Bridging Ligands

Triatomic EP_2 Triangles (E = Ge, Sn, Pb) as μ_2:η^3,η^3-Bridging Ligands**

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Three-membered, 2π-electron rings comprised of main-group elements are of interest as compact manifestations of $4n+2$ Hückel aromaticity in which $n=0$.[1] The cyclopropenium ion [*cyclo*-C_3H_3]$^+$ serves as the prototypical organic representative of this class,[2] while the prospect of substituting one or more CH units of the cyclopropenium ring by an isolobal heteroatom has spurred investigations seeking to extend the concept of π delocalization throughout the p block of the

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periodic table.[3,4] Reactive unsaturated rings, such as cyclobutadiene, may be stabilized through complexation with a metal center. With this idea in mind, we present herein a study on the synthesis of triatomic {*cyclo*-EP_2} triangles (E = Ge, Sn, and Pb) stabilized within the coordination sphere of a sterically protected diniobium unit. This particular family of {*cyclo*-EP_2} triangles has not been considered previously in either its free or complexed form. Furthermore, divalent atoms from Group 14 have received relatively little attention as components in three-membered, 2π-electron rings. In fact, only the neutral cyclopropene carbene *cyclo*-:$C(C_2H_2)$, diazacyclopropene carbene *cyclo*-:CN_2, and silacyclopropenylidene *cyclo*-:$Si(C_2H_2)$ molecules have been considered theoretically,[5,6] with three-membered rings containing the heavier atoms from Group 14 having been completely neglected to date.

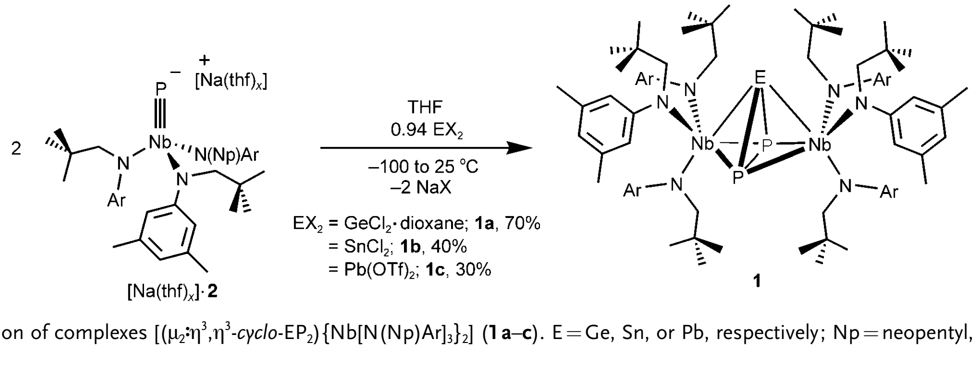
The title complexes $[(\mu_2{:}\eta^3,\eta^3$-*cyclo*-$EP_2)\{Nb[N(Np)Ar]_3\}_2]$ (**1a–c**; E = Ge, Sn, and Pb, respectively; Np = neopentyl, Ar = 3,5-$Me_2C_6H_3$) were formed as a consequence of the propensity of the niobium phosphide anion $[P{\equiv}Nb\{N(Np)Ar\}_3]^-$ (**2**)[7] to undergo electronic rearrangement when functionalized at the phosphorus atom.[7,8] This tendency has already afforded both a new synthesis of phosphaalkynes[8] and of diorganophosphanylphosphinidene complexes.[7] The current manifestation of this phenomenon, which is characterized by the exchange of a niobium/phosphorus multiple-bond interaction for a main-group element/phosphorus bonding interaction, is simply derived from salt elimination reactions of divalent Group 14 halides with the $[Na(thf)_x]^+$ derivative of anion **2**.[7]

$^{31}P\{^1H\}$ NMR spectroscopic analysis on a room-temperature solution containing equimolar quantities of $[Na(thf)_x]{\cdot}\mathbf{2}$ and $SnCl_2$ after mixing in cold THF revealed a single new resonance centered at $\delta = 47.8$ ppm, which is well upfield of the range expected for a niobium phosphinidene complex.[7,9] X-ray structural analysis of a crystal harvested from the reaction mixture established the identity of complex **1b** as containing a central $\{SnP_2\}$ ring and as the product of a double addition of $[Na(thf)_x]{\cdot}\mathbf{2}$ to $SnCl_2$ with elimination of NaCl. A purposeful synthesis was then devised and extended to the Ge- and Pb-containing derivatives. Accordingly, the slow addition of 0.47 equivalents of the respective divalent Group 14 source ($GeCl_2{\cdot}$dioxane, $SnCl_2$, or $Pb(OTf)_2$[10]) to $[Na(thf)_x]{\cdot}\mathbf{2}$ in cold THF provided dark-red **1a** and forest-green **1b** and **1c**, respectively, in moderate yields of isolated product (**1a**: 65%, **1b**: 40%, **1c**: 30%) after removal of the salt by-product and crystallization from Et_2O (Scheme 1).

Diamagnetic complexes **1a–c** are obtained as crystalline solids, which are soluble in ethereal and aromatic solvents. Complexes **1a** and **1b** retain their integrity in solution at elevated temperatures ([D_6]benzene, 80–100 °C, 2 days), whereas complex **1c** decomposed in solution at room temperature to Pb^0 and the known bridging diphosphide ligand complex $[(\mu_2{:}\eta^2,\eta^2\text{-}P_2)\{Nb[N(Np)Ar]_3\}_2]$ (**3**),[11] over several hours; furthermore, the absence of light did not retard the decomposition of **1c**. Therefore, considering the fragile nature of **1c**, the mild conditions of the present synthesis,[12] condition which permitted it to be isolated in pure form, can be further appreciated.

The solid-state structures for complexes **1a–c** are depicted in Figure 1. The $\mu_2{:}\eta^3,\eta^3$ disposition of the {*cyclo*-EP_2} ring between the two niobium centers is evident in each structure. The {*cyclo*-EP_2} units in **1b** and **1c** are near-perfect isosceles triangles, in which the ∢P-E-P angle in **1c** (48.85(5)°) is slightly more acute than that in **1b** (51.23(7)°) as a result of the larger covalent radius of the lead center. Indeed, the average E–P bond lengths in **1b** and **1c** (Sn–P: 2.571 Å, Pb–P: 2.677 Å) follow the trend of the covalent radii going from Sn to Pb and reflect values typical of Sn–P and Pb–P single bonds.[13] Additionally, the P–P distances of 2.223(2) and 2.213(3) Å for **1b** and **1c**, respectively, are in the range typical of P–P single bonds,[14] thus indicating a saturated electronic framework for these {*cyclo*-EP_2} rings when sandwiched between two reducing d^2 niobium centers.[11] Complex **1a**, however, was found to crystallize in the cubic space group $P2_13$ with its Nb–Nb vector coincident with a crystallographic C_3 axis. Unfortunately, this morphology resulted in a crystallographically imposed threefold compositional disorder of the ring atoms in the {*cyclo*-GeP_2} unit. Consequently, chemically suspect metrical parameters were obtained for the complexed $\{GeP_2\}$ ring, in which the edge distance of 2.460 Å clearly exceeds the value for a P–P single bond and reflects structural dominance by the larger Ge component.[15]

To garner further insight into the geometrical structure of **1a**, the model construct $[(\mu_2{:}\eta^3,\eta^3$-*cyclo*-$GeP_2)\{Nb(NH_2)_3\}_2]$ (**4a**) was subjected to full geometric optimization at the density functional level (ADF 2004.01, ZORA-TZ2P/BP86). Using the experimental metrical parameters of **1a** as the basis for the initial computational model structure, **4a** converged to a geometry with P–P (2.242 Å) and P–Ge (2.4465 Å av)



Scheme 1. Formation of complexes $[(\mu_2{:}\eta^3,\eta^3$-*cyclo*-$EP_2)\{Nb[N(Np)Ar]_3\}_2]$ (**1a–c**). E = Ge, Sn, or Pb, respectively; Np = neopentyl, Ar = 3,5-$Me_2C_6H_3$, OTf = O_3SCF_3.

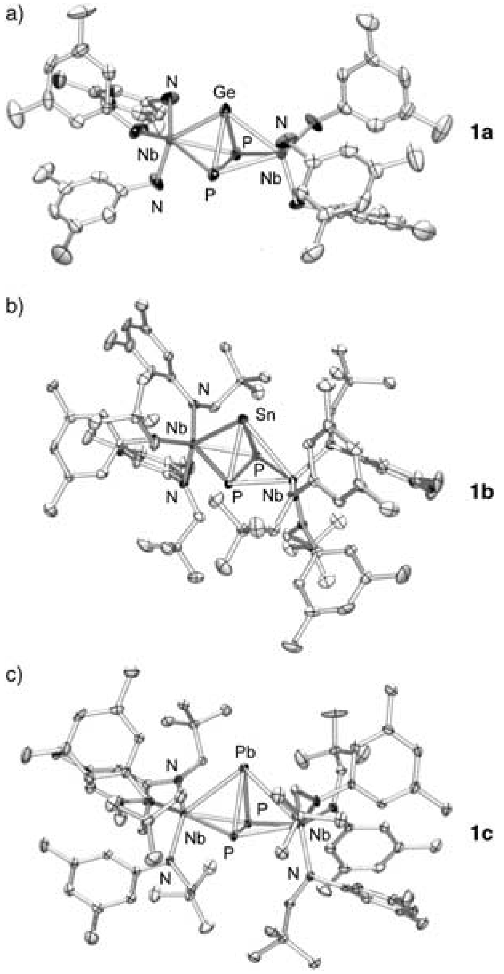


Figure 1. ORTEP diagrams of a) **1a**, b) **1b**, and c) **1c** at the 35% probability level. All the hydrogen atoms and the neopentyl residues of **1a** have been omitted for clarity.

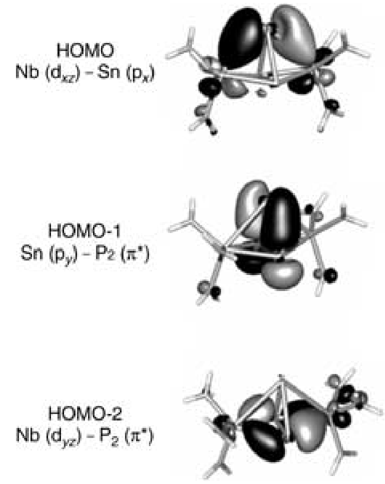


Figure 2. Selected frontier molecular orbitals calculated for **4b**.

separations consistent with both P–P and P–Ge single bonds.[13,14] All other overall structural features for **4a** were similarly consistent with those found experimentally for **1b** and **1c**. Furthermore, the calculated structural parameters for models **4b** and **4c** were in excellent agreement with their experimental counterparts (**1b** and **1c**, respectively). Therefore, we contend that **4a** represents the molecular geometry for complex **1a** in the absence of crystallographic disorder.

Of particular interest are the electronic-structure attributes attendant with {*cyclo*-EP_2} complexation in **1a**–**c**. The highest occupied molecular orbitals (HOMOs) calculated for **4b** are shown in Figure 2.[16] The HOMO-1 is part of the σ framework of the {*cyclo*-SnP_2} unit, whereas complexation of the Nb centers consists of a pair of mutually orthogonal two-electron π backbonds. The HOMO involves the out-of-plane valence p orbital of the Sn center as the acceptor component in one of these bonds, whereas the HOMO-2 utilizes a P–P π^* orbital as the acceptor component in the other bond. Accordingly, a pair of d^2 niobium trisamide fragments is seen to be electronically complementary to a formally neutral {*cyclo*-EP_2} ring. However, summation of the calculated multipole-derived charges (MDC-q)[17] on the ring atoms in **4a**–**c** indicate that each complexed {*cyclo*-EP_2} unit bears a net charge of approximately -1.0 ($\Sigma_{\text{MDC-q}} = -1.186$, -0.917, and -0.837 a.u. for **4a**–**c**, respectively). Thus, although formally neutral as free entities, complexation by two electropositive d^2 Nb centers renders these {*cyclo*-EP_2} rings moderately anionic. The latter interpretation is consistent with the saturated nature of the {*cyclo*-EP_2} framework, as determined crystallographically for **1b** and **1c**.

It is noteworthy that the net negative charge calculated for the {*cyclo*-EP_2} rings in models **4a**–**c** decreases in the order Ge > Sn > Pb according to the decreasing electronegativity of the Group 14 atom.[18] Indeed, the negative charge at the phosphorus center is calculated to remain relatively constant between models **4a**–**c** (-0.384 ± 0.016 a.u.), and the variation in the net charge between each {*cyclo*-EP_2} ring is dictated by the charge at the E center (MDC-q $= -0.390$, -0.185, and -0.057 a.u. for **4a**–**c**, respectively). A similar dependence on the identity of the Group 14 atom is observed experimentally in the $^{31}P\{^1H\}$ NMR spectra of complexes **1a**–**c** in solution ($\delta^{31}P = -15.7$, 47.8, and 115.2 ppm for **1a**–**c**, respectively). The downfield progression in the resonances is attributed qualitatively to the increase in the paramagnetic component σ_{para} of the total ^{31}P nuclei shielding tensor σ_{total} as the Group 14 atom becomes less electronegative.[19] NMR calculations performed on models **4a**–**c** are consistent with this suggestion, thus revealing that variation in σ_{para} dominates σ_{total} and increases in the order Pb > Sn > Ge.[20] Mapping the principal components of σ_{para} onto the molecular frame of **4a**–**c** (Figure 3) reveals that $R(\sigma_{11})$ mediates an occupied–virtual coupling between the Nb_2–P_2 π^* backbond (occupied) and the σ^* framework (virtual) of the {EP_2} ring in the presence of an applied magnetic field. Thus, a molecular-orbital description of ^{31}P nuclei deshielding as influenced[21] by the identity of the Group 14 atom[22] within the {*cyclo*-EP_2} ring is afforded.

In conclusion, new triatomic molecules are of interest both as synthetic targets and theoretical constructs.[3,4] We have identified that complexed forms of {*cyclo*-EP_2} triangles

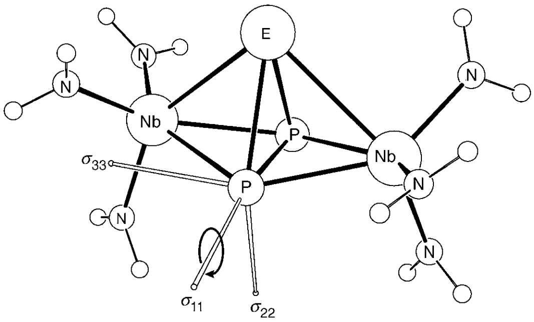


Figure 3. Principal components of σ_{para} for models **4a–c**.

containing germanium, tin, and lead can be synthesized as a direct consequence of the remarkable chemistry of the niobium–phosphorus triple bond in phosphide anion **2**.[7,8] Future prospects in this area include chemical liberation of the $\{\mathit{cyclo}\text{-}\mathrm{EP_2}\}$ triangles, with an aim of establishing their reactivity patterns.

Experimental Section

$[(\mu_2{:}\eta^3,\eta^3\text{-}\mathit{cyclo}\text{-}\mathrm{EP_2})\{\mathrm{Nb[N(Np)Ar]_3}\}_2]$ (**1a–c**):[10] Solutions of $[\mathrm{Na(thf)}_x]\cdot\mathbf{2}$ (0.300 g, 0.380 mmol) in THF (5 mL) and the corresponding divalent Group 14 salt (0.47 equiv; $\mathrm{GeCl_2\cdot dioxane}$, $\mathrm{SnCl_2}$, or $\mathrm{Pb(OTf)_2}$ for **1a–c**, respectively) in THF (2 mL) were frozen separately in a glove-box cold well. On removal of the solutions from the cold well, the thawing solution containing the salt was added dropwise (approximately 0.6 mL) over 1 min to the thawing solution of $[\mathrm{Na(thf)}_x]\cdot\mathbf{2}$. The reaction mixture was stirred for an additional 3 min, whereupon both solutions were placed back into the cold well. This procedure was repeated twice more until complete addition of the divalent Group 14 salt was achieved. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 30 min before being evaporated to dryness in vacuo. The residue was extracted with *n*-pentane (3 mL), the extract filtered through celite, and the filtrate evaporated to dryness in vacuo. Crystallization of each complex was effected by storing a saturated solution of $\mathrm{Et_2O}$ at −35 °C for 1–3 days.

1a: Red crystals, 70 % yield; ^{1}H NMR (500 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = 6.69$ (s, 6H, *o*-Ar), 6.60 (s, 3H, *p*-Ar), 4.42 (s, 6H, N-$\mathrm{CH_2}$), 2.20 (s, 18H, Ar-$\mathrm{C}\mathit{H}_3$), 1.02 ppm (s, 27H, *t*Bu); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = 155.9$ (*ipso*-aryl), 137.7 (*m*-Ar), 126.4 (*p*-Ar), 125.2 (*o*-Ar), 80.3 (N-$\mathit{C}\mathrm{H_2}$), 37.3 ($\mathit{C}(\mathrm{CH_3})_3$), 30.8 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 21.9 ppm (Ar-$\mathit{C}\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (202.5 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = -15.7$ ppm (s); elemental analysis (%) calcd for $\mathrm{C_{78}H_{120}N_6P_2GeNb}$: C 64.07, H 8.27, N 4.97; found: C 65.50, H 8.98, N 5.50.

1b: Green crystals, 40 % yield; ^{1}H NMR (500 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = 6.76$ (s, 6H, *o*-Ar), 6.60 (s, 3H, *p*-Ar), 4.35 (s, 6H, N-$\mathrm{CH_2}$), 2.22 (s, 18H, Ar-$\mathrm{C}\mathit{H}_3$), 1.02 ppm (s, 27H, *t*Bu); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = 156.2$ (*ipso*-aryl), 137.7 (*m*-Ar), 126.3 (*p*-Ar), 125.0 (*o*-Ar), 80.0 (N-$\mathit{C}\mathrm{H_2}$), 37.4 ($\mathit{C}(\mathrm{CH_3})_3$), 30.8 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 21.9 ppm (Ar-$\mathit{C}\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (202.5 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = 47.8$ ppm (t, $^1J(\mathrm{Sn\text{-}P}) = 205.2$ Hz); ^{119}Sn NMR (186.5 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = -696.4$ ppm (br s, $\nu_{1/2} = 1300.8$ Hz); elemental analysis (%) calcd for $\mathrm{C_{78}H_{120}N_6P_2SnNb}$: C 62.11, H 8.02, N 5.57; found: C 61.75, H 7.91, N 5.66.

1c: Green crystals, 30 % yield; ^{1}H NMR (500 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = 6.78$ (s, 6H, *o*-Ar), 6.62 (s, 3H, *p*-Ar), 4.45 (s, 6H, N-$\mathrm{CH_2}$), 2.23 (s, 18H, Ar-$\mathrm{C}\mathit{H}_3$), 1.02 ppm (s, 27H, *t*Bu); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (202.5 MHz, $[\mathrm{D_6}]$benzene, 20 °C): $\delta = 115.2$ ppm (s with shoulders); satisfactory $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectroscopic and elemental analyses could not be obtained because of the rapid decomposition of **1c**.[23]

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[12] An alternate synthesis of **1b** was attempted by treatment of **3** with an excess of Sn dust in THF; however, no reaction was observed when intermittently assayed for 24 h. We tentatively attribute this observation to the inability of elemental Sn to reduce the $\{\mathrm{P_2}\}$ unit in **3**.

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[15] Separation of the Ge and P centers within the asymmetric unit is possible by allowing each atom to refine freely with the appropriate site occupancy factor (namely, $\mathrm{Ge_{0.33}P_{0.67}}$); however, we suggest that the true molecular geometry in **1a** is marred by the crystallographically imposed symmetry, as the inherent

translations of the $\{Nb[N(Np)Ar]_3\}$ fragments, which are required to reveal a chemically sensible molecular geometry, are masked relative to the central ring (see the Supporting Information for full details).

[16] The molecular-orbital splitting patterns calculated for models **4a–c** are qualitatively identical.

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[20] The calculated σ_{para} values are −558.6, −626.9, and −682.7 ppm for models **4a–c**, respectively; the total ^{31}P nuclei chemical shielding σ_{total} is the sum of the individual paramagnetic σ_{para}, diamagnetic σ_{dia}, and spin orbit σ_{so} tensor components; note that σ_{dia} was found to be essentially invariant between models **4a–c** (961.9 ± 0.5 ppm) and σ_{so} made a negligible contribution (13–21 ppm).

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[22] Complex **1b** gives rise to a broad, upfield ^{119}Sn NMR signal at $\delta = -696.4$ ppm ($\nu_{1/2} = 1300.8$ Hz, $[D_6]$benzene, 20°C). Typical ^{119}Sn NMR chemical shifts for divalent Sn species are significantly deshielded relative to that of **1b**. We attribute this disparity to ground-state electronic population of the normally empty p orbital of the Sn^{II} center. For a discussion of ^{119}Sn NMR chemical shifts in divalent Sn complexes, see: a) B. E. Eichler, B. L. Phillips, P. P. Power, M. P. Augustine, *Inorg. Chem.* **2000**, *39*, 5450; b) B. E. Eichler, A. D. Phillips, S. T. Haubrich, B. V. Mork, P. P. Power, *Organometallics* **2002**, *21*, 5622. Attempts to locate the corresponding ^{203}Pb NMR shift for **1c** were unsuccessful.

[23] CCDC-262173–262175 contain the supplementary crystallographic data for $[(\mu_2{:}\eta^3,\eta^3\text{-}\mathit{cyclo}\text{-}SnP_2)\{Nb[N(Np)Ar]_3\}_2]$ (**1b**), $[(\mu_2{:}\eta^3,\eta^3\text{-}\mathit{cyclo}\text{-}GeP_2)\{Nb[N(Np)Ar]_3\}_2]$ (**1a**), and $[(\mu_2{:}\eta^3,\eta^3\text{-}\mathit{cyclo}\text{-}PbP_2)\{Nb[N(Np)Ar]_3\}_2]$ (**1c**), respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data request/cif.