$(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3\text{-}2,6\text{-}Mes_2$: A Transition-Metal Germylyne Complex

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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 carbyne[2] or nitrido complexes.[3] Rare exceptions to this generalization are the recently reported phosphido derivatives $Mo(P)(NRAr)_3$[4] ($R = -C(CD_3)_2CH_3$, $Ar = 3,5\text{-}(CH_3)_2C_6H_3-$) and $W(P)(NN_3)$[5] ($NN_3 = \{(Me_3SiNCH_2CH_2)_3N\}^{3-}$) which feature formal triple bonds between phosphorus and molybdenum or tungsten. Despite the existence of the donor stabilized silylyne complex $[(\eta^5\text{-}C_5Me_5)(Me_3P)_2RuSi\{(bipy)(SC_6H_4\text{-}4\text{-}Me)\}][OTf]_2$,[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 $(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3\text{-}2,6\text{-}Mes_2$ (**1**), which contains a molybdenum−germanium triple bond, is now described.

The compound (**1**) was synthesized[7] in THF solution by treatment of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ with $2,6\text{-}Mes_2C_6H_3GeCl$ (generated in situ) as shown in eq 1

$$Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3] + 2,6\text{-}Mes_2C_6H_3GeCl \xrightarrow[-CO]{THF,\ 50\ ^\circ C} (\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3\text{-}2,6\text{-}Mes_2 + NaCl \quad (1)$$

(**1**)

The formula of **1** was established by spectroscopic and structural characterization. The X-ray crystal structure[8] (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 $[Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$,[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 radii[10] of Mo (1.4 Å) and Ge (1.22 Å) and, in addition, the Mo−Ge single bond lengths in $(\eta^5\text{-}C_5H_5)(CO)_2Mo(GePh_3)\{C(OEt)Ph\}$[11] (2.658(2) Å) and $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_6H_{11})(NO)MoGePh_3$[12] (2.604(2) Å). Clearly, the shortening[13] 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 $(\eta^5\text{-}C_5H_5)(CO)_2Mo$ fragment and the $GeC_6H_3\text{-}2,6\text{-}Mes_2$ moiety.

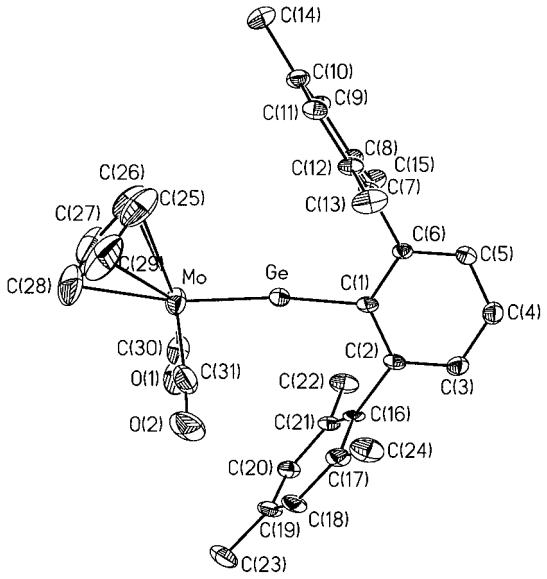

Figure 1. Thermal ellipsoid plot (30%) of **1** with hydrogen atoms not shown. Selected bond distances (Å) and angles (deg) are as follows: Mo−Ge = 2.271(1), Mo−C(25) = 2.379(12), Mo−C(26) = 2.34(1), Mo−C(27) = 2.31(1), Mo−C(28) = 2.30(1), Mo−C(29) = 2.34(1), Mo−C(30) = 1.950(9), Mo−C(31) = 1.960(13), 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).

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 phosphenum ion-Mo complex $(\eta^5\text{-}C_5H_5(CO)_2MoPNMe(CH_2)_2NMe$ featuring a Mo−P multiple bond.[14] The Mo−C($\eta^5\text{-}C_5H_5$) distances are also very similar, but the Mo−C(25) and C(26) bonds nearest the large -C_6H_3-

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(7) (a) All manipulations were carried out under anaerobic and anhydrous conditions. $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ (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 $2,6\text{-}Mes_2C_6H_3GeCl$, prepared in situ from $2,6\text{-}Mes_2C_6H_3Li$[7c] (0.64 g, 2.0 mmol) and $GeCl_2$·dioxane[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 $(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3\text{-}2,6\text{-}Mes_2$ (**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 (C_6D_6): δ 2.17 (s, 12H, *o*-CH_3), 2.22 (s, 6H, *p*-CH_3), 4.70 (s, 5H, η^5-C_5H_5), 6.86 (d, 2H, $J_{HH} = 7.5$ Hz, *m*-C_6H_3), 6.92 (s, 4H, *m*-Mes), 7.14 (tr, 1H, $J_{HH} = 7.2$ Hz, *p*-C_6H_3). ^{13}C NMR (C_6D_6): δ 20.94 (*o*-CH_3), 21.16 (*p*-CH_3), 86.27 (η^5-C_5H_5), 128.13 (*m*-Mes), 129.26 (*m*-C_6H_3), 131.35 (*p*-C_6H_3), 135.81 (*p*-Mes), 137.02 (*o*-Mes), 138.48 (*o*-C_6H_3), 144.35 (*i*-Mes), 165.03 (*i*-C_6H_3), 231.02 (CO). Anal. Calcd for $C_{31}H_{30}GeMoO_2$: 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) Fjelberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(8) Crystal data for **1** at 130 K with Mo Kα ($\lambda = 0.71073$ Å) radiation: $a = 13.185(3)$ Å, $b = 14.891(3)$ Å, $c = 15.576(3)$ Å, $\beta = 114.28(3)°$, $Z = 4$, 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 germylene structures, possessing a formal Mo−Ge double bond, appear to be available for comparison. For other transition metal germylene complexes, see: Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 741.

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2,6-Mes_2 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-$Mes_2C_6H_3$− ligand, and the plane of the central aromatic ring approximately bisects the angle between the carbonyl groups.

The solution ^{1}H and ^{13}C 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(η^5-C_5H_5)-$(CO)_2${C(C_6H_4-2,6-Me_2)}.[16a] Instead the frequencies resemble those in other (η^5-C_5H_5)$(CO)_2$Mo fragments involved in multiple bonding: e.g., 1947 and 1873 cm^{-1} found for (η^5-C_5H_5)$(CO)_2$-$MoAs(t\text{-}Bu)_2$[16b] or 1920 and 1856 cm^{-1} for (η^5-C_5H_5)$(CO)_2$-$Mo(NCPh_2)$.[16c]

The facile synthesis and the stability of **1** may be attributed to the stabilizing properties of the 2,6-$Mes_2C_6H_3$− substituent[17] 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 germylyne 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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