SHELXL-97;[11f] 371/370 free parameters; GOF = 0.785/1.074, R-value ($I \geq 2\sigma(I)$): $R1 = 0.0723/0.043$, $wR2 = 0.179/0.114$; max./min. residual electron density: $+1.9/+0.9$ and $-1.5/-1.0 \times 10^{-6}$ e$^-$pm^{-3}, respectively.[11c] c) Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411970 ($Cs_{10}Si_7O_9$), -411971 ($Rb_{14}Si_{10}O_{17}$), and -411972 ($Cs_{14}Ge_4Si_6O_9$).d) Bruker AXS, SAINT, and SADABS, **1983**; e) G. Sheldrick, SHELXS-97, Universität Göttingen, **1997**; f) G. Sheldrick, SHELXL-97, Universität Göttingen, **1997**.

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The First Biscarbene Complex of a Group 4 Metal: [Zr{C(Me$_2$P=NSiMe$_3$)$_2$}$_2$]**

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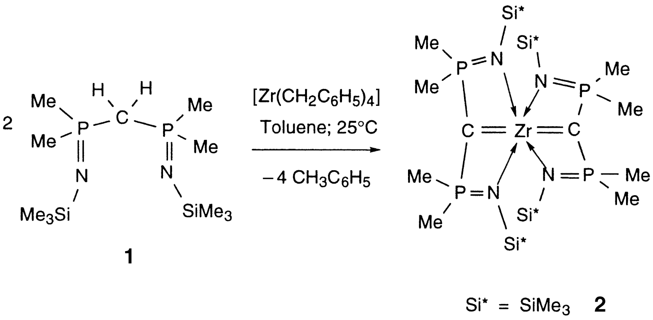
The wealth of chemistry demonstrated by metal–carbene species, summarized in a recent set of reviews,[1] illustrates the great versatility that can be expected from these compounds. Carbenes stimulate much interest because of the many applications to catalysis and organic syntheses.[2] We have recently reported on an extensive series of "pincer" and bridged dimer complexes derived from complete deprotonation of the methylene center in bis(iminophosphanyl)-methanes.[3–7] These complexes, which provide an alternative approach to the generation of this reactive metal–carbon center, were assembled in all cases with a metal/carbon combining ratio of 1:1 with only one phosphinimine ligand per metal atom. These complexes possess "carbene" character in that the metal is multiply bound to the carbon center.

These complexes provided a number of Group 4 examples which have been relatively rare[8] in contrast to the extensive examples of conventional Group 5, 6, and 7 metal carbenes.[2, 9–11] The reactivity patterns of these "pincer" carbenes with metals of Group 4 parallel the behavior of alkylidenes.[3, 6] We now report on a novel zirconium biscarbene complex of this ligand system that contains a linear assembly of two of these metal–carbon multiple bond units and is the first example of such a structure. The compound was obtained by a spontaneous double deprotonation of the methylene backbone of two ligands by a tetraalkylzirconium compound in the same fashion as that used previously to make some of the singly derivatized complexes. Biscarbene complexes of early transition metals are exceptionally rare there being only a few structurally characterized examples of biscarbene complexes of Group 5 metals.[12–15]

The reaction of $CH_2(Me_2P{=}NSiMe_3)_2$[16] (**1**) with $[Zr(CH_2C_6H_5)_4]$[17] in a 2:1 ratio in toluene gave the biscarbene complex $[Zr\{C(Me_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}_2]$ (**2**) in 30–40% yield as a result of complete deprotonation of the acidic methylene groups of the ligands [Eq. (1)]. Surprisingly, under similar reaction conditions, analogous reactions carried out with the ligands $CH_2(R_2P{=}NSiMe_3)_2$ (R = Ph or Cy) containing Ph or Cy instead of Me groups on the phosphorus center did not yield the desired biscarbene product. This demonstrates the uniqueness of the behavior of this methyl-substituted ligand and suggests that steric factors play a key role in the formation of this biscarbene complex.



(1)

The high symmetry of complex **2** is illustrated by the observation of a single sharp resonance signal in the $^{31}P\{^1H\}$ NMR spectrum. The absence of methylene backbone proton signals for the ligand in the ^1H NMR spectrum and the appearance of a positive triplet for the backbone (P-C-P) carbon atoms in the $^{13}C\{^1H\}$ APT spectrum (APT = attached proton test) confirms the double deprotonation of the methylene groups of the ligand. Both in the $^{31}C\{^1H\}$ and the ^1H NMR spectra, the signals of the P-methyl groups appear as "deceptively simple" triplets due to coupling with phosphorus centers that are chemically but not magnetically equivalent, commensurate with the high symmetry of the system.[18]

The molecular structure of **2** (Figure 1) is highly symmetric.[19] The core structure consists of two mutually perpendicular six-membered bicyclic planes, each containing the

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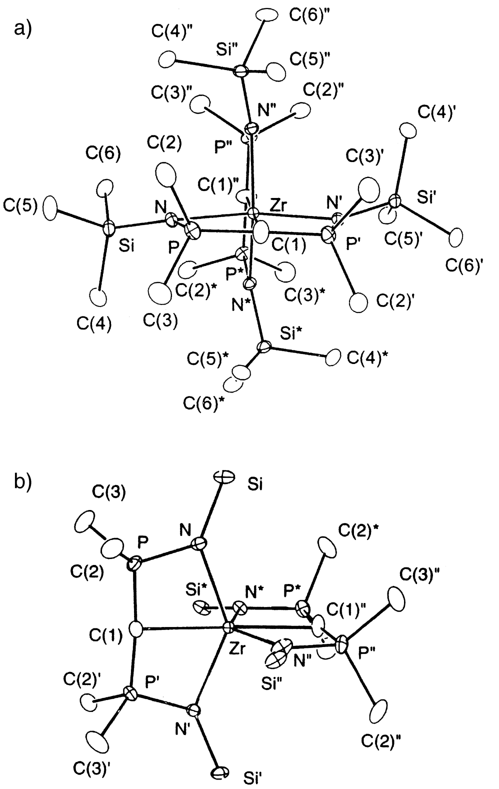

Figure 1. a) Molecular structure of **2** (ORTEP[19] view). All non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. Selected interatomic distances [Å] and angles [°]: Zr-C(1) 2.288(3), Zr-N 2.255(1), P-N 1.630(1), P-C(1) 1.6407(5), P-C(2) 1.811(2), P-C(3) 1.813(2); P-C(1)-P′ 173.9(2), Zr-C(1)-P 93.07(9), N-Zr-N′ 137.63(7), N-Zr-N″ 97.50(2), C(1)-P-N 103.4(1). b) Side view of the core structure of **2**.

tridentate pincer methanediide ligand moiety bound to the central metal center in a spirocyclic fashion. Each of the six-atom planes is formed from the two planar four-membered rings that share a common Zr–C(1) edge. The dihedral angle between these two planar, four-membered rings is 0°; thus, the two ligands are exactly mutually perpendicular and the six-membered bicyclic ring unit is planar. The sum of the angles around the carbene center C(1) is 360°, thus this center is also planar. The C(1)-Zr-C(1)″ angle is exactly 180° by symmetry.

The bonding features within each ligand–metal unit are similar to those which we have encountered in our previously reported systems.[3–7, 20–26] The only major difference between the present biscarbene structure and the monocarbene complex of zirconium is that the six-membered metallacycle in the monoligated structure was not planar but rather subtended a dihedral angle of 11.1(2)° between the two four-membered rings.[7] The Zr–C bond length (2.288(3) Å) in the bis complex is slightly longer than in the mono-ligated analogue,[7] presumably because of the steric crowding at the metal center. However, this M–C distance is shorter than those observed in secondary alkylzirconium derivatives,[27] which supports the assignment of multiple-bond character to the metal–carbene bond.

The bond lengths within the ligand framework of **2** are considerably altered in comparison with those in the free ligands.[28, 29] The P=N bond lengths are elongated and the endocyclic P–C bond lengths are significantly shortened; however, the exocyclic P–C distances are unaffected. The P-C-P bond angle (173.9(2)°) in **2** is considerably wider than in $CH_3CH\{Ph_2P{=}N(Tol)\}_2$ (112.39(19°)[28] and in $H_2C\{Ph_2P{=}NSiMe_3\}_2$ (124.9(2)°).[29] As noted before,[3] comparison of the bond parameters in the six-membered frame with those of similar bis(iminophosphoranyl)methane ligands suggests that there is π-electron delocalization within these frames.

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[27] See for example: a) $[Cp_2Zr(CPh_2H)_2]$: Zr–C 2.379(6), 2.396(6) Å (J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, R. Pearce, *J. Am. Chem. Soc.* **1977**, *99*, 6645–6652); b) $[Cp_2Zr(CH(CH_3)($*6*-ethylpyrid-*2*-yl$)Cl]$: Zr–C 2.421(4) Å (A. S. Guram, D. C. Swenson, R. F. Jordan, *J. Am. Chem. Soc.* **1992**, *114*, 8991–8996); c) $[\{Cp_2Zr(CH(Me)CH_2CH_2O)\}_2]$: Zr–C 2.382(11) Å (H. Takaya, M. Yamakawa, K. Mashima, *J. Chem. Soc. Chem. Commun.* **1983**, 1283–1284).

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[30] Preparation of **2**. All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox. To a pale yellow-brown solution of $[Zr(CH_2C_6H_5)_4]$[17] (0.2 g, 0.44 mmol) in toluene (10 mL) at room temperature was added solid **1** (0.273 g, 0.88 mmol). The reaction mixture was stirred for four days, then concentrated to half of the original volume and finally left at room temperature. After two days a pale brown crystalline solid deposited which was isolated by filtration and washed with few mL of hexane (0.09 g). A second fraction of product (0.02 g) was obtained after cooling the filtrate at $-15\,^{\circ}C$ for 8 h. (Total Yield: 0.11 g, 0.155 mmol, 35.4 %). IR (Nujol mull): $\tilde{\nu}$1457w, 1381s, 1287m, 1278m, 1243s, 1068s, 1038s, 940m, 924s, 897w, 838s, 765s, 751s, 725s, 712w, 685w, 670m, 645m, 615m; ^1H NMR (400.1 MHz, C_6D_6, 298 K): $\delta = 1.58$ (t, $^2J_{P,H} = 6$ Hz, 24 H), 0.39 (s, 36 H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): $\delta = 77.8$ (t, $^1J_{P,C} = 188$ Hz, 2 C; PCP), 25.4 (t, $J_{P,C} = 32$ Hz, 8 C; P-CH_3), 4.6 (s, 12 C, CH_3-$SiMe_3$); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): $\delta = 2.9$ (4P); elemental analysis (%) calcd for $C_{22}H_{60}N_4P_4Si_4Zr$: C 37.31, H 8.54, N 7.91; found: C 37.61, H 8.48, N, 7.64.

[31] Crystal structure analysis for **2**: tetragonal, $P4_2/n$ (no. 86), $a = 13.5050(4)$, $c = 10.5817(5)$ Å, $V = 1929.9(12)$ Å^3, $Z = 2$,. $\rho_{calcd} = 1.219\ g\,cm^{-3}$, $\mu = 0.593\ mm^{-1}$ ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å), $T = 193$ K; the structure was solved by direct methods and refined by full-matrix least-squares procedures: $R_1 = 0.0248$ and $wR_2 = 0.0738$ for 1982 reflections with $F_o^2 > 2\sigma(F_o^2)$ and all data respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171868. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Syntheses and Structures of Niobium Copper Chalcogenido Clusters: $[Cu_4Nb_6Se_{12}O(PMe_3)_{10}][Cu_4NbSe_4Cl_2(PMe_3)_4]\cdot 1.5\,DMF$, $[Cu_4Nb_2Se_6(PMe_3)_8]$, $(NEt_4)[Cu_6Nb_2S_6Cl_5(PEt_3)_6]$, and $[Cu_6NbTe_3(Te_2)_2(PEt_3)_6][CuCl_2]$**

Alexander Lorenz and Dieter Fenske*

Chalcogenometalates of molybdenum, tungsten, and vanadium, in particular the tetrachalcogenometalates $[ME_4]^{n-}$ ($M = Mo$, W, $n = 2$, $E = S$, Se; $M = V$, $n = 3$, $E = S$), have been successfully used as complexing ligands for the synthesis of heterodimetallic clusters, since Müller et al. first synthesized $(PPh_4)_2[Ni(WS_4)_2]$[1] in 1971.[2] As a result of the biochemical[3] and industrial[4] interest in the coordination chemistry of chalcogenomolybdates, -tungstenates, and -vanadates, these compounds have been extensively researched, and a multitude of M-M′-E clusters have been synthesized (M = V, Mo, W, M′ = Fe, Cu, Ag, Au, etc., E = S, Se). In contrast, the coordination chemistry of chalcogenoniobates or -tantalates has remained relatively unexplored. Recently, we reported on the reactivity of soluble chalcogenoniobates towards coinage metal salts in which a series of novel Nb–Cu or Nb–Au chalcogenide clusters were prepared by reactions of $Li_3[NbS_4]\cdot 4\,CH_3CN$,[5a,b] $(NEt_4)_4[Nb_6S_{17}]\cdot 3\,CH_3CN$,[5c] and $(NEt_4)_2[NbE_3(E'tBu)]$ (E = S, Se; E′ = S;[5d,e] E = E′ = Se[6]) with copper or gold salts in the presence of phosphane ligands.[6] For example, polynuclear complexes containing a $[Cu_2Nb_2E_4]$ heterocubane unit, such as $[Cu_2Nb_2E_4Cl_2(PMe_3)_6]\cdot DMF$ **I** (E = S, Se, DMF = *N*,*N*-dimethylformamide) with two terminal chloro ligands, can be isolated. Initial attempts to link the cluster units in **I** through bridging Se atoms by the use of $(Me_3Si)_2Se$ (and accompanying loss of Me_3SiCl) have not yet produced crystalline reaction products. However, Wu et al. reported the successful in situ condensation of cluster complexes.[7] Following this concept, we allowed $(NEt_4)_2[NbSe_3(Se\textit{t}Bu)]$ and $[CuCl(PMe_3)_3]$ to react in DMF[8] and isolated two novel Nb–Cu cluster compounds, the nature of which was dependent on the amount of $(Me_3Si)_2Se$ added during the reaction. The molecular structures of the ionic compound **1** and the neutral cluster **2** (Scheme 1) were determined by X-ray diffraction.[9] Compound **2** might have been formed by a reaction of intermediate $[Cu_2Nb_2Se_4Cl_2(PMe_3)_6]$ with $[CuCl(PMe_3)_3]$ and $(Me_3Si)_2Se$.

Compound **1** crystallizes in the orthorhombic space group *Pbcn* with eight formula units per unit cell. The ionic compound contains two heterodimetallic Nb-Cu-Se cluster ions, $[Cu_4NbSe_4Cl_2(PMe_3)_4]^{2-}$ and $[Cu_4Nb_6Se_{12}O(PMe_3)_{10}]^{2+}$. The anion is formed by a $[NbSe_4]$ tetrahedron, in which four

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