–Ge–C = 172.2(2)°) at the germanium and a short Mo–Ge bond length of 2.271(1) Å. There are no other close interatomic contacts involving germanium, and the shortest Ge–CO distances are greater than 2.9 Å. Thus, the carbonyls are terminal and not semibridging as they are in the related dimer [Mo(η^5 -C₅H₅)(CO)₂]₂,⁹ which features Mo–Mo triple bonds. The Mo–Ge distance may be compared to the single bond length (2.62 Å) predicted from the sum of the covalent radii¹⁰ of Mo (1.4 Å) and Ge (1.22 Å) and, in addition, the Mo–Ge single bond lengths in (η^5 -C₅H₅)(CO)₂Mo(GePh₃){C(OEt)Ph}₁₁ (2.658(2) Å) and (η^5 -C₅H₅)(η^3 -C₆H₁₁)(NO)MoGePh₃¹² (2.604(2) Å). Clearly, the shortening¹³ seen in **1** is of the order of 0.35 Å and is consistent with the presence of a Mo–Ge triple bond between the 15-electron (η^5 -C₅H₅)(CO)₂Mo fragment and the GeC₆H₃-2,6-Mes₂ moiety.

Most of the remaining structural features of the molecule are not unusual and are consistent with previously published data. The Mo–CO bonds 1.950(9) and 1.960(10) Å are slightly (ca. 0.01 Å) longer than those in the phosphonium ion-Mo complex (η^5 -C₅H₅)(CO)₂MoPNMe(CH₂)₂NMe featuring a Mo–P multiple bond.¹⁴ The Mo–C(η^5 -C₅H₅) distances are also very similar, but the Mo–C(25) and C(26) bonds nearest the large -C₆H₃-

(8) Crystal data for **1** at 130 K with Mo K α ($\lambda = 0.71073$ Å) radiation: $a = 13.185(3)$ Å, $b = 14.891(3)$ Å, $c = 15.576(3)$ Å, $\beta = 114.28(3)^\circ$, $Z = 4$, monoclinic, space group $P2_1/n$, $R_1 = 0.069$ for 3698 ($I > 2\sigma(I)$) data.

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(13) Unfortunately, no molybdenum germlyne structures, possessing a formal Mo–Ge double bond, appear to be available for comparison. For other transition metal germlyne complexes, see: Barrau, J.; Escudé, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. Jutzi, P.; Schmidt, H.; Neumann, B.; Stamm, H.-G. *Organometallics* **1996**, *15*, 741.

2,6-Mes₂ group are slightly longer (ca. 0.1 Å) than the others (Mo–C(27–29)). This is consistent with the greater steric congestion imposed by the germanium substituent. The Ge–C bond length, 1.933(7) Å, is at the shorter end of the range of Ge–C distances,¹⁵ perhaps as a result of the approximate sp hybridization of the Ge–C bonding orbital. There is little distortion apparent in the geometry of the 2,6-Mes₂C₆H₃–ligand, and the plane of the central aromatic ring approximately bisects the angle between the carbonyl groups.

The solution ¹H and ¹³C NMR spectra of **1** are consistent with the structure established by X-ray crystallography. No dynamic behavior could be detected at temperatures as low as –90 °C. The IR spectrum of **1** (Nujol mull) displayed the expected two stretching absorptions in the carbonyl region. The observed stretching frequencies, 1930 and 1872 cm^{–1}, do not suggest the unusually high π-acceptor properties seen in many carbynes:² e.g., 1992 and 1919 cm^{–1} in Mo(η⁵-C₅H₅)-(CO)₂{C(C₆H₄-2,6-Me₂)}.^{16a} Instead the frequencies resemble those in other (η⁵-C₅H₅)(CO)₂Mo fragments involved in multiple

bonding: e.g., 1947 and 1873 cm^{–1} found for (η⁵-C₅H₅)(CO)₂-MoAs(t-Bu)₂^{16b} or 1920 and 1856 cm^{–1} for (η⁵-C₅H₅)(CO)₂-Mo(NCPh₂).^{16c}

The facile synthesis and the stability of **1** may be attributed to the stabilizing properties of the 2,6-Mes₂C₆H₃– substituent¹⁷ which affords the germanium sufficient steric protection and facilitates the elimination of CO under mild conditions to afford the Mo–Ge triply bonded product. The complex **1** is unique not only because it is the first stable transition metal germylene complex but also it appears to be the first species in which a heavier group 14 element forms a triple bond in a compound that is stable at room temperature. Investigations of the chemical properties of **1** and the synthesis of related heavier main group 14 analogues are currently underway.

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Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances, angles, anisotropic thermal parameters and hydrogen coordinates (9 pages). See any current masthead page for ordering and Internet access instructions.

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