Molybdenum Hydrido Complex Containing a Novel Quinquidentate (*P,P,Ge,P,P*) Ligand

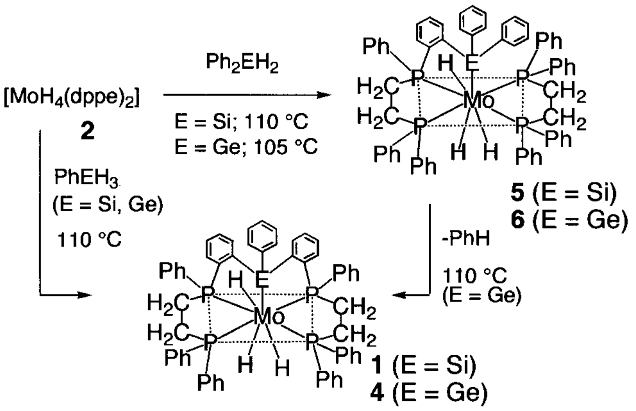
Makoto Minato, Ryo Hirabayashi, Takaomi Matsumoto, Yoshitaka Yamaguchi, and Takashi Ito*
Department of Materials Chemistry, Graduate School of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501

(Received June 8, 2001; CL-010534)

The reaction of $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ with $PhGeH_3$ or Ph_2GeH_2 resulted in the formation of a novel molybdenum–germyl complex $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]_2(Ph)Ge\text{-}P,P,P,P,Ge\}]$ (**4**) with a quinquidentate ligand comprised of a P~P~Ge~P~P framework, where activation of Ge–H bonds, two C–H bonds, and, in the case of Ph_2GeH_2, a Ge–C bond took place concurrently.

Compounds which contain an inter-element linkage of M–E (M = transition metals; E = Group 14 elements) are highly important as active species in catalytic addition of the linkage to unsaturated organic substrates. Especially, transition-metal silyl chemistry has grown immensely over the past two decades. However, much less studies have been carried out on the chemistry related to its higher homologue germanium.[1] Here we report the synthesis of a novel molybdenum–germyl complex having a Mo–Ge bond. In previous papers, we reported the unexpected formation of a novel complex, $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]_2(Ph)Si\text{–}P,P,P,P,Si\}]$ (**1**), which is obtained by the thermal reaction of $[MoH_4(dppe)_2]$ (**2**) with $PhSiH_3$.[2] Complex **1** represents the first example of the concomitant activation of Si–H bonds and two C–H bonds of the ortho positions of the phenyl groups in the dppe ligand giving rise to the formation of a quinquidentate ligand which consists of a P~P~Si~P~P girdle. A series of new complexes with this quinquidentate ligand has been synthesized from **1**. For example, **1** reacted with further mole of $PhSiH_3$ to afford a novel complex $[MoH_2\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]_2(Ph)Si\text{-}P,P,P,P,Si\}(SiH_2Ph)]$ (**3**). Whereas reaction of **1** with electrophilic dioxygen or dialkyl malonate yielded a peroxo type η^2-O_2 complex[3] or η^1-*O*-enolato type complex,[4] respectively.

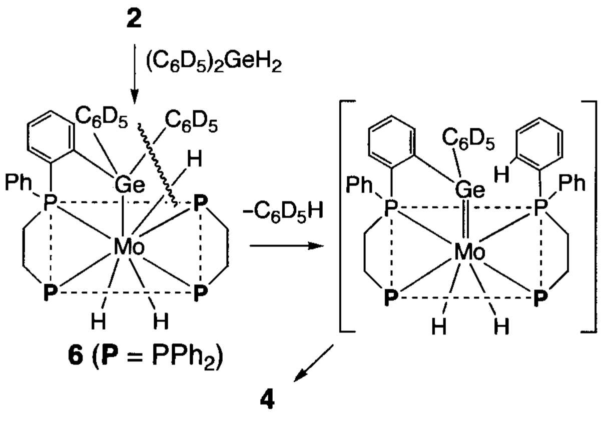
We thought that our methodology described above is also applicable to the synthesis of a molybdenum–germyl complex. Hence, we examined the reaction of **2** with $PhGeH_3$ in toluene under reflux and found that in fact it proceeded in a similar manner as in the case of $PhSiH_3$ giving $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]_2(Ph)Ge\text{-}P,P,P,P,Ge\}]$ (**4**),[5] the germanium congener of **1**, in 60% yield (Scheme 1): the reaction involving Ge–H oxidative addition and C–H activation took place, although $PhGeH_3$ was less reactive than $PhSiH_3$ and the reaction went to completion only after a long period of heating (6 h).



Scheme 1.

Noteworthy is the reaction of **2** with secondary Ph_2GeH_2, which resulted in the formation of **4** (85%) and this reaction proceeded with accompanying evolution of one mole of benzene. The result is quite contrast to that found in the similar reaction employing Ph_2SiH_2: the only isolated product being the trihydrido complex **5** (Scheme 1) with a tridentate ligand Si~P~P.[3] The reaction between **2** and Ph_2GeH_2 was found to be very sensitive to the reaction temperatures. At temperatures of 100 to 105 °C, the intermediary **6**[6] with a tridentate ligand, which is analogous to the silyl complex **5**, was formed (96%). The complex **6** was converted easily into **4** by heating the former in toluene at 110 °C in 13% yield.

In order to obtain some insights into the mechanism of the formation of **4** from **6**, we attempted the reaction of **2** with $(C_6D_5)_2GeH_2$ at 110 °C under argon. GC–MS analysis of the volatile product showed a peak at *m/z* = 83, which was ascribed to the pentadeuterated benzene, C_6D_5H, suggesting a cleavage of the Ge–C(Ph) bond (Scheme 2). This α-elimination reaction of **2** with Ph_2GeH_2 is proposed to occur via intervention of the germylene intermediate. The silyl complex **5** was found to be stable to prolonged heating in toluene and the similar transformation into **1** did not take place. It is quite difficult to rationalize these differences in the reactivity between the germane and



Scheme 2.

the silane because the strengths of chemical bonds in Ge–C(Ph) and Si–C(Ph) are similar.[7] In organogermanium compounds, intramolecular coordination between a germanium atom and a substituent (halogen, O–, S–, etc.) in the α-position to the germanium has been known to favor a homolytic cleavage of the germanium–carbon bond.[8] The Mo(dπ)—GeC(Ph)(σ*) interaction might have induced a weakening of the Ge–C bond. In the case of silyl–molybdenum complex **5** we may suppose that such interaction between d-electrons is weak since the Si–C(σ*) orbital lies much higher in energy than the Ge–C(σ*) orbital.

The ^{1}H NMR spectrum of **4** showed the multiplet signals between −3.7 and −4.6 ppm assignable to Mo–H protons, which were analyzed as a set of a broad triplet at −3.9 ppm with apparent coupling constant of 48 Hz and a broad quintet at −4.4 ppm with J = 29 Hz with the integration ratio 1:2. These results are quite similar to those of the silyl complex **1**.[2]

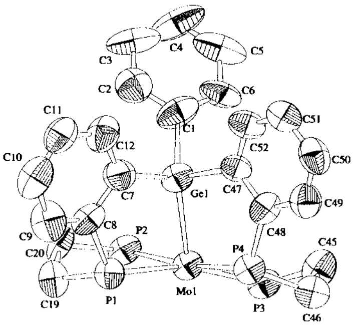


Figure 1. Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Mo1—Ge1 2.587(2), Mo1—P1 2.456(4), Mo1—P2 2.457(5), Mo1—P3 2.449(5), Mo1—P4 2.436(5), Ge1—C1 2.03(2); P1—Mo1—P2 80.6(2), P2—Mo1—P3 102.0(2), Mo1—Ge1—C47 106.6(5), Mo1—Ge1—C1 125.5(7).

The structure of **4** was confirmed by single crystal X-ray diffraction technique.[9] The complex **4** contains bonds between the germanium and the ortho carbons of the phenyl groups in the dppe ligand constructing a quinquidentate ligand, which is entirely analogous to that of **1**. The structure can be compared and contrasted with that of the above-mentioned disilyl complex **3**. The Mo–Ge bond distance is 2.587(2) Å, which is a little longer than that of the Mo–Si bond in **3** by ca. 0.03 Å. On the other hand, the mean Mo–P distance of 2.44 Å in **4** is a little shorter than that found in **3** (2.47 Å). The Ge–C1 bond distance of 2.03(2) Å is longer than that of Si–C(Ph) in **3** (1.90 Å), reflecting a difference in their covalent radii (Ge = 1.23 and Si = 1.17 Å). The total of the bond angles P1–Mo1–P2, P2–Mo1–P3, P3–Mo1–P4, and P4–Mo1–P1, is 362.2°, which confirms the planarity of P–P–Mo–P–P moiety.

We thank Professor Kunio Mochida (Gakushuin University) for providing us with $GeCl_4$. This work was supported by a Grant-in-Aid for Scientific Research (B) No. 10450340 and a Grant-in-Aid for Scientific Research on Priority Areas (No. 11120217) from the Ministry of Education, Science, Sports, and Culture of Japan.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

1 a) F. Riedmiller, G. L. Wegner, A. Jockisch, and H. Schmidbaur, *Organometallics*, **18**, 4317 (1999). b) H. Komoriya, M. Kako, Y. Nakadaira, and K. Mochida, *J. Organomet. Chem.*, **611**, 420 (2000).

2 D.-Y. Zhou, M. Minato, T. Ito, and M. Yamasaki, *Chem. Lett.*, **1997**, 1017.

3 D.-Y. Zhou, L.-B. Zhang, M. Minato, T. Ito, and K. Osakada, *Chem. Lett.*, **1998**, 187.

4 T. Ito, K. Shimada, T. Ono, M. Minato, and Y. Yamaguchi, *J. Organomet. Chem.*, **611**, 308 (2000).

5 Complex **4**: ^{1}H NMR (benzene-d_6, 25 °C, 270 MHz): δ −4.4 (br quint, J = 29 Hz, 2H, Mo–H), −3.9 (br t, J = 48 Hz, 1H, Mo–H), 1.5–2.5 (br m, 8H, PCH_2); $^{31}P\{^1H\}$ NMR (benzene-d_6, 109.4 MHz): δ 83.8 (br d, J = 55 Hz), 113.8 (br d, J = 55 Hz); Satisfactory elemental analysis data were not so far available, possibly due to the presence of germanium in the molecule.

6 Complex **6**: ^{1}H NMR (benzene-d_6, 25 °C, 270 MHz): δ −4.3 (br quint, 3H, Mo–H), 1.5–2.7 (br m, 8H, PCH_2); $^{31}P\{^1H\}$ NMR (benzene-d_6, 109.4 MHz): δ 76.9 (br 2P), 94.2 (br 1P), 115.5 (br 1P). These data were found to be quite similar to those of **5**, which was fully characterized by X-ray crystallography. D.-Y. Zhou, M. Minato, and T. Ito, unpublished results.

7 G. Pilcher and H. A. Skinner, "The Chemistry of the Metal–Carbon Bond. Volume 1. The Structure, Preparation, Thermochemistry, and Characterization of Organometallic Compounds," ed. by F. R. Hartley and S. Patai, John Wiley and Sons, Chichester (1982), p 43.

8 P. Riviere, M. Riviere-Baudet, and J. Satgé, "Comprehensive Organometallic Chemistry," ed. by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1982), Vol. 2, p 399.

9 Crystal data for **4** : green prism; 0.35 × 0.20 × 0.02 mm; $C_{58}H_{54}GeMoP_4$ fw = 1043.49; monoclinic, space group Pn(#7); a = 12.465(3) Å, b = 12.111(3) Å, c = 16.631(6) Å, β = 94.90(3)°, V = 2501(1) Å^3, Z = 2; D_{calcd} = 1.385 g/cm^3; Rigaku AFC7R diffractometer; 298 K; Mo Kα radiation (λ = 0.71069 Å); scan method ω-2θ; R = 0.082 for 2863 observed reflection.