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Synthesis and Structures of Novel Low-Valent Group 14 1,3-Dimetallacyclobutanes and a Mixed-Metal 1,3-Stanna−Plumbacyclobutane

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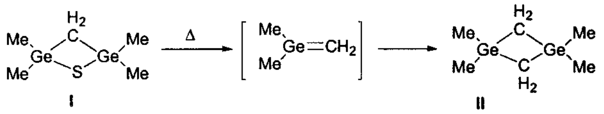
1,3-Digermacyclobutane $R_2Ge(CH_2)_2GeR_2$ (R = Me (**II**) or Ph) has been proposed as the cycloaddition product from the unstable intermediate [$R_2Ge{=}CH_2$] generated from the four-membered ring heterocycles **I** (Scheme 1)[1] or $Ph_2Ge(CH_2)_3$.[2]

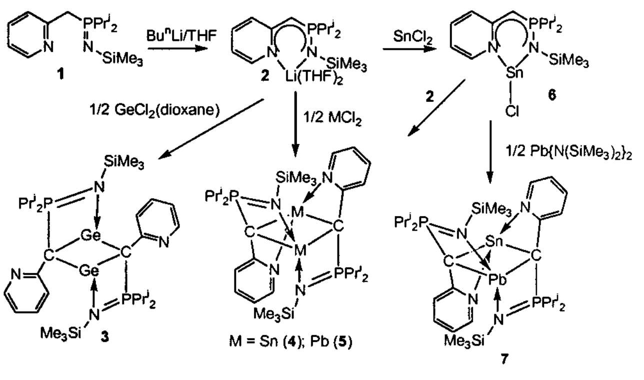
Synthetic methods and structures of stable group 14 compounds with M=C bond have been reviewed.[3,4] By contrast, the heavier congener plumbenes (>Pb=C<) and in particular the low-valent group 14 vinylidene analogues [**:**M=C<] are scarce. This could be due to the fact that less steric crowding at the low-coordinate metal center renders oligomerization more readily. Nevertheless, unstable silavinylidene [**:**$Si{=}CH_2$] and germavinylidene [**:**$Ge{=}CH_2$] had been detected and studied by laser-induced fluorescence spectroscopy.[5] Theoretical studies of the electronic states of germavinylidene [**:**$Ge{=}CH_2$] have also been carried out using ab initio quantum mechanical methods.[6] We here report the synthesis and structural characterization of a series of low-valent group 14 1,3-dimetallacyclobutanes and an unusual 1,3-stanna−plumbacyclobutane. These compounds represent the first series of low-valent group 14 1,3-dimetallacyclobutanes being isolated and structurally characterized.

The supporting ligand used is based on the deprotonation of the methylene backbone of iminophosphorano(pyridyl)methane ($Pr^i_2P{=}NSiMe_3$)(2-Py)CH_2 (**1**). Compound **1** was prepared by heating Pr^i_2P(2-Py)CH_2 with Me_3SiN_3 at 70−100 °C followed by vaccum distillation. Deprotonation of **1** using Bu^nLi in THF afforded yellow crystalline solids of lithium methanide ($Pr^i_2P{=}NSiMe_3$)(2-Py)$CHLi(THF)_2$ (**2**) in 89.5% yield. Treatment of 2 equiv of **2** with $GeCl_2$(dioxane) in diethyl ether afforded the low-valent 1,3-digermacyclobutane 1,3-[Ge{C($Pr^i_2P{=}NSiMe_3$)(2-Py)}]$_2$ (**3**) in good yield. Similar reactions with $SnCl_2$ and $PbCl_2$ afforded the 1,3-distannacyclobutane 1,3-[Sn{C($Pr^i_2P{=}NSiMe_3$)-(2-Py)}]$_2$ (**4**) and 1,3-diplumbacyclobutane 1,3-[Pb{C($Pr^i_2P{=}NSiMe_3$)(2-Py)}]$_2$ (**5**), respectively. The reaction of of **2** with $SnCl_2$ in 1:1 ratio afforded the chlorotin(II) complex [Sn{CH-($Pr^i_2P{=}NSiMe_3$)(2-Py)}Cl] (**6**). Further reaction of **6** with 1 equiv of **2** afforded compound **4**. However, similar reaction of 1 equiv of **2** with MCl_2 (M = Ge, Pb) afforded only intractable oily substances which could not be characterized. It is proposed that the reactions proceeded through the alkylmetal(II) chloride intermediate {($Pr^i_2P{=}NSiMe_3$)(2-Py)CH}MCl similar to **6**, followed by further abstraction of the methine proton by lithium complex **2** and elimination of LiCl and **1** to form the unstable metallavinylidene "**:**M=C($Pr^i_2P{=}NSiMe_3$)(2-Py)". This intermediate then undergoes a "head-to-tail" cycloaddition to form the 1,3-dimetallacyclobutanes. The lithium complex **2** acts both as the ligand-tranfer reagent and strong base for dehydrochlorination (Scheme 2).

Scheme 1



Scheme 2



The reaction of 2 equiv of **6** with Pb{N($SiMe_3$)$_2$}$_2$ afforded the mixed-metal 1,3-stanna−pumbacyclobutane [1-Sn{C($Pr^i_2P{=}NSiMe_3$)(2-Py)}3-Pb{C($Pr^i_2P{=}NSiMe_3$)(2-Py)}] (**7**). Compound **7** could also be a "head-to-tail" cycloaddition product from the stannavinylidene "**:**Sn=C($Pr^i_2P{=}NSiMe_3$)(2-Py)" and plumbavinylidene "**:**Pb=C($Pr^i_2P{=}NSiMe_3$)(2-Py)".

The structurally related ligand bis(iminophosphorano)methane CH_2\{($Ph_2P{=}N(SiMe_3)$)\}$_2$ has been used in the synthesis of metal methanide and bimetallic methandiide complexes of aluminum.[7] Furthermore, the dimeric and tetrameric Cr(II)-bridging carbene complexes [Cr{μ_2-C($Ph_2P{=}NSiMe_3$)$_2$-κ^4C,C′N,N′}]$_2$ and [Cr_2(μ_2-Cl)$_2${μ_2-C($Ph_2P{=}NSiMe_3$)$_2$-κ^4C,C′N,N′}(LiCl)(THF)$_2$]$_2$,[8] and the "Pincer" carbene complexes [Zr{C$Ph_2P{=}NR$)$_2$-κ^3C,N,N′}(CH_2-Ph)$_2$] (R = adamantyl or $SiMe_3$),[9] were also derived from the bis(iminophosphorano)methane ligand.

Compounds **2**−**7** were characterized by elemental analysis, ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectroscopy. The ^{13}C signals of the quarternary methandiide carbon in **3**−**5** and **7** were not observed. For compounds **3**−**7**, the single-crystal X-ray structures had been determined.

The molecular structure of 1,3-digermacyclobutane 1,3-[Ge-{C($Pr^i_2P{=}NSiMe_3$)(2-Py)}]$_2$ (**3**) as shown in Figure 1 comprises two germanium atoms bridged by two iminophosphorano-(pyridyl)methandiide carbon centers, forming a 1,3-digermacyclobutane ring.[10] The geometry around each of the three-coordinate germanium centers is trigonal pyramidal. The imino nitrogen arms of the ligands dangle back and coordinate to the germanium centers forming two nonplanar GeCPN four-membered rings. These four-membered rings together with the Ge_2C_2 ring form a "step-like" structure framework.

In contrast, the molecular structures of 1,3-distannacyclobutane 1,3-[Sn{C($Pr^i_2P{=}NSiMe_3$)(2-Py)}]$_2$ (**4**) and 1,3-diplumbacyclobutane 1,3-[Pb{C($Pr^i_2P{=}NSiMe_3$)(2-Py)}]$_2$ (**5**) are somewhat different from that of **3**. The environments around the metal centers in each of **4** and **5** are different due to coordination to different groups. One metal center adopts a tetrahedral geometry,

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[10] Crystal data for **3**: triclinic, space group: *P*-1, yellowish-orange crystals, a =12.2138(9) Å, b = 12.792(1) Å, c =13.206(1) Å, α = 80.997-(2)°, β = 85.355(2)°, γ = 63.923(1)°, V = 1830.3(2) Å^3, Z = 2, T = 293 K, R = 0.0369, R_w = 0.0753, GOF = 0.898.

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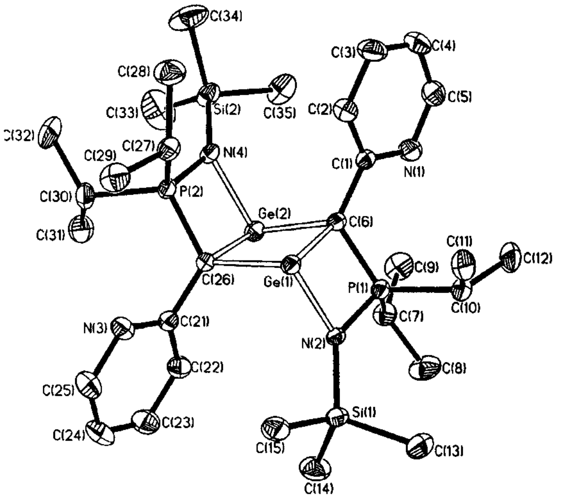

Figure 1. ORTEP drawing of **3**; 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge(1)−N(2) 2.055(2), Ge(1′)−N(2′) 2.064(2), Ge(1)−C(6) 2.107(3), Ge(1)−C(6′) 2.132(3), Ge(1′)−C(6′) 2.079(3), Ge(1′)−C(6)2.154-(3), P(1)−N(2) 1.632(2), P(1′)−N(2′) 1.630(2); Ge(1)−C(6)−Ge(1′) 90.29(10), Ge(1′)−C(6′)−Ge(1) 91.68(10), N(2)−Ge(1)−C(6) 74.66(9), N(2)−Ge(1)−C(6′) 98.35 (9), C(6)−Ge(1)−C(6′) 88.58(10), N(2)−Ge-(1)−P(1) 36.58(6), C(6)−Ge(1)−P(1) 40.13(7), C(6′)−Ge(1)−P(1) 104.04-(8), N(2′)−Ge(l′)−C(6′) 76.38(9), N(2′)−Ge(1)−C(6) 96.91(9), C(6′)−Ge(1)−C(6) 88.70(10), N(21)−Ge(1′)−P(1′) 36.62 (6)

being bonded to the methandiide carbons and coordinated to two imino nitrogens. The other metal center also adopts a tetrahedral geometry, but bonded to the methandiide carbons and coordinate to two pyridyl nitrogens. As compared to the Ge(II) centers in **3**, the additional coordination from the pyridyl groups is presumably due to the larger atomic sizes of the Sn(II) and Pb(II) atoms. The steric crowding of the smaller Ge(II) in **3** prevents the close approach of the pyridyl groups.

The molecular structure of mixed-metal cyclobutane analogue **7** (Figure 2)[11] also adopts the structure similar to **4** and **5**, with the Pb(II) atom coordinated to the slightly more bulky imino nitrogens, and the Sn(II) atom is coordinated to the two pyridyl nitrogens. With the M_2C_2 or SnCPbC ring as the base, the nonplanar MCC(py)N(py) and MCPN(imino) rings form the flaps of an "open box"-like structure framework.

The bond distances within the dimetallacyclobutane rings in each of compounds **3**−**5** are different. The average M−C distance of 2.118 Å in **3** is significantly longer than the Ge−C distance of 1.803(4) Å in fluorenylidene-substituted germene[12] and 1.970(2) Å in digermacyclopropane $Ar'_2GeCH_2GeAr'_2$ (Ar'_2 = 2,4,6-$Pr^i_3C_6H_2$).[3,13] The average Sn−C distances of 2.325 Å (in **4**) and 2.320 Å (in **7**) are longer than the Sn−C distance of 2.025(4) Å in stannene $[\{(Me_3Si)_2CH\}_2Sn{=}C\{(BBu^t)_2C(SiMe_3)_2\}]$.[3,14] The metal−metal distances in these dimetallacyclobutanes are too long to consider the existence of bonding interactions. The stability of these low-valent dimetallacyclobutanes are presumably attributed to the coordination from the imino and pyridyl groups.

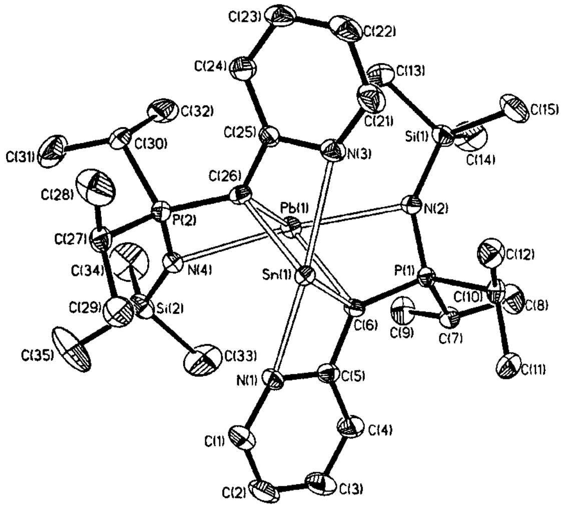

Figure 2. ORTEP drawing of **7**; 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pb(l)−C(26) 2.434(7), Pb(1)−C(6) 2.451(8), Pb(1)−N(2) 2.617(6), Pb(1)−N(4) 2.640(6), Sn(1)−C(6), 2.329(7), Sn(1)−C(26) 2.310(8), Sn(1)−N(3) 2.500(6), Sn(1)−N(1) 2.503(6), P(1)−N(2) 1.601-(6), P(2)−N(4) 1.580(7); C(26)−Pb(1)−C(6) 87.7(2), C(26)−Pb(1)−N(2) 102.8(2), C(6)−Pb(1)−N(2) 62.5(2), C(26)−Pb(1)−N(4) 62.2(2), C(6)−Pb(1)−N(4) 102.3(2), N(2)−Pb(1)−N(4) 160.31(19), C(26)−Sn(1)−C(6) 93.6(3), C(26)−Sn(1)−N(3) 57.8(2), C(6)−Sn(1)−N(3) 104.5(2), C(26)−Sn(1)−N(1) 103.9(2), C(6)−Sn(1)−N(1) 57.9(2), N(3)−Sn(1)−N(1) 155.8(2).

In summary, lithium iminophosporano(pyridyl)methanide complex reacts with MCl_2 (M = Ge, Sn, Pb) to give novel low-valent group 14 1,3-dimetallacyclobutanes. The reaction of tin(II)-methanide chloride **6** with $Pb\{N(SiMe_3)_2\}_2$ gave the mixed-metal 1,3-stanna−plumbacyclobutane. These metallacyclobutanes could be the products from cycloaddition of the unstable metallavinylidene "**:**$M{=}C(Pr^i_2P{=}NSiMe_3)$(2-Py)".

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Supporting Information Available: Experimental procedures for preparation of **1**−**7**, spectral data, and crystallographic data (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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[11] Crystal data for **7**: orthorhombic, space group: *Pbca*, orange crystals, a = 13.4402(7) Å, b = 18.2669(10) Å, c = 31.5543(18) Å, V = 7746.9(7) $Å^3$, Z = 8, T = 293 K, R = 0.0404, R_w = 0.1022, GOF = 0.962.

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