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Germylene and Silylene Complexes of Molybdenum via E−H (E = Ge, Si) Bond Activations: Steric Influences on Intramolecular MoH···E Interactions

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Reactions of Cp*(dmpe)Mo(η^3-CH_2Ph) with organogermanes ($RR'GeH_2$) afforded germylene complexes Cp*(dmpe)Mo(H)GeRR′ (RR′ = Ph_2 (**2**), Et_2 (**3**), (Mes)H (**4**), (^{t}Bu)H (**5**)). Compound **2** does not possess an intramolecular H···Ge interaction of the type exhibited by its silicon analogue and by **3**. The existence of such interactions appears to depend on the steric properties of substituents on the Ge (or Si) atom. For comparison, a silylene complex was prepared by reaction of 9-silafluorene with **1**, to give Cp*(dmpe)Mo(H)Si($C_{12}H_8$), which on the basis of NMR spectroscopy does not possess a significant Si···H interaction.

In recent years, metal silylene complexes have become well-established as isolable chemical species with unusual chemical properties.[1] Of particular interest are examples of hydrogen-substituted silylene complexes, which serve as catalysts in a new type of hydrosilylation reaction involving the direct addition of a Si−H bond to the olefin[2] and have been observed to mediate unusual stoichiometric reductions of nitriles and organic carbonyl compounds.[3] Many of the known silylene complexes possess hydride ligands, which can participate in the observed transformations and are often found to interact with the silylene silicon center via a nonclassical, interligand H···Si interaction. For example, a series of molybdenum silylene complexes of the type Cp*(dmpe)MoH(SiRR′), obtained by reaction of Cp*(dmpe)Mo(η^3-CH_2Ph) (**1**) with $RR'SiH_2$ via double Si−H bond activation, exhibit this structural feature.[4] Given the versatility of this synthetic route to molybdenum silylene complexes, it seems that this system is well suited for investigations of substituent effects on structure, bonding, and reactivity in closely related complexes with other metal−main group multiple bonds.

Although germylene transition metal complexes have been known for a long time, little is known about their chemical properties.[5,6] To address this issue, and to establish a general route to germylene complexes that possess reactive bonds to hydrogen (M−H, Ge−H), reactions of complex **1** with hydrogermane compounds have been examined. As reported here, these transformations provide germylene hydride complexes of the type Cp*(dmpe)Mo(H)GeRR′, including some of the first examples that possess Ge−H bonds.[7]

The benzyl complex **1** reacted with secondary germanes with loss of toluene at room temperature in benzene to afford germylene complexes Cp*(dmpe)Mo(H)GeR_2 (**2**, R = Ph; **3**, R = Et; Scheme 1). Interestingly, the ^{1}H NMR chemical shifts for the hydride ligands in these complexes, −4.34 (J_{HP} = 41 Hz) for **2** and −10.53 ppm (J_{HP} = 25 Hz) for **3**, are markedly different. Also, these chemical shifts are significantly downfield with respect to those observed for the analogous silylene complexes, at −11.36 (J_{HP} = 18 Hz) and −13.91 ppm (J_{HP} = 25 Hz), respectively.[4] Note that the significantly larger J_{HP} value for **2** (41 Hz) versus its silylene analogue (19 Hz) suggests that these two complexes have somewhat different stuctures.

The structures of **2** and **3** (Figures 1 and 2), determined by X-ray crystallography, show that the Ge atoms exhibit a trigonal-planar bonding arrangement (summations of angles

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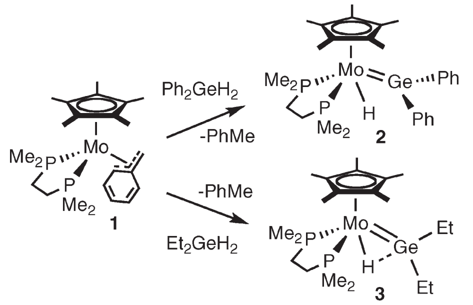
[7] The complexes Cp*(^{i}Pr_3P)(H)Ru=GeHR (R = trip, ^{t}Bu) have recently been reported: Hayes, P. G.; Waterman, R.; Glaser, P. B.; Tilley, T. D. *Organometallics*, in press.

Scheme 1



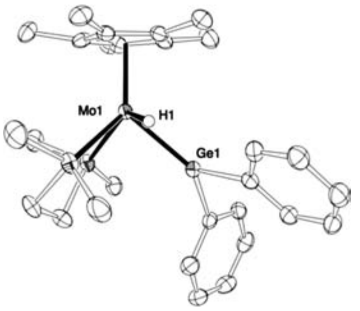


Figure 1. ORTEP drawing of one of the two independent molecules of **2** in the unit cell (ellipsoids at 50% probability). Hydrogen atoms (except for H1) are omitted for clarity.

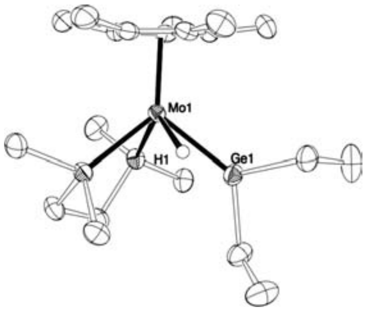


Figure 2. ORTEP structure of **3** with thermal ellipsoid plots (50% probability). Hydrogen atoms (except for H1) are omitted for clarity.

about Ge: 359.4 and 358.5°, respectively). The Mo−Ge bond lengths (2.4142(7) Å for **2** and 2.4111(4) Å for **3**) lie between values that might be expected for Mo−Ge single (2.67 Å) and triple (2.28 Å) bonds.[8,9] The mean Mo−P bond length in **2** (2.43 Å) is longer than that for **3** (2.39 Å). In both cases, the molybdenum-bound hydrogen atom was located from the Fourier difference map, and this allowed determination of a long Ge−H distance of 2.32 Å, and a Mo−H bond length of 1.56(10) Å, for **2**. For compound **3**, the Ge−H separation (1.89(3) Å) clearly corresponds to a bonding distance, and the Mo−H bond distance is relatively long at 1.84(4) Å.[10] Note that the Mo−H bond distance in **2** is consistent with the value expected for a terminal, unperturbed Mo−H bond,[11] and the H−Mo−Ge−C dihedral angles in **2** (19.9 and 124.0°) imply that the Mo−H bond is roughly coplanar with the GeC_2 fragment. Furthermore, the hydride ligand in **2** is displaced by only 0.56 Å from the $MoGeC_2$ least-squares plane (Figure 3). In contrast, the hydride ligand in **3** appears to be located over the Mo═Ge double bond, such that the H−Mo−Ge−C dihedral angles are 91.3 and 72.1° (Figure 3). Thus, the hydride ligand in **3** is clearly involved in a secondary bonding interaction with the germanium atom, resulting in a longer Mo−H bond distance for this complex. Unlike **3** and the analogous silylene complex, **2** does not exhibit this nonclassical bonding interaction. This difference appears to be reflected in the ^{1}H NMR shifts for the hydrides (vide supra). A greater upfield shift, to ca. −10.5 ppm, reflects the presence of this interaction in such complexes. For both complexes, the NMR spectra at room temperature are consistent with equivalent substituents on Ge and rapid rotation about the Mo−Ge bond, as for the analogous silylene derivatives.[4]

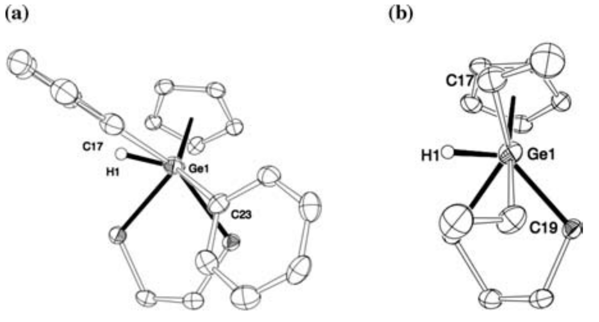


Figure 3. View along the Mo−Ge bonds of **2** (a) and **3** (b), with groups on the H atoms removed for clarity.

Hydrogen-substituted germylene complexes were readily obtained by the method of Scheme 1. Thus, reactions of **1** with the primary germanes $MesGeH_3$ and $^tBuGeH_3$ allowed isolation of Cp*(dmpe)Mo(H)GeH(R) (**4**, R = Mes; **5**, R = ^{t}Bu) complexes in 48 and 40% yields, respectively. Interestingly, the ^{1}H NMR chemical shifts for the germanium-bound protons are quite downfield-shifted (12.32 (**4**), 11.43 (**5**) ppm), as observed for analogous silylene complexes.[1g] Although the NMR data for these complexes do not conclusively define the environments about germanium, the relatively downfield hydride shifts (**4**, −8.40 ppm, J_{HP} 26 Hz; **5**, −5.59 ppm, J_{HP} 27 Hz) suggest the presence of little to no MoH···Ge interactions.

The results described above suggest that intramolecular H···Ge interactions in this system may be highly sensitive to steric properties for the germanium substituents. For the analogous silylene complexes, and for **3**, the preferred geometry is one with the silylene or germylene plane roughly perpendicular to the plane of the Cp* ligand. This orientation allows the hydride ligand to interact with the E atom. Apparently, steric interactions between the Cp* ligand and the silylene (or germylene) substituents may favor rotation about the Mo−E bond (as might be preferred for the presumably weaker Mo−Ge bond) such that MoH···E interactions are no longer possible. It is worth noting,

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[8] Vincent, J. L.; Luo, S.; Scott, B. L.; Butcher, R.; Unkefer, C. J.; Burns, C. J.; Kubas, G. J.; Lledós, A.; Maseras, F.; Tomàs, J. *Organometallics* **2003**, *22*, 5307.

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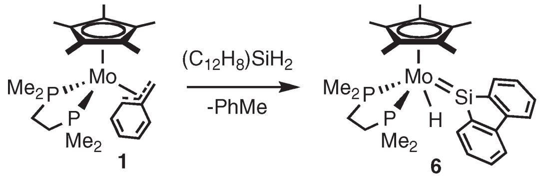
[10] There are two independent molecules of **2** in the unit cell, one of which is disordered.

[11] Pleune, B.; Poli, R.; Fettinger, J. C. *Organometallics* **1997**, *16*, 1581.

however, that electronic factors may play some role in determining the structures, since the Ge center with the most electronegative substitutents (Ph) is associated with complete cleavage of the Ge–H bond.[8]

It therefore seemed of interest to determine whether or not a silylene complex could adopt the basic structure exhibited by **2**, with no MoH···E interaction. This would seem to require sterically demanding silylene substituents rigidly confined to the SiC_2 plane, and for this purpose, a biphenylene group was chosen. Thus, reaction of 9-silafluorene, $(C_{12}H_8)SiH_2$, with **1** in benzene at 50 °C gave the silylene complex **6** in 54% yield (eq 1). The ^1H NMR chemical shift of the hydride ligand appears at −4.92 ppm (J_{HP} = 32 Hz), and the ^{29}Si NMR shift (296 ppm) implies significant silylene character for the silicon-based ligand.[1] For comparison, the hydride shifts for known Cp*-(dmpe)Mo(H)SiRR′ silylene complexes range from −14 to −10 ppm.[4] In addition, the J_{SiH} coupling constant for **6** (24 Hz) is distinctly less than corresponding values for the related silylene complexes (30–48 Hz).[4] Thus, the NMR parameters lead us to suggest that **6** is the only silylene complex in this series that does not possess a MoH···Si interaction. Unfortunately, X-ray-quality crystals of **6** have not yet been obtained.



1 **6** (1)

In conclusion, it would appear that intramolecular MoH···E interactions of the type described here are rather weak, and somewhat dependent on steric interactions within the metal's coordination sphere. Future structural studies on silylene– and germylene–hydride complexes are expected to contribute substantially to an understanding of these interactions.

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Supporting Information Available: Experimental details for all new compounds and cif files of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.