Inorg. Chem. **2003**, *42*, 2836–2838

Inorganic Chemistry
Communication

Formation and Structure of *fac*-[$Mo(CO)_3(C_2H_2[N(CH_2Bu^t)]_2Ge)_3$]: The First Structurally Characterized Group 6 Transition Metal Complex of an Unsaturated Diaminogermylene

Olaf Kühl,*,[†] Peter Lönnecke,[‡] and Joachim Heinicke*,[†]

Institut für Chemie und Biochemie, Ernst-Moritz-Arndt-Universität Greifswald,
Soldmannstrasse 16, D-17487 Greifswald, Germany, and Institut für Anorganische Chemie,
Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

Received September 4, 2002

The title compound was obtained from the cyclic diaminogermylene $C_2H_2[N(CH_2Bu^t)]_2Ge$ and *cis*-[$Mo(CO)_4(NCEt)_2$] and its crystal structure determined revealing structural changes in the coordinated ligand indicative of strong π-acceptor properties.

Whereas N-heterocyclic carbenes (NHC) have received tremendous interest ever since their discovery by Arduengo in 1991,[1] their longer known germanium counterparts (Meller 1989)[2] have found less attention. This is undoubtedly due to the growing application of NHC as replacements of phosphines (diagonal relationship) in catalytic processes.[3] However, as shown recently, the higher homologues may also be useful as catalysts.[4,5] Since π-interactions between the group 14 element and nitrogen decrease in the order C−N ≫ Si−N > Ge−N, the electron density in the p_π-orbital of the heavier homologues should be rather low and thus enhance the π-acceptor strength and modify the properties of such ligands and catalysts. While complexes of NHSi were reported for a broader variety of transition metals,[6] studies on complexes of the more easily accessible NHGe and their structures are still quite limited and restricted to few transition metals.[7−9] In context with investigations on electronic anellation effects in NHC[10] and their higher homologues[11−15] that cause further modification of the donor−acceptor properties, we performed a preliminary study of the formation of a molybdenum complex with the nonanellated reference ligand 1,3-dineopentyl-1,3,2-diazagermoline-2-ylidene (L)[13] (same N-substituents as in the anellated derivatives). The resulting title compound is to our knowledge the first example of a structurally characterized NHGe complex of a less electron-rich transition metal, in particular of group 6. Structural changes as compared to **1** and related compounds are discussed.

When *cis*-[$Mo(CO)_4(NCEt)_2$] is reacted with 2 equiv of L, a mixture of the expected *cis*-[$Mo(CO)_4L_2$] (**1**) and a small amount of *fac*-[$Mo(CO)_3L_3$] (**2**) is readily formed[16] (eq 1).

---

* Authors to whom correspondence should be addressed. J.H.: fax, +49 3834 864319; tel, +49 3834 864337; e-mail, heinicke@uni-greifswald.de; kuhl@uni-greifswald.de (O.K.).

[†] Ernst-Moritz-Arndt-Universität Greifswald.

[‡] Universität Leipzig.

(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(2) Pfeiffer, J.; Maringgelle, M.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245−252.

(3) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

(4) Fürstner, A.; Krause, H.; Lehmann, C. W. *Chem. Commun.* **2001**, 2372−2373.

(5) (a) Litz, K. E.; Bender, J. E.; Kampf, J.; Banaszak-Holl, M. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 496. (b) Bender, J. E.; Shusterman, A. J.; Banaszack-Holl, M. M.; Kampf, J. W. *Organometallics* **1999**, *18*, 1547−1552.

(6) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617−618*, 209−223.

(7) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485.

(8) (a) Veith, M.; Stahl, L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 106. (b) Veith, M.; Müller, A.; Stahl, L.; Nötzel, M.; Jarcyk, M.; Huch, V. *Inorg. Chem.* **1996**, *35*, 3848−3855. (c) Veith, M.; Stahl, L.; Huch, V. *Organometallics* **1993**, *12*, 1914−1920.

(9) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162−11167.

(10) Oprea, A. Ph.D. Thesis, Universität Greifswald, 2000.

(11) Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpati, T.; Nyulászi, L.; Veszprémi, T. *Chem. Eur. J.* **1998**, *4*, 541−545.

(12) Heinicke, J.; Oprea, A. *Heteroat. Chem.* **1998**, *9*, 439−444.

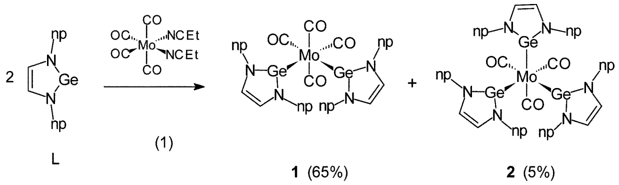
(13) Kühl, O.; Lönnecke, P.; Heinicke, J. *Polyhedron* **2001**, *20*, 2215−2222.

(14) Pause, L.; Robert, M.; Heinicke, J.; Kühl, O. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1383−1388.

(15) Kühl, O.; Lönnecke, P.; Heinicke, J. *New J. Chem.* **2002**, *26*, 1304−1307.

(16) $C_2H_2[N(CH_2Bu^t)]_2Ge$ (550 mg, 2.06 mmol) was dissolved in 25 mL of toluene, and 328 mg (1.03 mmol) of *cis*-[$Mo(CO)_4(NCEt)_2$] was added. After 4 h the solution was concentrated under reduced pressure. **2** (50 mg, 5%) precipitated as pale yellow rectangular crystals. The remainder was concentrated to a dark yellow-brown oil, and 20 mL of hexane was added. The solution was filtered and the hexane removed in a vacuum. **1** (496 mg, 65%) was obtained as a viscous yellow-brown oil. NMR data for **1**: ^1H (C_6D_6, 300.1 MHz) δ 6.61 (s, 2H, CH), 3.55 (s, 4H, CH_2), 0.89 (s, 18 H, CH_3); ^{13}C (75.5 MHz) δ 215.3 (*trans*-CO), 210.1 (*cis*-CO), 127.3 (CH), 61.8 (CH_2), 33.6 (C), 28.7 CH_3). NMR data for **2**: ^1H (C_6D_6, 300.1 MHz) δ 6.68 (s, 2 H, CH), 3.58 (s, 4 H, CH_2), 0.89 (s, 18 H, CH_3); ^{13}C (75.5 MHz) δ 219.7 (CO), 127.0 (CH), 61.2 (CH_2), 33.5 (C), 28.7 (CH_3). EI-MS (*m*/*z*, %) for **1**: [**2**]$^+$ 984.1 (6), [M]$^+$ 746.2 (44), [$MoL_2(CO)_2$]$^+$ 692.1 (75), [MoL_2]$^+$ 634.6 (29), [$MoL(CO)_3$]$^+$ 451.6 (43), [L]$^+$ 270.5 (67), [L − Bu^t]$^+$ 213.1 (100). Elemental anal. for $C_{28}H_{48}Ge_2MoN_4O_4$ (746.07): calcd C 45.07, H 6.48, N 7.54; found C 45.75, H 7.36, N 7.62.

10.1021/ic0259991 CCC: $25.00



However, no trace of *mer*-**2** could be detected in any of the NMR spectra. The solubility of **1** and **2** is very high even in hydrocarbons. Sensitivity toward OH groups prevented chromatographic separation. Neither the oil containing mostly **1** nor the crystals of **2** (coated with a thin film of oily **1**) could be obtained in a completely pure form by fractionated crystallization. Both the mass spectrum and the elemental analysis of the oil containing mostly **1** showed evidence of the presence of a small amount of **2** (M^+ peak of **2** at m/z 984, rel int 6%). However, recrystallization from toluene provided **2** in low yield as single crystals suitable for an X-ray structure investigation.[17]

2 crystallizes monoclinic in the space group $P2_1/c$ with four molecules in the unit cell. The compound is monomeric and the *fac* isomer with C_3 symmetry. The molybdenum atom is octahedrally coordinated by three CO and three germylene ligands. Each CO ligand is trans to a germylene entity with almost linear Ge−Mo−C bond angles [175.0(2)°, 176.6(2)°, and 179.27(19)°] and Mo−C bond lengths [195.5(7), 196.4(8), 198.5(7) pm] that are in the same range as those for Mo−CO complexes with phosphine ligands trans to CO.[18] The comparable trans influence indicates similar acceptor properties of the germylene ligand. This is further supported by the changes of bond lengths in L on complexation (see below) and the short Mo−Ge distances in **2** [253.25(8), 253.39(10), and 254.44(9) pm, respectively] at the lower end of Mo(0)−Ge(IV) bond lengths, except GeH_3 species, ranging from 251 to 265.8 pm.[19] That is surprising since Ge(II) as in **2** [20] is certainly bigger than Ge(IV) in the structures found in the literature[19] and thus we would have expected the Mo(0)−Ge(II) bond length at the long end of the range. A significant amount of π-back-bonding would explain this finding. The IR spectra of **1** (2026, 1940, 1923, 1892 cm^{-1}) and **2** (1961, 1853 cm^{-1}) in Nujol support this as they are similar to related phosphorus-based complexes, but displaying slightly better back-bonding character. This is manifested by a shift to higher wavenumbers of the νCO bands of the *trans*-CO ligands. The complex *fac*-$[Mo(CO)_3(PPh_3)_3]$[21] displays bands at 1949 and 1835 cm^{-1} and the complex $[TpZr(\mu\text{-}OCH_2PPh_2)_3Mo(CO)_3]$ (Tp = tris(pyrazolyl)hydroborate)[22] at 1932 and 1834 cm^{-1}.

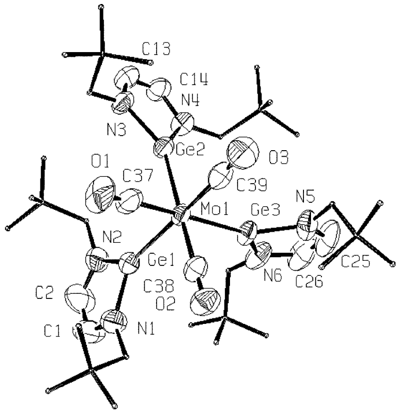


Figure 1. Crystal structure of **2**.Thermal ellipsoids are drawn at 50% probability. H-atoms have been omitted and np-substituents stylized.

The germylene ligands exhibit the neopentyl substituents in the cis orientation, i.e., on the same side of the respective ring plane. This was observed also in anellated NHGe and seems to be the preferred orientation in these germylenes, although there is trans orientation in the crystal of the free ligand due to packing effects.[13] The N−Ge−N bond angles [85.7(2)−86.5(3)°] within the five-membered ring of **2** are only slightly smaller than in the free ligand [87.75(6)°] whereas the Ge−N bond lengths [181.9(6)−183.7(6) pm] are somewhat longer [180.8(1) pm in L]. Although the elongation of the Ge−N bond lengths upon coordination is only slightly larger than the minimum required to be considered significant (3 times the sum of the standard deviations), it is indeed real as the $N-C_{ring}$ bond lengths [N(1)−C(1) 137.7(10), N(2)−C(2) 138.5(10), N(3)−C(13) 136.2(8), N(4)−C(14) 136.9(8), N(5)−C(25) 137.4(10), and N(6)−C(26) 140.5(10) pm] shorten simultaneously to an even greater extent compared to those in the corresponding free ligand [143.7(3) pm]. This is in agreement with π-acceptor properties of L. Back-donation of electron density from molybdenum into the π-orbital of germanium weakens the demand for electron density by Ge−N π-interactions in favor of the carbon skeleton competing with Ge(II) for the electron lone pairs at nitrogen and strengthening of the C−N π-bonds. This accounts for both the observed elongation of the Ge−N and the shortening of the $N-C_{ring}$ bond lengths, usually only observed in the anellated free ligands. The explanation suggests that in NHGe anellated by benzene[13,23] or even more extended or electron-withdrawing π-systems like naphthalene,[12] pyridine,[11] or quinoxaline,[15] competing more strongly with Ge(II) for the nitrogen electron lone pairs, the acceptor strengths should be even higher than in

---

(17) Crystallographic data for **2**: $C_{39}H_{72}Ge_3MoN_6O_3$, $M = 986.74$, monoclinic, space group $P2_1/c$, $a = 1952.5(3)$ pm, $b = 1053.25(17)$ pm, $c = 2394.9(4)$ pm, $\beta = 96.398(3)°$, $V = 4.8944(13)$ nm^3, $Z = 4$, $\mu = 2.112$ mm^{-1}, $T = 223(2)$ K, 10011 unique reflections ($R_{int} = 0.0894$, R1 = 0.1387, wR2 = 0.1460) and 5201 reflections with $I > 2\sigma(I)$ (R1 = 0.0601, wR2 = 0.1209).[24,25]

(18) Kühl, O.; Blaurock, S.; Sieler, J.; Hey-Hawkins, E. *Polyhedron* **2001**, *20*, 111−117.

(19) Holloway, C. E.; Melnik, M. *Main Group Met. Chem*. **2002**, *25*, 331−410.

(20) The electronegativity of both Mo and Ge is 1.8 according to Pauling, and thus there will be no change of oxidation states following the complexation of L by the Mo fragment.

(21) Elschenbroich, C.; Salzer, A. *Organometallchemie*, 2nd ed.; B. G. Teubner: Stuttgart, 1988; p 279.

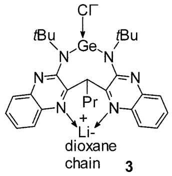
(22) Kühl, O.; Blaurock, S.; Sieler, J.; Hey-Hawkins, E. *Polyhedron* **2001**, *20*, 2171.

(23) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans*. **2000**, 3094.

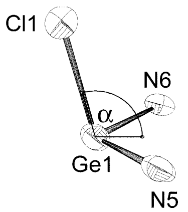
(24) SHELXTL PLUS, XS, Program for Crystal Structure Solution, XL, Program for Crystal Structure Determination, XP, Interactive Molecular Graphics, Siemens Analytical X-ray Institute Inc., 1990.

(25) Sheldrick, G. M. *SADABS, A Program for Empirical Absorption Correction*; Georg-August-Universität Göttingen: Göttingen, Germany, 1998.

L. This was indeed found to be the case. A structurally characterized crystalline adduct of the benzoanellated NHGe $1,2\text{-}C_6H_4[N(CH_2Bu^t)]_2Ge$ to the homologous NHC $1,2\text{-}C_6H_4[N(CH_2Bu^t)]_2C$ reveals strong π-acceptor properties of the germylene and rather Lewis-base properties of the carbene. The fold angles of the ring plane to the Ge−C bond are 77.5° ± 2.5° for the germylene but only 29° ± 2° for the carbene.[23] An even stronger acceptor is a 2-fold quinoxaline anellated non-cyclodelocalized eight-membered NHGe **3** which coordinates LiCl. The chloride anion bonds to germanium (fold angle of Cl−Ge to the N−Ge−N plane $\alpha = 99.5(3)°$) and the lithium cation to two nitrogen atoms of the quinoxaline rings and two dioxane molecules, forming a polymer Li−dioxane backbone.[15] The addition of LiCl was observed neither in the synthesis of L nor in the synthesis of less electron-withdrawing benzo-, naphtho/(2,3)-, or pyrido(2.3)-anellated NHGe.[11−13]



3



Other structurally characterized transition metal complexes of N-heterocyclic germylenes, $[\{(CH_2NBu^t)_2Ge\}_2Ni(CO)_2]$,[7] $[CpNi\{Ge(NBu^t)_2SiMe_2\}_2(\mu\text{-}Cp)]$, $[Rh\{Ge(NBu^t)_2SiMe_2\}_4(\mu\text{-}Cl)]$, $[\{CpFe(CO)_2\}_2\{Ge(NBu^t)_2SiMe_2\}]$,[8] and $[\{naphtho\text{-}1,8\text{-}(NPr^i_2)Ge\}_4Ni]$,[9] are distinguished apart from the different metal by the electron distribution within the ligand from that in **2**. The former have no cyclodelocalized π-electron system whereas the naphthoanellated NHGe contains a rare example of an electron-rich six-membered NGeN heterocycle possessing seven π-electrons including the two electron lone pairs on nitrogen. The corresponding hydrocarbon perinaphthene is a nonplanar cyclic polyolefin with 12 π-electrons. Incorporation of two nitrogen atoms and one germanium atom results in a planar 14 π-electron ring system with formally seven π-electrons (three from carbon and four from nitrogen) in the heterocycle. This increased electron density results in the shortening of the Ge−N (ca. 3.9 pm) and elongation of the C−N (ca. 4.1 pm) bonds upon complexation. This is the inverse effect of that observed during the complexation of L to **2**. A second consequence is a weaker π-acceptor strength which becomes evident in a Ni−Ge distance of 224.00(16) pm[9] close to that in $[(CH_2NBu^t)_2Ge]_2Ni(CO)_2$ (229.69(4) and 229.13(3) pm)[7] and to the sum of the covalent radii. In the latter π-back-donation was considered to be poor by the authors.[7] In the silylamido- and arylgermylene nickel complexes $[CpNi\{Ge(NBu^t)_2SiMe_2\}_2(\eta^1\pi\text{-}Cp[Ge])]$ (208.5(3) pm),[8a] $(Ph_3P)_2Ni\{Ge[N(SiMe_3)_2]_2\}$[5a] (220.6(1) pm), and bis(2,4,6-trifluoromethylphenyl)germylene-$Ni(PPh_3)_2$ (218.14(7) pm)[5b] the Ni−Ge distances are shorter due to π-back-bonding, for the latter established on the basis of DFT investigations.[5b]

The present results shed some light on the donor/acceptor properties of cyclic diaminogermylenes possessing a delocalized 6-π-electron system. They complement the findings on the influence of anellation in unsaturated heterocyclic diaminogermylenes. They show that this influence is mirrored by complexation to transition metals. In particular the extent of π-back-bonding seems to be dependent on the degree of π-electron delocalization of the NHGe. However, to understand the coordination properties of the anellated derivatives better, further comparative studies are necessary.

Acknowledgment. The authors are grateful to Prof. Dr. E. Hey-Hawkins for her support in carrying out the X-ray structural investigations, to I. Stoldt for the measurement of IR spectra, and to the EMA Universität Greifswald and the Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0259991