A Nucleophilic Tin(II) Cation Salt

Chaopeng Hu and Liu Leo Liu*

Department of Chemistry and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055 (China)
*liuleoliu@sustech.edu.cn

We show that one of the tris(carbene)borate (TCB) ligands, namely PhB(^{t}BuIm)$_3$ (PhB(^{t}BuIm)$_3$ = phenyltris(3-*tert*-butylimidazol-2-ylidene)borato), is capable of stabilizing an unprecedented nucleophilic Sn(II) cation salt. Unlike known Sn(II) cations, the strong electron-donating ability of PhB(^{t}BuIm)$_3$ makes the cationic tin atom electron-rich, σ-donating yet slightly π-accepting, which allows for the ensuing facile oxidation with *o*-chloranil and S_8 as well as coordination with coinage metals. The former oxidations give rare Sn(IV) cation salts, while the latter reactions produce novel metal complexes. The electronic structures of these species are thoroughly probed by quantum chemical computations. These results unravel an added role for TCB ligands in isolating unprecedented p-block species.

Introduction

Low-valent group 14 (poly)cations have garnered much attention over the past few decades.[1-8] Among them, (di)cations of [R–E]$^+$ and E^{2+} (E = heavier group 14 elements) have been of paramount interest due to not only the fundamental significance of their electronic structure and bonding but also the associated reactivity for synthetic chemistry.[1-8] As a result of the high s-character of the lone pair orbital at low-valent tin centers,[9-12] stannylenylium cations [R–Sn]$^+$ and Sn^{2+} dications are in their ground-state singlet (Figure 1a).[8,13] The former compounds possess a monocoordinated Sn atom featuring a lone pair of electrons and two vacant p orbitals, isoelectronic with group 13 neutral metallylenes,[14-16] while Sn^{2+} contains an electron pair and three vacant p orbitals. These electronic characteristics render such species extremely reactive, so much so they cannot be isolated in their free state. However, these unfilled valence orbitals where shown to be stabilized by Lewis basic ligands, leading to isolable Sn(II) cation salts. On the basis of coordination modes at Sn, these species can be classified into three broadly defined categories, namely Cp-ligated Sn(II) cations **I** (Cp = cyclopentadienyl),[17-21] base-stabilized [R–Sn]$^+$ cations **II**,[22-43] and base-stabilized Sn^{2+} dications **III** (Figure 1b).[44-54] Archetypical examples involve Jutzi's [Cp*Sn]$^+$ **A** (Cp* = pentamethylcyclopentadienyl),[17] Jones' arene-stabilized amido-Sn(II) cation **B**,[27] Nicholson's crown ether complex of Sn^{2+} **C**,[44] and Krossing's [(MeCN)$_6$Sn]$^{2+}$ **D** (Figure 1c).[52] Significant to note is that the electrophilic tendency of these cationic Sn centers dominates because of the energetically low-lying 5s^2 lone pair at Sn.[17-54] Even for neutral stannylenes without donor-stabilization, they usually function as a Lewis acid with high electrophilicity, and almost all their reactivity is initiated by the nucleophilic reaction of the reagents toward the vacant p orbital albeit behaving overall ambiphilicity.[12] This points out the challenges for isolating a nucleophilic Sn(II) cation as the cationic nature further diminishes the energy of the Sn 5s^2 lone pair. In fact, free Sn(II) cations with predominant nucleophilicity are hitherto unknown. None of the Sn(II) cations have been utilized as a free nucleophilic Sn ligand for the synthesis of transition metal (TM) complexes although a handful of examples of TM-bound Sn(II) cations have been prepared exclusively via a halide abstraction method.[55-58]

Ligand design plays a central role in modern synthetic chemistry, providing access to various isolable compounds with unusual properties. Among the most prevalent organometallic ligands are 6-electron aromatic anionic Cp groups (Figure 1d).[59-61] Similarly as an anionic 6-electron donor, ligands based on tris(pyrazolyl)borate (Tp)[62-64] and tris(carbene)borate (TCB)[65-66] architectures (Figure 1d) have proven to be superior in stabilization of low-valent compounds. To our surprise, while TCB ligands were first documented by Fehlhammer as early as 1996[67] and have been extensively employed in TM chemistry,[68-69] such ligands are completely absent from the chemistry of low-valent p-block compounds.

In the present work, we demonstrate that one of the TCB ligands originally reported by Smith, namely PhB(^{t}BuIm)$_3$ (PhB(^{t}BuIm)$_3$ = phenyltris(3-*tert*-butylimidazol-2-ylidene)borato),[70] is able to stabilize an elusive nucleophilic Sn(II) cation salt (Figure 1e). This cation is isoelectronic with phosphines R_3P and amines R_3N. Most strikingly, the strong electron-donating ability of PhB(^{t}BuIm)$_3$ enables an umpolung characteristic of the cationic Sn atom with predominant nucleophilicity.

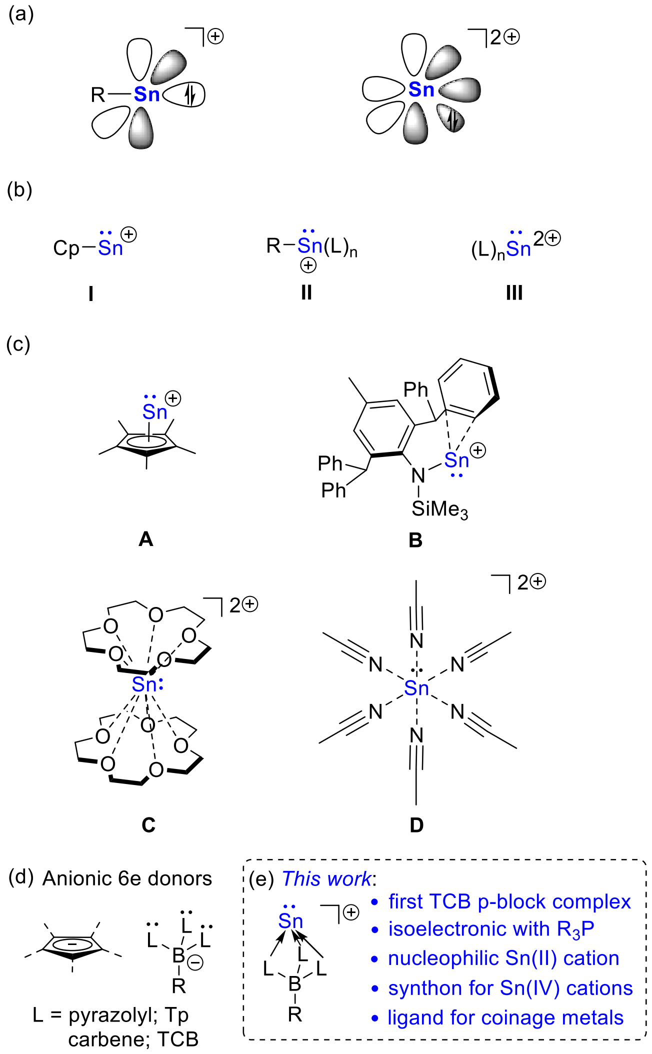
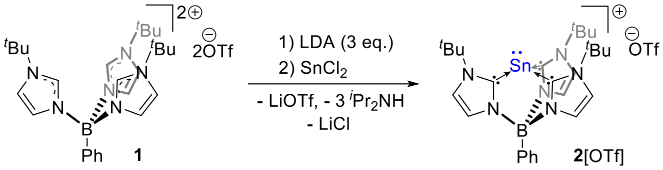


Figure 1. (a) Singlet stannylenylium cation $[R{-}Sn]^+$ and Sn^{2+} dication. (b) Representations of Cp-ligated Sn(II) cations **I**, base-stabilized stannylenylium cations **II**, and base-stabilized Sn(II) dications **III**. (c) Selected examples of isolable Sn(II) cations **A** and **B** and dications **C** and **D**. (d) Electronic analogy of Cp, Tp and TCB ligands. (e) This work.

Results and discussion

Isolation of a Nucleophilic Sn(II) Cation Salt

In targeting a nucleophilic Sn(II) cation, we sought to install Sn^{2+} with a strong electron-donating tripodal TCB ligand that can not only increase the energy of the Sn lone pair but also enhance the directionality of the lone pair.[8, 37, 71-74] By analogy with the synthesis of transition metal TCB complexes,[70, 75-78] compound **1** was deprotonated by lithium diisopropylamide (LDA), followed by a salt metathesis reaction with $SnCl_2$ (Scheme 1). After workup, **2**[OTf] (OTf = triflate) was obtained as a white solid in 45% yield. This species exhibited ^{119}Sn, ^{11}B and ^{19}F NMR chemical shifts at -429.4, 1.1 and -78.1 ppm, respectively. The ^{119}Sn NMR signal is low-frequency shifted in comparison with those of three-coordinate Sn(II) cations supported by a bis(oxazoline) ligand (-389.2 and -377.1 ppm).[29] The ^{1}H NMR spectrum displayed a singlet for the ^{t}Bu groups at 1.8 ppm, and the carbene carbon resonance at 170.4 ppm was observed via a ^{13}C NMR spectroscopic study. These data reveal the C_3 symmetric nature of **2**.



Scheme 1. Synthesis of **2**[OTf].

Single crystals of **2**[OTf] suitable for X-ray crystal structure determination were grown by slow evaporation of a concentrated THF solution at -35 °C. The crystallographic data confirmed the formulation of **2**[OTf] as $[PhB(^{t}BuIm)_3Sn][OTf]$ ($PhB(^{t}BuIm)_3$ = phenyltris(3-*tert*-butylimidazol-2-ylidene)borato) (Figure 2a). In the asymmetric unit of the crystal lattice of **2**[OTf], two independent molecules are included as a monomer. The Sn(1) atom is supported by the tripodal TCB ligand. In contrast to neutral species TpSnX (X = Cl, OTf) bearing a Sn–X bond,[79-82] the solid-state structure of **2**[OTf] clearly demonstrates its ionic nature as the oxygen atoms of the triflate anion are over 7.0 Å away from Sn(1). This is attributed to the stronger electron-releasing ability of TCB over that of Tp[83] and indicates the electron-rich character of Sn(1) in **2**[OTf]. The average length of Sn–C bonds (2.240 Å) is longer than the Pyykkö standard value for a Sn–C single bond (2.15 Å),[84] whereas slightly shorter than those found in $IDippSnCl_2$ (2.341(7) Å) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)[85] and $LSnCl_2$ (2.323(9) and 2.309(9) Å) (L = chelating dicarbene ligand).[86] Of note, species **2**[OTf] is the first example of a p-block complex with a TCB ligand.[86-88]

Electronic Structures and Bonding

The electronic structure of **2** was investigated by quantum chemical calculations (M06-2X/def2-SVP). The HOMO of **2** (-10.1 eV) is mainly the non-bonding electron pair at Sn, while the LUMO (-2.7 eV), LUMO+1 (-2.4 eV), LUMO+4 (-1.3 eV) and LUMO+5 (-1.2 eV) are highly delocalized with contributions from the Sn atom and TCB ligands (Figure S33). For comparison, the assumed analogous species $[PhB(^{t}BuPy)_3Sn]^+$ ($PhB(^{t}BuPy)_3$ = phenyltris(3-*tert*-butylpyrazolyl)borato) and known species $[Cp^*Sn]^+$ are predominantly electrophilic as their HOMOs do not involve the lone pair at Sn and LUMOs primarily comprise the vacant p orbitals at Sn (Figures S34 and S35). Moreover, natural bond orbital (NBO) calculations of **2** shows a less positively charged Sn atom (0.98 a.u.) compared to those in $[PhB(^{t}BuPy)_3Sn]^+$ (1.42 a.u.) and $[Cp^*Sn]^+$ (1.34 a.u.). The NBO charge of the TCB ligand is 0.02 a.u., in which each 3-*tert*-butylimidazol-2-ylidene unit carries the negative charge of approximately -0.26 a.u. This charge distribution is in agreement with the observations from the electrostatic potential analysis of **2** (Figure S37). These are also in accordance with the $PhB(^{t}BuIm)_3$ ligand being a much stronger 6e donor than $PhB(^{t}BuPy)_3$ and Cp*.[83]

Intrinsic bond orbital (IBO) calculations, which has been proven to give an exact representation of any Kohn–Sham density functional theory (DFT) wave function,[89-90] clearly reveal the 6e donations from the ligand to Sn (Figures 2c-2e) as well as a lone pair of electrons at Sn (Figure 2b).

The dual descriptor (DD) from conceptual DFT calculations,[91] which typically provide an overall description of reactivity behaviors for molecules (positive value: electrophilic; negative value: nucleophilic), give a highly negative value of the dual descriptor at Sn (-0.44) in **2** (Figure 2f). The DD values for $[Cp^*Sn]^+$ and $[PhB(^tBuPy)_3Sn]^+$ are 0.51 and 0.34, respectively (Figures 2g and S36). Combined with aforesaid results, **2** should exhibit predominant nucleophilicity.

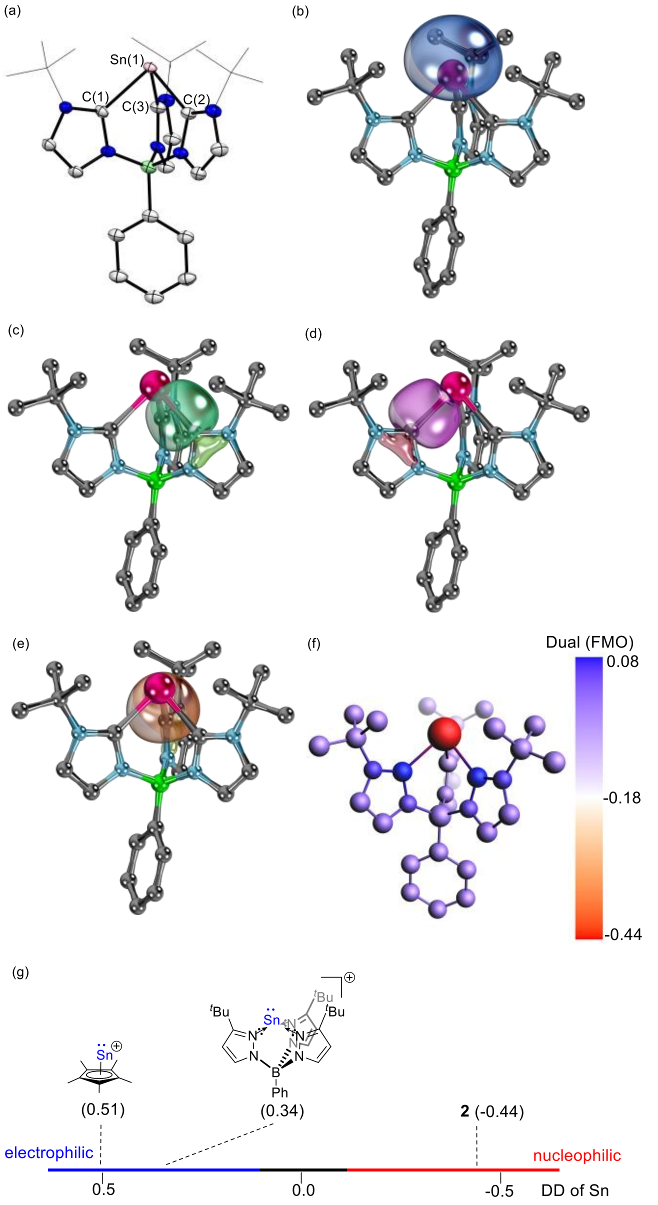
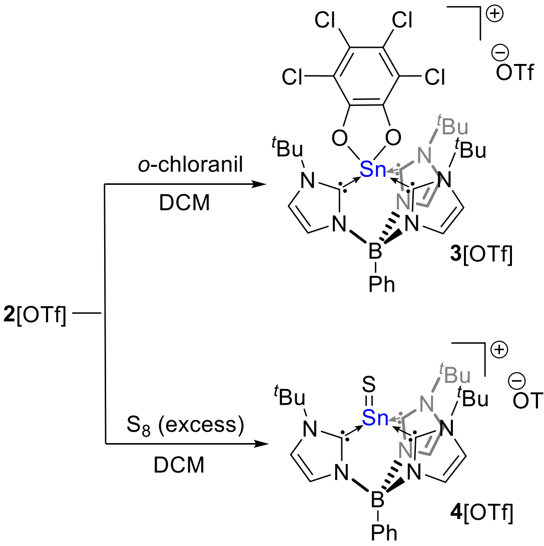


Figure 2. (a) Solid-state structure of **2**[OTf]. Hydrogen atoms and the non-interacting triflate anion are omitted for clarity. Thermal ellipsoids are set at the 40% probability level. (b-e) Selected IBOs of **2** with enclosing 80% of the density of the orbital electron. (f) The condensed values of the dual descriptor (DD) that corresponds to the difference between frontier molecular orbitals (FMOs) electron densities. Positive values correspond to atomic sites where electrophilicity is predominant, and negative values refer to atomic sites where nucleophilic tendencies dominate. (g) DD of Sn for $[Cp^*Sn]^+$, $[PhB(^tBuPy)_3Sn]^+$ and **2**.

Isolation of Sn(IV) Cation Salts

In line with the computational results, no reaction was observed upon combining **2**[OTf] with Lewis bases such as PMe_3 and 4-dimethylaminopyridine in DCM. We thus envisioned that the electron-rich Sn center of **2**[OTf] should have a high propensity for oxidation reactions. Treatment of **2**[OTf] with 3,4,5,6-tetrachloro-1,2-benzoquinone (*o*-chloranil) or S_8 in DCM gave rise to **3**[OTf] (^{119}Sn NMR: -375.3 ppm) or **4**[OTf] (^{119}Sn NMR: -201.5 ppm) in 85 or 65 % yield, respectively (Scheme 2). Characterization that included X-ray diffraction showed the formation of two novel Sn(IV) cation salts (Figure 3). In both cases, Sn(1) forms two new chemical bonds and the $PhB(^tBuIm)_3$ ligand remains completely intact. This contrasts with the facile hapticity shifts of the Cp ring in $[Cp^*Sn][OTf]$.[22] The bond length of Sn(1)–S(1) (2.246(2) Å) in **4**[OTf] correlates favorably with those seen for $(CyNC(^tBu)NCy)_2Sn{=}S$ (2.280(5) Å)[92] and Bbt(Titp)Sn=S (2.221(3) Å)[93] (Bbt = 2,6-bis[bis(trimethylsilyl)-methyl]-4-[tris(trimethylsilyl)methyl]phenyl; Titp = 2,2'',4,4''-tetraisopropyl-*m*-terphenyl-2'-yl). While neutral compounds featuring a Sn=S double bond have been known for decades,[92-96] cationic Sn=S species are extremely rare. It was reported recently by Ghadwal that oxidation of a cationic distannabarrelene with S_8 yielded a cationic Sn=S species.[41] **4**[OTf] represents a scarce example of this sort of species. These results showcase the potential of TCB ligands for stabilization of hitherto unknow main group species, as well as the potent synthetic ability of **2**[OTf] for Sn(IV) cations.



Scheme 2. Oxidations of **2**[OTf] leading to tin(IV) salts **3**[OTf] and **4**[OTf].

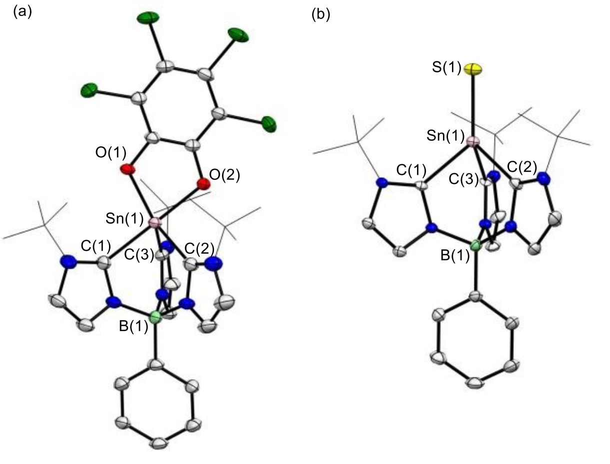


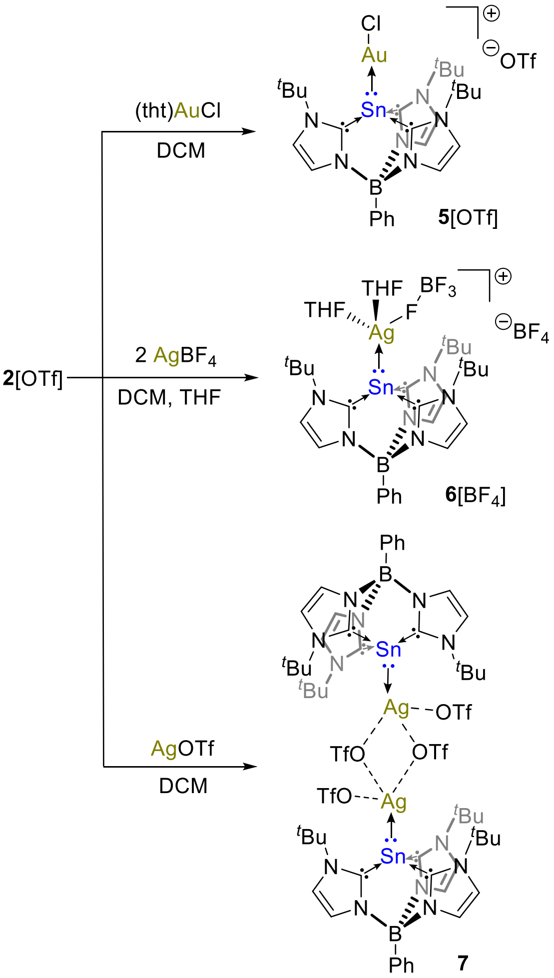
Figure 3. Solid-state structures of **3**[OTf] (a) and **4**[OTf] (b). Hydrogen atoms and the non-interacting triflate anion each are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Coordination Behavior toward Coinage Metals

Whereas numerous TM stannylene complexes have been documented,[97] coinage metal complexes ligated with a Sn(II) cation are hitherto unknown. We thus examined the nucleophilic behavior of Sn(1) in **2**[OTf] towards coinage metals (Scheme 3). The combination of **2**[OTf] and (tht)AuCl (tht = tetrahydrothiophene) in DCM immediately led to a ligand exchange reaction, in which **5**[OTf] (^{119}Sn NMR: -118.8 ppm) was isolated as a white powder in 73% yield. Further structural authentication of **5**[OTf] as a rare monomeric gold complex with a cationic Sn(II) ligand was established by X-ray diffraction (Figure 4a). The Sn(1)–Au(1) bond length at 2.4904(3) Å is comparable to that of stannylene gold complexes L^1(Cl)SnAuCl (2.4848(3) Å) (L^1 = 2,6-$(Me_2NCH_2)_2C_6H_3$)[73] whereas slightly shorter than that in $[L_2SnAuSnL_2]$[OTf] (2.555(8) Å, av.) (L = (2,6-diisopropylphenyl)(1-(pyridin-2-yl)vinyl)amide).[37] It is noteworthy that TM-bound Sn(II) cations have been seldom encountered; they are exclusively prepared via a halide abstraction route.[55-58] Previous attempts by Inoue for coordination of a bisNHCP Sn(II) cation (bisNHCP = ferrocene-bridged N-heterocyclic carbene stabilized bis-phosphinidenes) with CuCl only gave a transmetalation product.[98] The group of Majumdar attempted to establish nucleophilic behavior of a bis(a-iminopyridine)-stabilized Sn^{2+} toward TMs but they were unsuccessful as well.[53] The success in isolating **5**[OTf] demonstrates a straightforward synthetic method for coinage metal Sn(II) cation complexes.

The reaction of **2**[OTf] with $AgBF_4$ in DCM followed by crystallization in THF gave rise to **6**[BF_4] in 43% yield (Scheme 3). We observed, via ^{11}B (0.1 and -1.2 ppm) and ^{19}F NMR (-150.9 and -155.8 ppm) spectroscopies, two magnetically inequivalent $[BF_4]^-$ anions in **6**[BF_4]. The monomeric structure of **6**[BF_4] is elucidated by crystallographic studies (Figure 4b). Ag(1) adopts in a tetrahedral coordination geometry and is bound not only to Sn(1) with the Sn(1)–Ag(1) bond length of 2.5809(4) Å, but also to two THF molecules and a fluoride of $[BF_4]^-$. The second $[BF_4]^-$ anion is away from the cation **6**.

Upon adding AgOTf to a DCM solution of **2**[OTf], we isolated a neutral species **7** in 51% yield (Scheme 3). Similar to the tetrahedral geometry of Ag(1) in **6**[BF_4], to fulfill four coordination sites at Ag **7** appears to be a dimeric structure (Figure 4c), featuring a $Ag_2S_2O_4$ eight-membered ring with two bridging OTf anions. Each Ag center bears a cationic ligand of **2** and an additional OTf anion. The average Ag–O bond length in the ring is computed to be 2.369 Å, which is similar to those of exocyclic Ag(1)–O(1) (2.367(3) Å) and Ag(2)–O(2) bonds (2.371(3) Å). The isolation of **5**[OTf], **6**[BF_4], and **7** demonstrates the nucleophilic ligand behavior of **2**[OTf] for coordination chemistry.



Scheme 3. Synthesis of gold and silver complexes **5**[OTf], **6**[BF_4] and **7**.

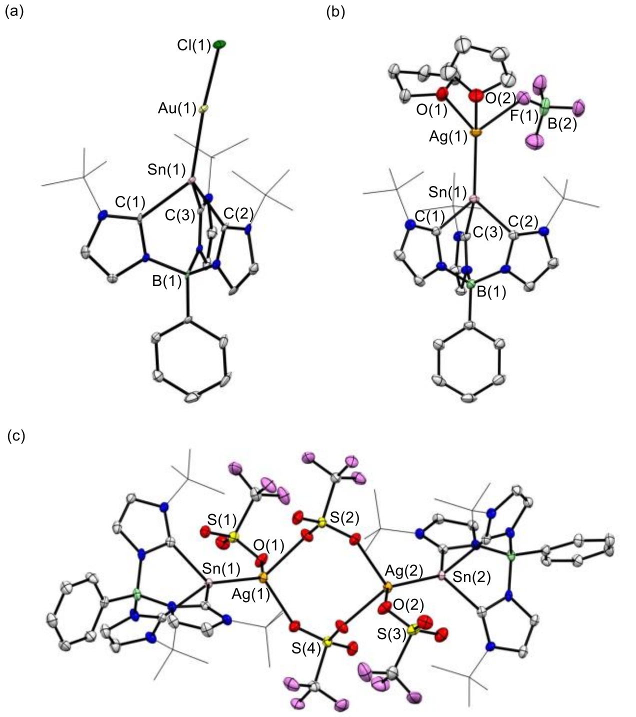


Figure 4. Solid-state structures of **5**[OTf] (a), **6**[BF$_4$] (b) and **7** (c). Hydrogen atoms and the non-interacting anions are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

DFT calculations were carried out to understand the ligand features of **2**[OTf]. We selected **5**[OTf] as an example. The presence of the donor-acceptor interaction between the cationic ligand **2** and [AuCl] is suggested by means of energy decomposition analyses with natural orbitals for chemical valence (EDA-NOCV)[99-101] (Figure S38). The electrostatic interaction term ($\Delta E_{\mathrm{elstat}}$) is dominant with -113.1 kcal mol^{-1}, while the orbital interaction term (ΔE_{orb}) is -55.2 kcal mol^{-1}. Investigations of the deformation density plots enable visualization of the donor-acceptor interaction (Figure 5), in which the Sn-to-Au σ-donation (-37.5 kcal mol^{-1}, 67.9%) plays a major role in contributions to ΔE_{orb}, and twofold Au-to-Sn π-backdonation contributes minorly (-10.2 kcal mol^{-1}, 18.5%). Furthermore, principal interacting orbital (PIO)[102-103] analysis, which has provided a clear illustration for donor-acceptor interactions, agrees well with the EDA-NOCV results. The first PIO pair suggests a σ-bonding interaction between the Sn(1) and the Au(1) atoms (Figure S39a), whereas the second and third PIO pairs represent Au(1)-Sn(1) π-backdonation (Figures S39b and S39c). Taken as a whole, these imply strong σ-donating and weak π-accepting ligand features of **2**[OTf].

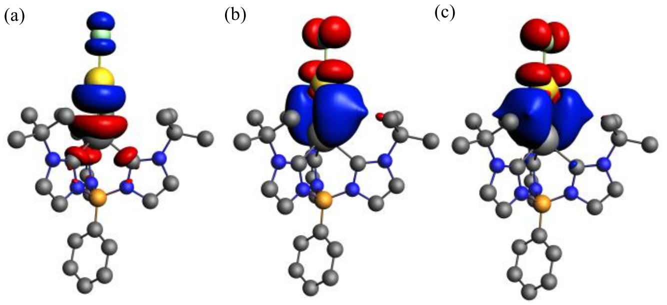


Figure 5. The strong pairwise orbital interactions (< -5.0 kcal mol^{-1}) in **5**. (a) Sn-to-Au σ-donation (-37.5 kcal/mol). (b) Au-to-Sn π-backdonation (-5.1 kcal mol^{-1}). (c) Au-to-Sn π-backdonation (-5.1 kcal mol^{-1}). The direction of charge flow is red to blue.

Conclusions

To conclude, we have introduced Smith's PhB(^{t}BuIm)$_3$ ligand for the chemistry of p-block elements, with the isolation of a nucleophilic Sn(II) cation salt. This anionic TCB ligand features stronger 6e donating ability with respect to those of the well-established Tp and Cp ligands. Unlike the previous electrophilic Sn(II) cations, we have shown the nucleophilic cationic Sn(II) ligand behavior of **2**[OTf] for coinage metals. Experimental and theoretical results unveil σ-donating and π-accepting ligand features of **2**[OTf]. Given that p-block compounds ligated with Cp and Tp ligands are pervasive, we believe that the present work has a significant impact on the future synthesis of unusual p-block species based on these TCB frameworks. Development of novel TCB ligands and their usage in main group chemistry are subjects of ongoing work in our laboratory.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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