σ-Acceptor Ligands

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Gold–Silane and Gold–Stannane Complexes: Saturated Molecules as σ-Acceptor Ligands**

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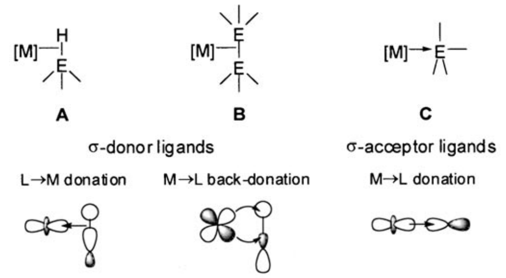
The discovery that saturated molecules may form σ complexes by side-on coordination of a σ bond to a transition metal represents a major breakthrough in transition-metal chemistry.[1–3] Over the years, considerable progress has been made in the understanding of this bonding situation. The coordination and activation of σ bonds involving Group 14 elements ($E = C$, Si, Ge, Sn, Pb) is at the forefront of developments in this area. An increasing variety of complexes **A**[3–5] and **B**[6,7] (Scheme 1) featuring side-on coordinated σ(E−H) and σ(E−E) bonds have been isolated, and the key factors governing the delicate balance between dissociation and oxidative addition have been progressively identified. The common feature and believed prerequisite for the coordination of saturated molecules free of lone pairs to transition metals is the superposition of ligand→metal donation (from a filled σ orbital of the ligand to an empty d orbital of the metal) and metal→ligand back-donation (from a filled d orbital of the metal to an empty σ* orbital of the ligand).



Scheme 1. Complexes **A**–**C** featuring Group 14 saturated molecules coordinated to transition metals ($E = C$, Si, Ge, Sn, Pb).

Aiming at identifying new types of metal–ligand interactions, and stimulated by our work on Group 13 Lewis acids as acceptor ligands,[8–10] we recently became interested in complexes of type **C**, in which a saturated Group 14 element could behave as an end-on, σ-acceptor ligand toward a transition metal. Heavier Group 14 elements such as silicon and tin are known to readily form hypervalent compounds through donor→acceptor interactions with organic Lewis bases.[11–13] A related situation is envisioned in complexes **C**, with a transition metal acting as a Lewis base. Such donor→acceptor interactions between transition metals and silanes or stannanes have been invoked in a few highly strained complexes on the basis of relatively short M−E distances.[14] Furthermore, the presence of a $Pd^{II} \rightarrow Sn^{IV}$ dative bond was recently evidenced structurally and theoretically in a palladastannatrane cage complex supported by four methimazolyl groups.[18] Herein, we report the straightforward synthesis and complete characterization of three gold complexes supported by diphosphino silane and stannane ligands. The presence of metal→silane and metal→stannane interactions in these complexes has been substantiated spectroscopically, structurally, and theoretically, thus providing unambiguous evidence for the existence of complexes of type **C**.

From our previous studies on Group 13 Lewis acids,[8] the use of two phosphine buttresses ligated by *ortho*-phenylene spacers was considered as a good compromise in order to support, but not impose, the coordination of the Group 14 element. We thus targeted the two complexes [*o*-$\{(iPr_2P)C_6H_4\}_2E(Ph)FAuCl$] **2** ($E = Si$) and **4** ($E = Sn$). The

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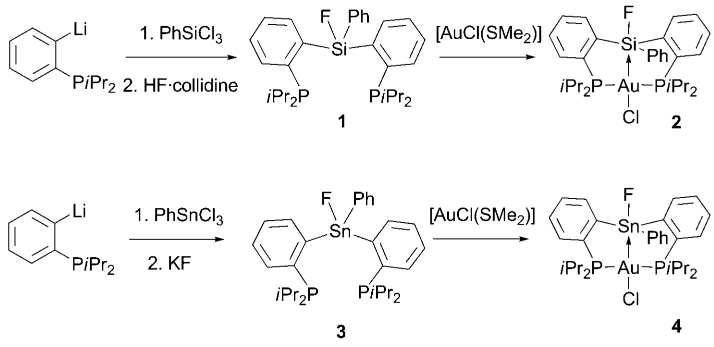
diphosphino silane ligand **1** was prepared by treating the *o*-lithiated diisopropylphenylphosphine with $PhSiCl_3$ and then with HF·collidine (collidine = 2,4,6-trimethylpyridine).[19] The chlorine–fluorine exchange imparts higher stability to the ligand. By allowing **1** to react with $[AuCl(SMe_2)]$, the desired gold complex **2** was obtained in 88 % yield as an analytically pure white solid (Scheme 2). Complex **2** exhibits a single signal by ^{31}P NMR spectroscopy ($\delta = 57.1$ ppm), indicating the symmetric coordination of the two phosphorus atoms. The signal in the ^{29}Si NMR spectrum ($\delta = -21.4$ ppm) is shifted by $\delta = 16$ ppm from that of the free ligand **1** ($\delta = -5.2$ ppm). This shift to lower frequency parallels those typically observed for pentacoordinate neutral silicon adducts[11,20] and strongly suggests the presence of a gold→silane interaction in **2**.



Scheme 2. Synthesis and coordination of the diphosphino silane and stannane ligands **1** and **3**.

According to X-ray diffraction analysis (Figure 1 a), complex **2** adopts a discrete mononuclear structure in the solid state. The gold center is surrounded by the chlorine and the two phosphorus atoms organized in a quasi-planar arrangement halfway between trigonal and T-shape geometries (P-Au-P 140.14(5)°). The silicon atom also comes close to the metal center (Au–Si 3.090(2) Å). This distance is beyond the sum of covalent radii (2.47 Å)[21] but is well within the sum of the van der Waals radii (4.20 Å),[22] suggesting the presence of a gold→silane interaction. This unusual bonding situation is further supported by the geometry around the silicon atom, which evolves from approximately tetrahedral in the free ligand **1** (Σ(C-Si-C) 327.6°) to slightly distorted trigonal-bipyramidal in complex **2** (Σ(C-Si-C) 353.1° and F-Si-Au 166.11(12)°). Moreover, the Si–F bond is noticeably elongated upon coordination (from 1.600(2) Å in the free ligand **1** to 1.635(3) Å in complex **2**), as observed in fluorosilane adducts with organic Lewis bases.[11,20]

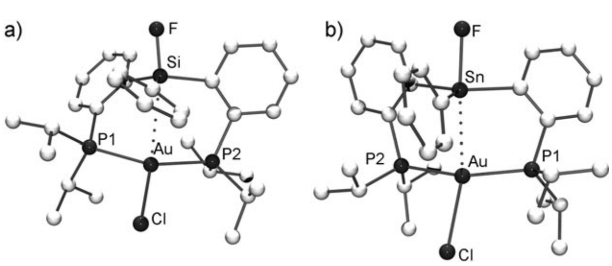


Figure 1. Molecular views of complexes **2** (a) and **4** (b) in the solid state (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: **2**: P1–Au 2.323(2), P2–Au 2.305(2), Au–Cl 2.577(2), Si–F 1.635(3), Au–Si 3.090(2); P1-Au-P2 140.14(5), Cl-Au-Si 141.54(4), Au-Si-F 166.11(12). **4**: P1–Au 2.334(2), P2–Au 2.330(2), Au–Cl 2.601(2), Sn–F 2.018(3), Au–Sn 2.891(2); P1-Au-P2 159.91(6), Cl-Au-Sn 151.36(4), Au-Sn-F 176.27(9).

To confirm and further demonstrate the ability of saturated heavier Group 14 elements to behave as σ-acceptor ligands, the related tin complex **4** was then targeted. The Lewis acidity of Group 14 compounds towards organic Lewis bases increases on going from silicon to tin.[23,24] The diphosphino stannane ligand **3** was readily prepared according to a slightly different procedure,[19] the chlorine–fluorine exchange at tin being performed in this case with KF in DMF at reflux (Scheme 2). Upon reaction with $[AuCl(SMe_2)]$, the desired complex **4** was isolated in 87 % yield as a white solid. The single resonance in the ^{31}P NMR spectrum, observed at 79 ppm with the expected tin satellites ($^{3}J_{^{117/119}Sn\text{-}P} = 53/56$ Hz), indicates the symmetric coordination of the two phosphorus atoms. Consistently, the signal in the ^{119}Sn NMR spectrum appears as a triplet at −147 ppm ($^{3}J_{^{119}Sn\text{-}P} = 56$ Hz). This chemical shift is at distinctly lower frequency than those of tetracoordinate Ar_3SnF derivatives ($\delta = -65$ to -85 ppm)[25] but approaches those reported for related nitrogen adducts ($\delta = -195$ to -200 ppm).[26] This finding suggests an increase in the coordination number of the tin atom and thus the presence of a gold→stannane interaction.

This hypothesis was confirmed by X-ray diffraction (Figure 1 b). Despite the larger size of tin than silicon, the Au–Sn separation in complex **4** (2.891(2) Å) is shorter than the Au–Si distance in **2** (3.090(2) Å), and only slightly exceeds the sum of the covalent radii (2.75 Å). The tin center adopts a quasi-ideal trigonal-bipyramidal coordination. The F and Au atoms define the apical axis (F-Sn-Au 176.27(9)°), while the three C atoms occupy the basal positions (Σ(C-Sn-C) 359.9°). The Sn–F bond length (2.018(3) Å) significantly surpasses those of tetracoordinate Ar_3SnF compounds (1.96–1.97 Å)[25] and falls in the same range as their nitrogen adducts (2.02 Å).[26] These geometric features indicate that tin is more strongly bound to gold than silicon.[27] In turn, this finding suggests that the higher Lewis acidity of tin toward organic Lewis bases can be extended to metallobases. Furthermore, the geometry around the gold center in complex **4** approaches square-planar (P-Au-P 159.91(6)° and Cl-Au-Sn 151.36(4)°), whereas tetracoordinate gold(I) complexes usually adopt tetrahedral arrangements. This situation is reminiscent of that observed in diphosphino borane gold complexes.[8d] Interestingly, the chlorostannane complex [*o*-$\{(iPr_2P)C_6H_4\}_2Sn(Ph)ClAuCl$] (**5**)[19] displays a dative Au→Sn interaction as well, with similar magnitude to that encountered in **4**. This comparison provides further evidence for metal→stannane interaction and demonstrates that the coordination of saturated heavier Group 14 elements is also possible with nonfluorinated moieties.

To gain a deeper insight into these unusual Au→silane and Au→stannane interactions, DFT calculations were car-

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ried out on the actual complexes **2**, **4**, and **5**.[19,28] The optimized geometries nicely match those determined crystallographically. In particular, the geometries around Au, Si, and Sn, including the key Au–Si and Au–Sn separations, are reliably reproduced. Interestingly, structural optimizations carried with the ADF program in the absence of the zero-order regular approximation (ZORA) lead to significantly elongated Au–Si and Au–Sn separations.[19] This trend reflects the importance of relativistic effects, which destabilize the 5d orbitals and thus increase the donor ability of the gold center. Natural bond orbital (NBO) analyses identify in all three complexes as donor–acceptor interaction between the gold center and the heavier Group 14 element. The corresponding delocalization energy ΔE_{NBO} is about three times greater for tin (**4**: 22.8 $\mathrm{kcal\,mol^{-1}}$ and **5**: 26.6 $\mathrm{kcal\,mol^{-1}}$) than for silicon (**2**: 7.6 $\mathrm{kcal\,mol^{-1}}$), in agreement with the conclusions drawn from the metric data. The bonding situation in complexes **2**, **4**, and **5** was further assessed by atoms in molecules (AIM) calculations (Figure 2). The electron density maps show the presence of bond paths between Au and Si and Au and Sn with localized bond critical points (BCPs). The electron density $\rho(r)$ at the BCP is higher for complexes **4** ($3.50\times10^{-2}\,\mathrm{e\,bohr^{-3}}$) and **5** ($3.56\times10^{-2}\,\mathrm{e\,bohr^{-3}}$) than for **2** ($2.13\times10^{-2}\,\mathrm{e\,bohr^{-3}}$), corroborating the stronger binding of tin than silicon to gold. Furthermore, charge depletion at the BCP is consistent with the closed-shell, donor–acceptor nature of the Au–E interactions.

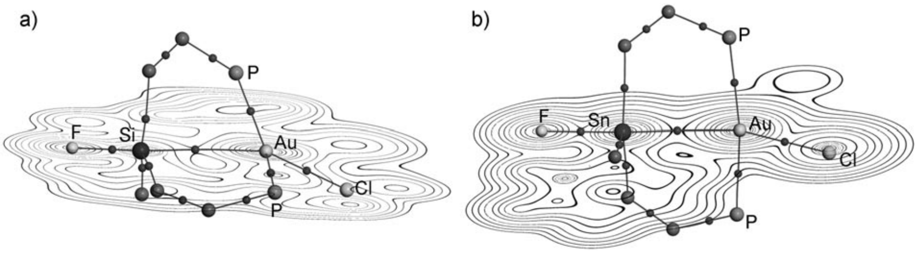
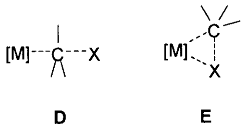


Figure 2. Calculated electron density maps for complexes **2** (a) and **4** (b) with relevant bond paths and bond critical points. The isopropyl substituents at phosphorus are omitted, and the *o*-phenylene linkers are simplified for clarity.

To date, the variety of complexes derived from saturated molecules free of lone pairs has been limited to σ complexes. The Au→silane and Au→stannane interactions exhibited by complexes **2**, **4**, and **5** provide unambiguous evidence for an alternative coordination mode, in which the saturated Group 14 element behaves as a σ acceptor ligand toward the transition metal. Accordingly, the concept of σ acceptor ligands appears to be much more general than previously anticipated.[29] Moreover, compounds **2**, **4**, and **5** are novel neutral hypervalent derivatives of heavier Group 14 elements. The donation from a metal center, as illustrated herein with gold, opens access to hypervalent derivatives featuring a transition metal as a substituent. Importantly, the geometric and electronic features of complexes **2**, **4**, and **5** parallel those predicted computationally for the transition-state structures **D** associated with the $\mathrm{S_N2}$-type oxidative addition of $\mathrm{C_{sp^3}}$–X bonds to transition metals (Scheme 3).[30,31] Accordingly, with heavier Group 14 elements, the nucleophilic attack of the metal can be frozen, and stable compounds that mimic their carbon congeners can be isolated.



Scheme 3. The two possible pathways for the oxidative addition of $\mathrm{C_{sp^3}}$–X bonds (X = halogen, sulfonate, etc.) to transition metals.

Experimental Section

All reactions and manipulations were carried out in an atmosphere of dry argon using standard Schlenk techniques.

2: A solution of **1** (79 mg, 0.15 mmol) in dichloromethane (1 mL) was added to a suspension of $[\mathrm{AuCl(SMe_2)}]$ (44 mg, 0.15 mmol) in dichloromethane (1 mL) at −78 °C. After warming to room temperature, volatile components were removed in vacuo, and complex **2** was isolated as a white powder (98 mg, 88 %). Colorless crystals suitable for X-ray crystallography were obtained from dichloromethane/pentane (3:7) at room temperature. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: $\delta = 57.1$ ppm (s); $^{29}\mathrm{Si}$ NMR: $\delta = -21.4$ ppm (d, $^1J_{\text{Si-F}} = 259$ Hz); $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: $\delta = -135.8$ ppm (s). HRMS (ESI+) calcd for $[M{-}\mathrm{Cl}]^+$ ($\mathrm{C_{30}H_{41}P_2FSiAu^+}$): 707.2102, found: 707.2113.

4: A solution of **3** (102 mg, 0.17 mmol) in dichloromethane (1 mL) was added to a suspension of $[\mathrm{AuCl(SMe_2)}]$ (50 mg, 0.17 mmol) in dichloromethane (1 mL) at −78 °C. After warming to room temperature, volatile components were removed in vacuo, and complex **4** was isolated as a white powder (123 mg, 87 %). Colorless crystals suitable for X-ray crystallography were obtained from dichloromethane/pentane (3:7) at −30 °C. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: $\delta = 79.1$ ppm (d, $^3J_{\text{P–}^{117}\text{Sn}} = 53.4$ Hz; $^3J_{\text{P–}^{119}\text{Sn}} = 55.7$ Hz, $^4J_{\text{P-F}} = 14.9$ Hz); $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR: $\delta = -147.8$ ppm (td, $^1J_{\text{Sn-F}} = 2110.3$ Hz, $^3J_{\text{Sn-P}} = 55.7$ Hz); $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: $\delta = -189.6$ ppm (t, $^1J_{\text{F–}^{117}\text{Sn}} = 2016.6$ Hz; $^1J_{\text{F–}^{119}\text{Sn}} = 2110.3$ Hz; $^4J_{\text{F-P}} = 14.9$ Hz). HRMS (ESI+) calcd for $[M{-}\mathrm{Cl}]^+$ ($\mathrm{C_{30}H_{41}P_2SnFAu^+}$): 799.1355, found: 799.1316.

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