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N-Coordinated Tin(II) Trifluoromethanesulfonates and Their Reactions with Transition Metal Carbonyls

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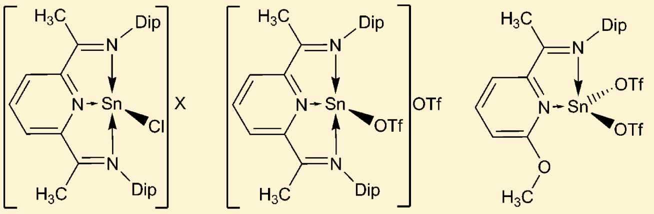
Supporting Information

ABSTRACT: The syntheses of the compounds $[L^1SnCl][M(CO)_5(SnCl_3)]$ (**3**, M = W; **4**, M = Cr), $[L^1SnCl]OTf$ (**5**), $[L^1SnCl][W(CO)_5(SnCl_2OTf)]$ (**6**), $[L^1SnOTf][OTf]$ (**7**), and $[L^2Sn(OTf)_2]$ (**8**) with L^1 = $\{2,6\text{-}[(CH_3)C{=}N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)_2]C_5H_3N\}$ (DIMPY) and L^2 = $\{2\text{-}[(CH_3)C{=}N\text{-}(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]\text{-}6\text{-}(CH_3O)\}C_5H_3N)$ is reported. The compounds were characterized by elemental analyses, ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectroscopy, electrospray ionization mass spectrometry, and single-crystal X-ray diffraction analyses (**3**·$1.5C_7H_8$, **5**·CH_2Cl_2, **7**·C_7H_8, **8**). For compounds **7** and **8**, the experimental work is accompanied by density functional theory calculations.



3, X = $[W(CO)_5(SnCl_3)]$
4, X = $[Cr(CO)_5(SnCl_3)]$
5, X = OTf
6, X = $[W(CO)_5\{Sn(OTf)Cl_2\}]$

7

8

Dip = 2,6-*i*-$Pr_2C_6H_3$

INTRODUCTION

The field of group 14 element(II) monocation RE^+ chemistry remains a challenge for inorganic chemists.[1] While the pioneering works reported on the stabilization of RE^+ (E = Si, Ge, Sn, Pb) cations by cyclopentadienyl-, *N*-isopropyl-2-(isopropylamino)troponimine-, or cyclophane-groups,[2] further studies conducted by Jutzi, Power, Driess, Müller, Krossing, and Jones, respectively, dealt with the synthesis of two- or even one-coordinated RE^+ cations being stabilized by sterically demanding ligands.[3] Autoionization of GeX_2 (X = Cl, Br) induced by bi- or multidentate ligands was reported by Reid and Baines, respectively.[4] Spontaneous dissociation of ECl_2 (E = Ge, Sn) was observed by Roesky et al. reporting the syntheses and structures of $[(DIMPY)ECl]^+$ cations (DIMPY = $\{2,6\text{-}[(CH_3)C{=}N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)_2]C_5H_3N\}$) that contain four-coordinated metal centers E (**A** in Chart 1),[5,6] and a similar result was observed by Ragogna, who employed a novel bis(imino)pyridine ligand containing redox-active cobaltocene and ferrocenyl functionalities (**B** in Chart 1).[7] Rowley et al. also used the DIMPY ligand for the synthesis of $[(DIMPY)SnX][SnX_3]$ complexes (X = Cl, Br; **C** in Chart 1).[8] A fascinating result was achieved by Fischer applying the DIMPY-type ligand for the stabilization of tin in oxidation state zero (**D** in Chart 1) and demonstrating the MeDIMPY ligand to give an Sn^{II} enamine complex (**E** in Chart 1).[9] The synthesis of three-coordinated tin and germanium monocations using neutral chelating ligand $\{2\text{-}[(CH_3)C{=}N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]\text{-}6\text{-}(CH_3O)\}\text{-}C_5H_3N$ (**F** in Chart 1) was also reported.[10]

As the $[L^1SnCl][SnCl_3]$ (**1**)[6] (L^1 = DIMPY) and $[L^2SnCl][SnCl_3]$ (**2**)[10] (L^2 = $\{2\text{-}[(CH_3)C{=}N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]\text{-}6\text{-}(CH_3O)\}C_5H_3N$) complexes, which differ by the coordination number of the tin atom, contain two potential sites to bind transition metal carbonyl moieties, reactions of **1** and **2** toward transition metal complexes $[M(CO)_5(thf)]$ (M = Cr, W; thf = tetrahydrofuran) were performed. These reactions provided the complexes $[L^1SnCl][W(CO)_5(SnCl_3)]$ (**3**) and $[L^1SnCl][Cr(CO)_5(SnCl_3)]$ (**4**), respectively. The analogous products containing the ligand L^2 were not isolated. Additionally, reactions of **1** and **3** with AgOTf gave the compounds $[L^1SnCl][OTf]$ (**5**), $[L^1SnCl][W(CO)_5(SnCl_2OTf)]$ (**6**), $[L^1SnOTf][OTf]$ (**7**), and $[L^2Sn(OTf)_2]$ (**8**), respectively.

RESULT AND DISCUSSION

Synthesis of Compounds 3−8. The treatment of $[L^1SnCl][SnCl_3]$ (**1**) with 1 equiv of $[M(CO)_5(thf)]$ (M = W, Cr) yielded the complexes $[L^1SnCl][W(CO)_5SnCl_3]$ (**3**) and $[L^1SnCl][Cr(CO)_5SnCl_3]$ (**4**), respectively, (Scheme 1). In contrast, from the reaction between $[L^2SnCl][SnCl_3]$ (**2**) and $[W(CO)_5(thf)]$, only the complex $[L^2H][W(CO)_5SnCl_3]$ being the product of hydrolysis was isolated (see Supporting Information).

Following the synthesis of compound **3**, we further studied the reactivity of both **1** and **3** with AgOTf. When complex **1** was reacted with 1 equiv of AgOTf, the compound $[L^1SnCl][OTf]$ (**5**) was isolated. In contrast, reaction of **3** with 1 equiv of AgOTf provided $[L^1SnCl][W(CO)_5\{Sn(OTf)Cl_2\}]$ (**6**), where one chloride anion of the $[SnCl_3]^-$ moiety was

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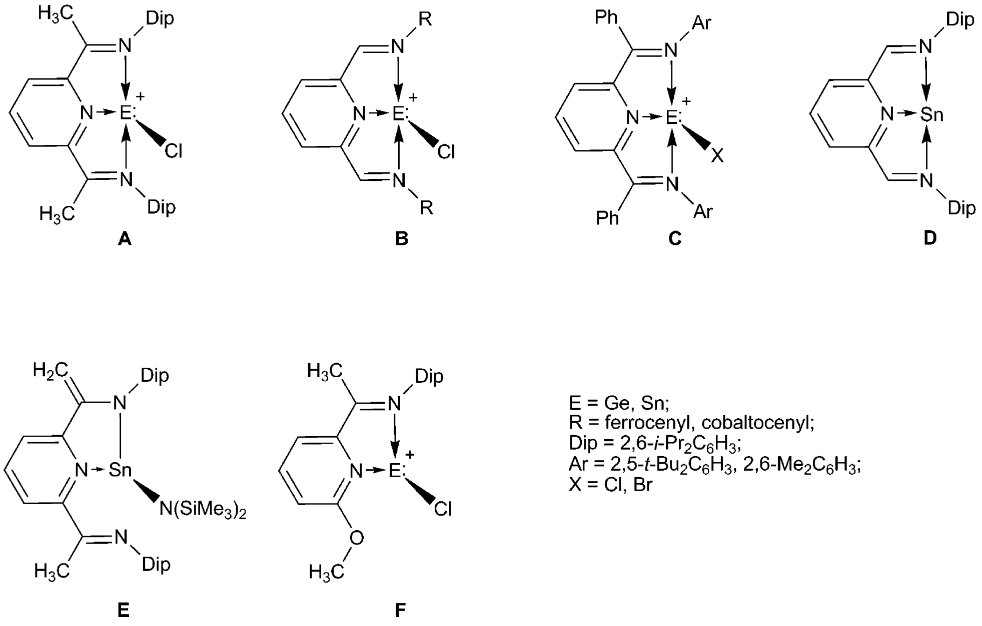
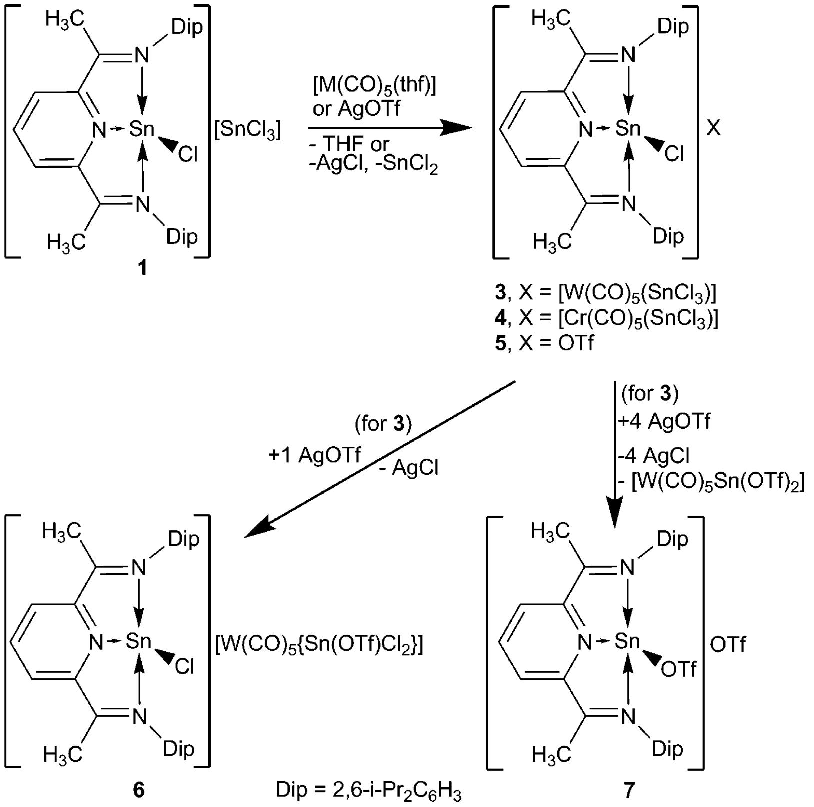
Chart 1. Selected Element(II) Cations Stabilized by Pincer-Type Ligands



E = Ge, Sn;
R = ferrocenyl, cobaltocenyl;
Dip = 2,6-*i*-$Pr_2C_6H_3$;
Ar = 2,5-*t*-$Bu_2C_6H_3$, 2,6-$Me_2C_6H_3$;
X = Cl, Br

Scheme 1. Synthesis of Compounds 3−7



substituted by a triflate anion. In addition, the reaction of complex **1** with 2 equiv of AgOTf again provided complex **5**. In contrast, the reaction of **3** with 4 equiv of AgOTf yielded compound [L^1SnOTf][OTf] (**7**). Interestingly, attempts at preparing **7** directly by treatment of ligand L^1 with $Sn(OTf)_2$ failed. However, the reaction of ligand L^2 with $Sn(OTf)_2$ provided complex [$L^2Sn(OTf)_2$] (**8**) (eq 1), as an analogue of **7**.

Molecular Structures of 3, 5, 7, and 8. Single crystals suitable for X-ray diffraction analysis of **3** and **5** (as their toluene and dichloromethane solvates **3**·$1.5C_7H_8$ and **5**·CH_2Cl_2), respectively, were obtained at room temperature from saturated toluene or CH_2Cl_2 solutions. The molecular structures of **3**·$1.5C_7H_8$ and **5**·CH_2Cl_2 are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are given in Table 1. The crystallographic data are given in Table S1 (see Supporting Information).

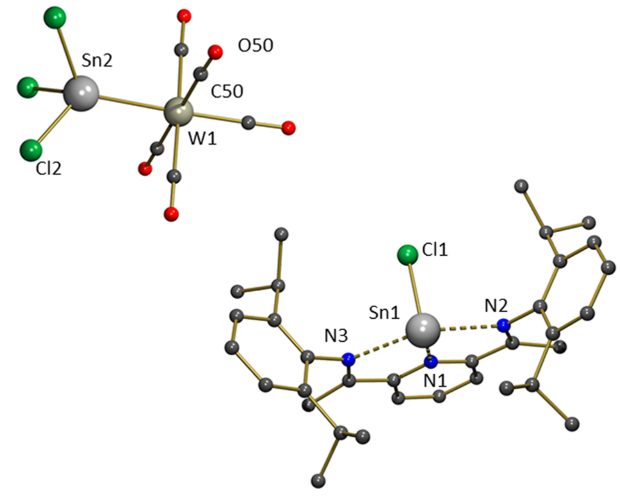


Figure 1. Povray schematic representation of the molecular structure of **3**·$1.5C_7H_8$. The hydrogen atoms and the toluene solvate molecule are omitted.

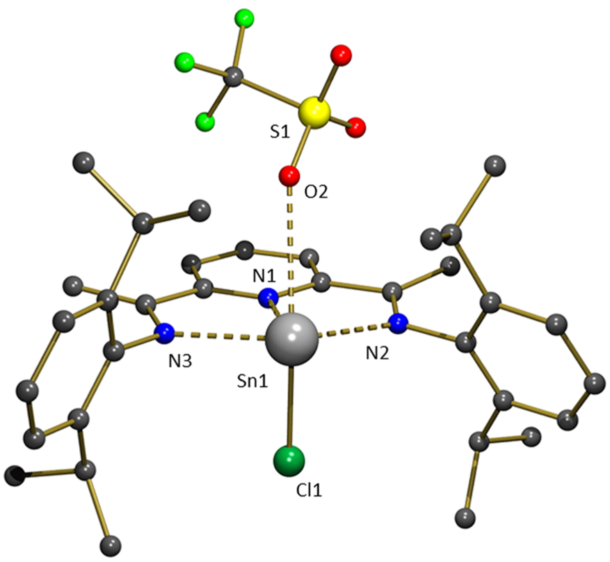


Figure 2. Povray schematic representation of molecular structure of **5**·CH_2Cl_2. The hydrogen atoms and dichloromethane solvate molecule are omitted for clarity.

The molecular structure of **3**·$1.5C_7H_8$ reveals an ion pair consisting of well-separated $[L^1SnCl]^+$ cation and $[W(CO)_5(SnCl_3)]^-$ anion. In the $[L^1SnCl]^+$ cation, the Sn(1) atom is four-coordinated as the result of three strong N → Sn interactions with distances ranging between 2.314(3) (Sn1−N1) and 2.420(3) Å (Sn1−N3), and one chlorine atom (Sn1−Cl1 2.405(1) Å). The Sn(1) atom shows a distorted pseudosquare pyramidal environment with the N(1), N(2), N(3) atoms and the lone electron pair located in equatorial positions, while the Cl(1) atom occupies the axial position. The geometry is similar as compared with that of the complex $[L^1SnCl][SnCl_3]$ reported by Roesky et al.[6] and will not be discussed in more detail. The W(1) atom is hexacoordinated by five carbon atoms and one tin atom. It has an octahedral geometry. The W(1)−Sn(2) distance of 2.7381(4) Å is close to the corresponding distances reported for $[W(CO)_5\{SnCl_2(thf)_2\}]$ (2.737(1) Å),[11] $[W(CO)_5\{Sn(C_6H_4CH_2NMe_2\text{-}o)_2\}]$ (2.749(1) Å),[12] $[W(CO)_5\{Sn(Cl)(2,6\text{-}[P(O)(Oi\text{-}Pr)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2)\}]$ (2.7263(11) Å),[13] and $[W(CO)_5\{Sn(C_{10}H_6NMe_2\text{-}8)_2\}]$ (2.822(2) Å) complexes.[14]

The molecular structure of **5**·CH_2Cl_2 reveals it being an ion pair consisting of $[L^1SnCl]^+$ cation and $[OTf]^-$ anion. The triflate anion interacts electrostatically with the Sn(1) center at a Sn(1)−O(2) distance of 3.042(2) Å being shorter than the sum of the van der Waals radii of the corresponding atoms ($\sum_{vdw}$(Sn,O) = 3.60 Å).[15] As a consequence, the Sn(1) atom in **5** is [4 + 1]-coordinate by N(1)−N(3), Cl(1), and O(2) and shows a strongly distorted pseudo-octahedral environment. The N(1), N(2), and N(3) atoms, and the lone electron pair occupy the equatorial positions, while the Cl(1) and O(2) atoms are located in axial positions. The distortion from the ideal octahedral geometry is especially expressed by the Cl(1)−Sn(1)−O(2) angle of 154.23(5)° deviating from 180° and illustrates the stereochemical activity of the lone electron pair at Sn(1). The Sn−N distances range between 2.318(2) (Sn1−N1) and 2.431(2) Å (Sn1−N2), similarly as compared to **3** or $[L^1SnCl][SnCl_3]$.[6] Interestingly, while the O → Sn interaction does not affect the Sn−N distances, it causes, via its trans-influence, an increase of the Sn(1)−Cl(1) distance to 2.4651(8) Å as compared to the corresponding distance of 2.405(1) Å in **3**·$1.5C_7H_8$.

Single crystals of **7** suitable for X-ray diffraction analysis were obtained as toluene solvate **7**·C_7H_8 from a saturated toluene solution at room temperature. The molecular structure of **7**·C_7H_8 is given in Figure 3, selected bond lengths and angles are given in Table 1, and the crystallographic data are given in Table S1 (see Supporting Information).

In **7**·C_7H_8, the Sn(1) atom is five-coordinate by N(1), N(2), N(3), O(1), and O(4) atoms. The Sn−N distances range between 2.269(2) (Sn1−N1) and 2.479(2) Å (Sn1−N3). The latter value indicates a weaker N → Sn interaction of the C═N imine moiety as compared with the $[L^1SnCl]^+$ cations in **3** (2.420(3) Å) and in **5** (Sn1−N3 2.431(3) Å). The Sn(1)−O(1) (2.350(2) Å) and Sn(1)−O(4) (2.554(2) Å) distances indicate that both triflate moieties are in closer contact with the tin atom than in the ion-separated complex $[L^1SnCl][OTf]$ (**5**) (Sn(1)−O(2) = 3.042(2) Å). The covalent radii of Sn and O are 1.40 and 0.73 Å,[15] respectively, and the ionic radii for Sn^{2+} and O^{2-} are 0.93 and 1.40 Å, respectively.[16] It thus appears that only the Sn−O bond to the closest triflate anion, at a distance of 2.350(2) Å, could possibly be treated as a slightly longer "normal" single bond. This prolongation may indicate considerable electrostatic character of these Sn−O interactions. The shortest Sn−O distance for the other triflate moiety is 2.554(2) Å, which falls within the sum of the van der Waals radii for Sn (2.19 Å) and O (1.52 Å), but is far longer than a typical single bond.[15] As a consequence, the bonding situation in **7**·C_7H_8 can be best described as an ion pair consisting of $[L^1SnOTf]^+$ cation and OTf^- anion. A similar situation has been found for crown ether-coordinated tin(II) triflates reported by Baines and MacDonald. They described the complexes [SnOTf([18]-crown-6)][OTf][17] and $Sn(OTf)_2$·triglyme,[18] each consisting of a monocationic moiety composed of the crowned tin(II) center to which one of the triflate groups is bound at Sn−O distances of 2.282(9) Å and 2.331(6) Å, respectively, and a second triflate moiety at Sn−O distances of 2.596(9) Å and 2.741(6) Å, respectively.[17,18]

Single crystals of **8** were obtained from a saturated CH_2Cl_2 solution at room temperature. The molecular structure of **8** is shown in Figure 4; selected bond lengths and angles are given

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $3{\cdot}1.5C_7H_8$, $5{\cdot}CH_2Cl_2$, $7{\cdot}C_7H_8$, and 8

	$3{\cdot}1.5C_7H_8$	$5{\cdot}CH_2Cl_2$	$7{\cdot}2C_7H_8$	7	7	8	8	8
	experimental	experimental	experimental	BP86[a]	wB97xD[a]	experimental	BP86[a]	wB97xD[a]
Sn(1)−N(1)	2.314(3)	2.318(2)	2.269(2)	2.3122	2.3289	2.258(2)	2.3708	2.2772
Sn(1)−N(2)	2.400(3)	2.431(2)	2.411(2)	2.4846	2.4341	2.364 (2)	2.4911	2.3518
Sn(1)−N(3)	2.420(3)	2.400(2)	2.479(2)	2.4966	2.4218			
Sn(1)−O(1)			2.350(2)	2.3867	2.3576	2.959(2)	3.1928	3.0043
Sn(1)−O(2)		3.042(2)				2.3822(19)	2.6061/2.6247	2.3880/3.9393
Sn(1)−O(4)			2.554(2)	2.4592	2.4269			
Sn(1)−O(5)						2.443(2)	2.3037/3.0638	2.2798/3.2864
Sn(1)−Cl(1)	2.4050(10)	2.4651(8)						
N(1)−Sn(1)−N(2)	68.26(10)	67.60(8)	69.69(7)	69.29	68.27	68.57(8)	67.31	68.933
N(1)−Sn(1)−N(3)	67.97(10)	68.70(8)	69.26(8)	69.27	68.41			
N(2)−Sn(1)−N(3)	136.23(10)	135.95(8)	138.93(7)	138.66	136.67			
O(1)−Sn(1)−O(4)			152.25(8)	155.37	151.32			
O(2)−Sn(1)−O(5)						145.63(7)	148.59	147.39
O(2)−Sn(1)−Cl(1)		154.23(5)						
N(1)−Sn(1)−Cl(1)	87.95(7)	88.42(6)						

[a] Basis sets Sn: def2-TZVP; H, C, N, O, S, F: 6-31g(d).

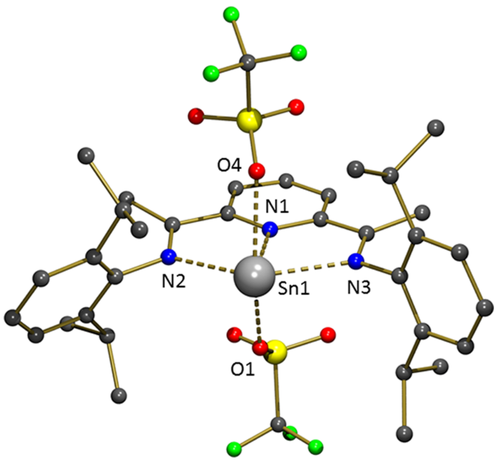


Figure 3. Povray schematic representation of the molecular structure of $7{\cdot}C_7H_8$. Hydrogen atoms and the toluene solvate molecule are omitted for clarity.

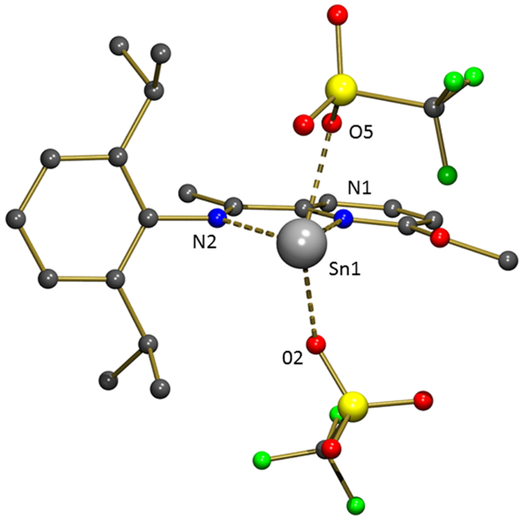


Figure 4. Povray schematic representation of the molecular structure of **8**. Hydrogen atoms are omitted for clarity.

in Table 1. The crystallographic data are given in Table S1 (see Supporting Information).

At first sight, the Sn(1) atom in **8** is four-coordinate and exhibits a distorted *ψ*-trigonal bipyramidal environment with N(1), N(2), and the lone electron pair in the equatorial and (O2) and O(5) in the axial positions. The stereochemical activity of the lone electron pair at Sn(1) is expressed by the extreme deviation from 180° of the O(2)−Sn(1)−O(5) angle (145.63(7)°). The rather narrow N(1)−Sn(1)−N(2) angle of 68.57(8)° is also in line with this but more likely the result of ligand constraint. Both the Sn(1)−N(1) (2.258(2) Å) and Sn(1)−N(2) (2.364(2) Å) distances reveal strong N → Sn interactions. The latter distance indicates a stronger N → Sn interaction of the C═N imine moiety in complex **8** as compared with those in $\mathbf{3}{\cdot}1.5C_7H_8$ (Sn(1)−N(2) 2.400(3), Sn(1)−N(3) 2.420(3) Å), $\mathbf{5}{\cdot}CH_2Cl_2$ (Sn(1)−N(2) 2.431(2), Sn(1)−N(3) 2.400(2) Å) and $\mathbf{7}{\cdot}2C_7H_8$ (Sn(1)−N(2) 2.411(2), Sn(1)−N(3) 2.479(2) Å). Despite the strong N → Sn interactions, both triflate anions coordinate the tin atom at Sn(1)−O(2) and Sn(1)−O(5) distances of 2.3822(19) and 2.443(2) Å, respectively. These distances are very close to the sum of the ionic radii for Sn^{2+} cation and O^{2-} anion (2.33 Å)[16] and suggest considerable ionic character of the Sn−O bonds. Similarly to **8**, a narrow range of distances between the tin atom and the triflate anions has been found in the complex $Sn(OTf)_2{\cdot}$tetraglyme, where one triflate anion has a closest Sn−O distance of 2.408(5) Å, and the other one has a closest such distance of 2.519(6) Å.[18]

Baines and MacDonald demonstrated that cyclic or acyclic polyether ligands react with $Sn(OTf)_2$ providing either neutral complexes, $Sn(II)^+$, or even $Sn(II)^{2+}$ cations stabilized by O → Sn donor−acceptor interactions, with the actual outcome depending on the identity of the polyether ligands.[17−19] In analogy, the use of the *N*,*N*,*N*-chelating ligand L^1 provided an ionic complex **7** consisting of $[L^1SnOTf]^+$ cation and OTf^- anion, while the *N*,*N*-chelated tin(II) triflate **8** contains both OTf moieties in close proximity to the tin atom. The Sn−O bond in **8** possesses highly ionic character as both Sn−O distances are close to the sum of the ionic radii for Sn^{2+} and O^{2-}. This implies the positive charge being located at the tin center and as the result of this, strong C═N → Sn donation takes place.

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Nuclear Magnetic Resonance Studies in Solution. Compounds **3**−**6** show excellent solubility in chlorinated solvents. In the ^{1}H NMR spectra of **3**−**6**, the aromatic protons of the pyridine ring are shifted downfield (δ 8.58 and 8.81 ppm for **3**, δ 8.72 and 8.94 ppm for **4**, δ 8.52 and 8.70 ppm for **5**, δ 8.67 and 8.88 ppm for **6**) when compared with the spectrum of the free L^1 ligand (δ 8.04 and 8.52 ppm).[6] Similarly, the signal of the N=CCH_3 protons are shifted downfield (δ 2.62 ppm for **3**, δ 2.69 ppm for **4**, δ 2.57 ppm for **5**, δ 2.64 ppm for **6**) in comparison to that of ligand L^1 (δ 2.34 ppm).[6] These observations are typical for the presence of the [L^{1}SnCl]$^+$ cation.[6] The ^{119}Sn NMR spectra of **3**, **4**, and **6** revealed for each compound two resonances (−37 and −431 ppm for **3**, 226 and −424 ppm for **4**, and −34 and −430 ppm for **6**), while one signal at δ −469 ppm was found in a ^{119}Sn NMR spectrum of **5**. The high field-shifted values of δ ^{119}Sn in **3**−**6** (range from −424 to −469 ppm) are comparable with the value found for the cationic part of the complex [L^{1}SnCl][SnCl$_3$] (**1**) (δ −435)[6] and support the existence of the [L^{1}SnCl]$^+$ cation in **3**−**6**. In contrast, the downfield-shifted ^{119}Sn NMR resonances in **3**, **4**, and **6** are assigned to their anionic parts [W(CO)$_5$(SnCl$_3$)]$^-$ (−37 ppm in **3**), [Cr(CO)$_5$(SnCl$_3$)]$^-$ (226 ppm in **4**), and [W(CO)$_5${Sn(OTf)Cl$_2$}]$^-$ (−34 ppm in **6**). These values are shifted downfield when compared with those found for the noncoordinated [SnCl$_3$]$^-$ anion (δ −60 ppm) in **1**.[6] In addition, the presence of $^1J(^{119}\text{Sn}-^{183}\text{W})$ = 397 Hz in the ^{119}Sn NMR spectrum of **3** unambiguously proves the coordination of the [SnCl$_3$]$^-$ anion to the W(CO)$_5$ moiety. A ^{19}F NMR spectrum of **6** revealed a resonance at δ −78.1, while a ^{13}C NMR spectrum showed a quartet resonance at δ 120.2 with $^1J(^{13}\text{C}-^{19}\text{F})$ = 318 Hz supporting the presence of a triflate anion in **6**.

In contrast to the complexes **3**−**6**, a ^{1}H NMR spectrum of compound **7** showed one broad signal for the pyridine protons (δ 8.41 ppm) that is high field-shifted in comparison with relevant signals of the [L^{1}SnCl]$^+$ cationic parts (range between 8.58 and 9.01). Similarly, the signal for the N=CCH_3 protons in **7** (δ 2.50 ppm) is also high field-shifted in comparison to those found for the [L^{1}SnCl]$^+$ cations (range of 2.62−2.69). A ^{119}Sn NMR spectrum of **7** showed a resonance at δ −447 being comparable with the values found for the [L^{1}SnCl]$^+$ cations of **1** (δ −435),[6] **3** (δ −431), **4** (δ −424), and **6** (δ −430). It demonstrates the existence of the [L^{1}SnOTf]$^+$ cation in **7**. The NMR data suggest a symmetrically bonded L^1 ligand in the [L^{1}SnOTf]$^+$ cation, where the imine moieties are involved in weaker N → Sn coordination (high field shift of N=CCH_3 protons) as compared with the [L^{1}SnCl]$^+$cation, which is consistent with the data found for the solid state. A ^{13}C NMR spectrum showed a quartet at δ 120.1 with $^1J(^{13}\text{C}-^{19}\text{F})$ = 316 Hz proving the presence of a triflate anion. In spite of the structural features observed in the solid state, a ^{19}F NMR spectrum of **7** revealed only a single resonance at δ −77.5 (even at 250 K) indicating the exchange between free and bound triflate groups to be fast on the NMR time scale. A similar observation was made for [Sn([18]crown-6)OTf][OTf].[17] The ^{19}F NMR resonance found for **7** is high field-shifted when compared with the chemical shift of MeOTf as a representative for a covalently bonded organic triflate (δ −75.4)[20] but shifted downfield in comparison with [Bu$_4$N][OTf] as a representative for an ionic triflate (δ −78.7).[21]

Similarly, in the ^{1}H NMR spectrum of **8**, the signals for the aromatic protons of the pyridine ring are shifted to high field (δ 7.48, 7.77, and 8.33 ppm) as compared with the corresponding resonances for the [L^{2}SnCl]$^+$ cation (7.48, 8.12, and 8.37 ppm) of **2**[10] but shifted downfield as compared with the resonances of the free ligand L^2 (δ 6.75, 7.68, and 7.95 ppm).[10] The signal of the N=CCH_3 protons is also high field-shifted (δ 2.30 ppm) in comparison to those found in the [L^{2}SnCl]$^+$ cation (δ 2.87 ppm) of **2**. A ^{119}Sn NMR spectrum of **8** revealed a resonance at δ −165 ppm being shifted downfield as compared with both the [L^{2}SnCl]$^+$ cation in **2** ($\delta\delta$ −330.4 ppm)[10] and the [L^{1}SnOTf]$^+$ cation in **7** (δ −447 ppm). The data indicate compound **8** existing as neutral species [L^{2}Sn(OTf)$_2$] in solution, with weaker N → Sn coordination (high field shift of N=CCH_3 proton resonance) as compared with the [L^{2}SnCl]$^+$ cation in **2**.[10] A ^{13}C NMR spectrum showed a quartet at δ 119.7 with $^1J(^{13}\text{C}-^{19}\text{F})$ = 322 Hz supporting the presence of triflate moieties in **8**. A ^{19}F NMR spectrum revealed a resonance at δ −77.9 ppm, very close to the value of [Bu$_4$N][OTf] as a representative for ionic triflate (δ −78.7),[21] thus supporting the presence of the highly ionic character of both Sn−O (triflate) bonds.

Density Functional Theory Calculations. To get an insight into the electronic structure of compounds **7** and **8** and information about donor−acceptor interactions between the ligands and the tin atom, density functional theory (DFT) calculations with Gaussian09[22] were performed. The pure BP86[23] functional and the dispersive wB97xD[24] functional with the basis set combination of def2-TZVP[25] basis on tin and 6-31g(d)[26] on the other atoms were used for geometry optimization. The resulting geometry parameters for **7** and **8** are listed in Table 1.

Overall, the calculated values, and here especially the angles, show reasonably good agreement with the experimentally determined ones. In general, the calculated interatomic distances are longer than those obtained experimentally. Exceptions are the Sn(1)−N(2) (**8**, wB97xD), Sn(1)−N(3) (**7**, wB97xD), Sn(1)−O(4) (**7**, both BP86 and wB97xD), and Sn(1)−O(5) (**8**, both BP86 and wB97xD). Interestingly, for compound **8** the triflate coordination is differently described by the pure functional BP86 and the wB97xD functional taking into account dispersive interactions. While in the experimentally established structure both triflate moieties coordinate the tin atom in a monodentate fashion, the calculation employing the BP86 functional results in one of the triflate anions in a bidentate coordination mode and for the second one in an anisobidentate coordination. Apparently, the differences are associated with a conformational change in the calculated structure with respect to the experimental one (Figure 5).

To get more insight into the donor−acceptor interactions, natural bond order (NBO) calculations were performed on Lewis structures involving interactions between lone electron pairs LP of the donor atoms nitrogen and oxygen and empty orbitals LP* at the tin atom (Table 2). For both compounds **7** and **8**, the strongest such interaction is calculated for the nitrogen atom N1 of the pyridine ring. In case of compound **8**, the values obtained from the calculation with the wB97xD functional are systematically bigger than those obtained from the pure BP86 functional. For compound **8**, the bidentate coordination mode of one triflate anion, as suggested from the calculated bond distances given in Table 1, is again reflected by the BP86-based calculation.

The Wiberg bond indices (hereafter referred to as WBIs) are given in Table 3. For compound **7**, the values are bigger for the BP86- than they are by the wB97xD-based calculations. This is

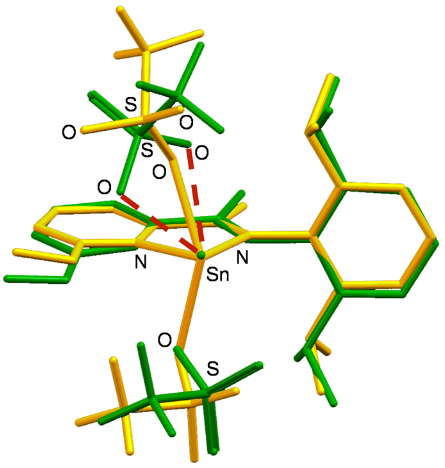

Figure 5. Superposition of the experimentally established structure of compound **8** (yellow) and the calculated one based on the BP86 functional (green). The red dashed lines illustrate the bidentate coordination mode of the triflate anion.

not the case for compound **8**, however. Most importantly, the WBIs found for the N(1) → Sn(1) interaction (0.22 (BP86)/0.16 (wB97xD) in **7** and 0.21 in **8**) suggest strong coordination of the pyridine N(1) atom to the tin atom in **7** and **8**, respectively. The WBIs of the Sn(1)−O(4) (triflate) interaction are 0.18 (BP86)/0.14 (wB97xD) in **7** (the WBI of the Sn(1)−O(2) (triflate) is 0.14 (BP86)/0.17 (wB97xD) in **8**) that are not significantly bigger than the bond indices for the O → Sn interactions in the dicationic cryptand[2.2.2] complex of $Sn(OTf)_2$ (range between 0.10 and 0.14)[19b] or in the dicationic crown ether complex of $Sn(OTf)_2$ (range from 0.10 to 0.18).[17] The WBIs thus suggest that there is no significant bonding beetween the tin center and one triflate moiety in both **7** and **8**. In contrast, the WBI of the Sn(1)−O(1) (triflate) interaction is 0.21 (BP86)/0.16 (wB97xD) in **7** (the WBI of the Sn(1)−O(5) (triflate) is 0.24 (BP86)/0.20 (wB97xD) in **8**). These values are comparable to the WBIs found for N(1) → Sn(1), which supports the idea that the other triflate moiety is involved in the strong O → Sn interaction in both complexes **7** and **8**.

The calculated residual positive charges on each tin center gave similar results with values of +1.356 (BP86)/+1.515 (wB97xD) for **7** and +1.325(BP86)/+1.465 (wB97xD) for **8**. While these values are bigger than the expected +1 charge for a generic monocation, they are rather similar to the values calculated for cryptand[2.2.2] complex of $Sn(OTf)_2$ (+1.44)[19b] and the crown ether complexes of $Sn(OTf)_2$ (range between +1.36 and +1.50).[17] However, they are not as large as the NBO charges reported for the crown ether/glyme complexes of $Sn(OTf)_2$ (+1.64).[18]

Table 3. Wiberg Bond Indices[26] for the N → Sn and O → Sn Interactions in Compounds 7 and 8 Determined by Natural Bond Order Calculations

7	BP86^a	wB97xd^a	8	BP86^a	wB97xd^a
N(1) → Sn(1)	0.2211	0.1640	N(1) → Sn(1)	0.2147	0.2140
N(2) → Sn(1)	0.1895	0.1465	N(2) → Sn(1)	0.1907	0.2117
N(3) → Sn(1)	0.1895	0.1470	O(2) → Sn(1)	0.1425	0.1706
O(4) → Sn(1)	0.1787	0.1378	O(3,4) → Sn(1)	0.1511	0.0690
O(1) → Sn(1)	0.2076	0.1580	O(5) → Sn(1)	0.2426	0.2037

^{a}Basis sets Sn: def2-TZVP; H, C, N, O, S, F: 6-31g(d).

■ CONCLUSION

In conclusion, we have demonstrated that the ionic compound **1** reacts with $[M(CO)_5(thf)]$ (M = Cr, W) in a uniform manner. Only the $[SnCl_3]^-$ anion coordinates the $M(CO)_5$ moieties, yielding the complexes $[L^1SnCl][W(CO)_5(SnCl_3)]$ (**3**) and $[L^1Sn^{II}Cl][Cr(CO)_5(SnCl_3)]$ (**4**), respectively. In contrast, the analogous reactions of compound **2** containing a three-coordinated tin atom in the $[L^2SnCl]^+$ cation failed. Further studies showed that complex **1** also reacts with 1 equiv of AgOTf providing $[L^1SnCl]OTf$ (**5**) as the result of the $[SnCl_3]^-$ anion substitution. In contrast, a similar reaction of **3** provided compound $[L^1Sn^{II}Cl][W(CO)_5\{Sn(OTf)Cl_2\}]$ (**6**), where one chloride anion of the $SnCl_3^-$ moiety is substituted by a OTf^- moiety at the $[W(CO)_5(SnCl_3)]^-$ anionic part, leaving the $[L^1SnCl]^+$ cation noneffected. The reaction between 4 equiv of AgOTf and **3**, however, provided the complex $[L^1SnOTf][OTf]$ (**7**), where the ligand L^1 and one triflate anion coordinates to the tin center. In contrast, the treatment of L^2 with $Sn(OTf)_2$ yielded neutral $[L^2Sn(OTf)_2]$ (**8**) with the ligand L^2 and both triflate anions being in the coordination sphere of the tin atom. The complexes **3**−**6** are well-separated ionic compounds consisting of the $[L^1SnCl]^+$ cation and different anions. Compound **7** can be seen as ion separated pair of $[L^1SnOTf]^+$ cation and OTf^- anion. In contrast, complex **8** can be interpreted as a neutral complex of ligand L^2 with $Sn(OTf)_2$. For both complexes **7** and **8**, the DFT calculations define highly positive charge at the tin center and hint at high ionic character of the Sn−O bonds.

■ EXPERIMENTAL SECTION

General Methods. The starting ligands L^1 and L^2 were prepared according the literature methods.[6,10] The $Sn(OTf)_2$, AgOTf, $W(CO)_6$, and $Cr(CO)_6$ were purchased from Sigma-Aldrich. All reactions were performed under argon, using standard Schlenk techniques. Solvents were dried by standard methods, distilled prior to use. The ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra were recorded on a Bruker Avance500

Table 2. Donor−Acceptor Interactions (*E* [kcal/mol]) between Nitrogen and Oxygen Atoms and the Tin Center in Compounds 7 and 8 as Determined by Natural Bond Order Calculations

7	BP86^a kcal/mol	wB97xD^a kcal/mol	8	BP86^a kcal/mol	wB97xD^a kcal/mol
LP N(1) → LP* Sn	49	49	LP N(1) → LP* Sn	42	60
LP N(2) → LP* Sn	25	34	LP N(2) → LP* Sn	28	59
LP N(3) → LP* Sn	25	34	LP O(2) → LP* Sn	11	40
LP O(1) → LP* Sn	36	22	LP O(3,4) → LP* Sn	11	
LP O(4) → LP* Sn	33	34	LP O(5) → LP* Sn	32	45

^{a}Basis sets Sn: def2-TZVP; H, C, N, O, S, F: 6-31g(d). LP = lone electron pair.

spectrometer at 300 K in $\mathrm{CDCl_3}$ or thf-d_8. The ^{1}H, ^{13}C, and ^{119}Sn NMR chemical shifts δ are given in parts per million and referenced to external $\mathrm{Me_4Sn}$ (^{119}Sn) and $\mathrm{Me_4Si}$ (^{13}C, ^{1}H). Elemental analyses were performed on an LECO−CHNS-932 analyzer.

*Synthesis of [L^1SnCl][W(CO)$_5$(SnCl$_3$)] (**3**).* Compound **1** (0.61 g, 0.71 mmol) in thf (80 mL) was added with stirring to $[\mathrm{W(CO)_5(thf)}]$, prepared in situ from $\mathrm{W(CO)_6}$ (0.5 g, 1.42 mmol)) in 200 mL of thf at room temperature. The reaction mixture was stirred for an additional 24 h. The solution was evaporated, and the orange powder was dissolved in toluene (30 mL). The solution was stored for 2 d at 5 °C giving orange crystals of **3** as the toluene solvate **3**$\cdot 1.5\mathrm{C_7H_8}$ (yield 0.68 g, 81%). mp 194.4 °C dec. Anal. Calcd for $\mathrm{C_{38}H_{33}Cl_4N_3O_5Sn_2W\cdot 1.5C_7H_8}$ (MW = 1322.33): C, 44.1; H, 3.4; Found: C, 44.3; H 3.6%. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.13 MHz): $\delta\delta$ = 1.13 (d, 6H, $\mathrm{CH}(CH_3)_2$), 1.15 (d, 6H, $\mathrm{CH}(CH_3)_2$), 1.20 (d, 6H, $\mathrm{CH}(CH_3)_2$), 1.25 (d, 6H, $\mathrm{CH}(CH_3)_2$), 2.62 (s, 6H, $(CH_3)\mathrm{C{=}N}$), 2.95 (m, 4H, $CH(\mathrm{CH_3})_2$), 7.15−7.35 (m, 6H, ArH), 8.58 (d, 2H, ArH), 8.81 (t, 1H, ArH). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.5 MHz): δ = 19.4 $(CH_3)\mathrm{C{=}N}$, 24.6 $\mathrm{CH}(CH_3)_2$, 24.9 $\mathrm{CH}(CH_3)_2$, 28.4 $CH(\mathrm{CH_3})_2$, 124.8, 129.0, 130.4, 136.8, 139.4, 145.6, 150.0, 169.0 $(\mathrm{CH_3})C\mathrm{{=}N}$, 194.4 ($^1J(^{13}\mathrm{C}-^{183}\mathrm{W})$ = 124.3 Hz), 200.1. ^{119}Sn NMR ($\mathrm{CDCl_3}$, 111.92 MHz): δ = −37 ($^1J(^{119}\mathrm{Sn}-^{183}\mathrm{W})$ = 397 Hz), −431 ppm.

*Synthesis of [L^1SnCl][Cr(CO)$_5$(SnCl$_3$)] (**4**).* Compound **1** (0.40 g, 0.46 mmol) in thf (30 mL) was added with stirring to $[\mathrm{Cr(CO)_5(thf)}]$ prepared in situ from $\mathrm{Cr(CO)_6}$ (102 mg, 0.46 mmol) at room temperature. Reaction mixture was stirred for an additional 24 h. The solution was evaporated, and the orange powder was dissolved in toluene (30 mL). The solution was stored for 2 d at 5 °C giving orange solid material of **4** (yield 0.32 g, 67%). mp 213.8 °C dec. Anal. Calcd for $\mathrm{C_{38}H_{43}Cl_4N_3O_5Sn_2Cr}$ (MW = 1052.97): C, 43.4; H, 4.1; Found: C 43.6; H 4.3%. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.13 MHz): δ = 1.20 (d, 12H, $\mathrm{CH}(CH_3)_2$), 1.28 (d, 12H, $\mathrm{CH}(CH_3)_2$), 2.69 (s, 6H, $(CH_3)\mathrm{C{=}N}$), 2.91 (bs, 4H, $CH(\mathrm{CH_3})_2$), 7.17−7.27 (m, 6H, ArH), 8.72 (bs, 2H, ArH), 8.94 (bs, 1H, ArH). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.5 MHz): δ = 19.6 $(CH_3)\mathrm{C{=}N}$, 24.8 $\mathrm{CH}(CH_3)_2$, 28.9 $CH(\mathrm{CH_3})_2$, 124.9, 128.3, 130.7, 136.8, 139.9, 146.1, 150.0, 169.3 $(\mathrm{CH_3})C\mathrm{{=}N}$, 216.9 ($\mathrm{CO_{ax}}$), 224.7 ($\mathrm{CO_{eq}}$). ^{119}Sn NMR ($\mathrm{CDCl_3}$, 111.92 MHz): δ = 226, −424 ppm.

*Synthesis of [L^1SnCl]OTf (**5**).* Compound **1** (0.30 g, 0.35 mmol) in $\mathrm{CH_2Cl_2}$ (30 mL) was added with stirring to AgOTf (90 mg, 0.35 mmol) at room temperature. Reaction mixture was stirred for an additional 24 h. The solution was filtered, and the filtrate was concentrated to a volume of ∼10 mL. The storage for 6 d at room temperature gave orange crystals of **5** as the dichloromethane solvate **5**$\cdot\mathrm{CH_2Cl_2}$ (yield 0.23 g, 85%). mp 310.4 °C dec. Anal. Calcd for $\mathrm{C_{34}H_{43}ClF_3N_3O_3SSn\cdot CH_2Cl_2}$ (MW = 879.86) C, 49.1; H, 4.9; Found: C, 48.9; H, 5.0%. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.13 MHz): $\delta\delta$ = 1.11 (d, 12H, $\mathrm{CH}(CH_3)_2$), 1.21 (d, 12H, $\mathrm{CH}(CH_3)_2$), 2.57 (s, 6H, $(CH_3)\mathrm{C{=}N}$), 2.95 (bs, 4H, $CH(\mathrm{CH_3})_2$), 7.25−7.31 (m, 6H, ArH), 8.52 (d, 2H, ArH), 8.70 (t, 1H, ArH). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.5 MHz): δ = 19.2 $(CH_3)\mathrm{C{=}N}$, 24.6 $\mathrm{CH}(CH_3)_2$, 24.8 $\mathrm{CH}(CH_3)_2$, 28.4 $CH(\mathrm{CH_3})_2$, 120.1 (CF_3, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 317 Hz), 124.7, 127.9, 129.4, 137.2, 140.2, 144.7, 150.5, 168.8 $(\mathrm{CH_3})C\mathrm{{=}N}$. ^{119}Sn NMR ($\mathrm{CDCl_3}$, 111.92 MHz): δ = −469 ppm. Positive-ion electrospray ionization mass spectrometry (ESI-MS): *m*/*z* $[\mathrm{L^1SnCl}]^+$ = 636.3, $[\mathrm{L^1}]^+$ = 482.3; negative-ion ESI-MS: *m*/*z* $\mathrm{OTf^-}$= 149.0.

*Synthesis of [L^1SnCl][W(CO)$_5$(SnCl$_2$OTf)] (**6**).* Compound **3** (0.35 g, 0.28 mmol) in toluene (30 mL) was added with stirring to AgOTf (70 mg, 0.28 mmol) at room temperature. The reaction mixture was stirred for an additional 24 h. The solution was filtered, and the filtrate was concentrated to a volume of ∼10 mL. Storage of this solution for 4 d at room temperature gave orange solid material of **6** (yield 0.22 g, 63%). mp 204.4 °C dec. Anal. Calcd for $\mathrm{C_{39}H_{43}Cl_3F_3N_3O_8SSn_2W}$ (MW = 1298.44): C, 36.1; H, 3.3; Found: C 36.5; H, 3.3%. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.13 MHz): δ = 1.17 (d, 12H, $\mathrm{CH}(CH_3)_2$), 1.26(d, 12H, $\mathrm{CH}(CH_3)_2$), 2.64 (s, 6H, $(CH_3)\mathrm{C{=}N}$), 2.87 (m, 4H, $CH(\mathrm{CH_3})_2$), 7.33−7.37 (m, 6H, ArH), 8.67 (d, 2H, ArH), 8.88 (t, 1H, ArH). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.5 MHz): δ = 19.5 $(CH_3)\mathrm{C{=}N}$, 23.6 $\mathrm{CH}(CH_3)_2$, 28.5 $CH(\mathrm{CH_3})_2$, 120.2 (CF_3, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 318 Hz), 124.7, 128.4, 130.7, 137.0, 139.7, 145.8, 150.3, 169.3 $(\mathrm{CH_3})C\mathrm{{=}N}$, 196.6 ($\mathrm{CO_{ax}}$, $^1J(^{13}\mathrm{C}-^{183}\mathrm{W})$ = 124 Hz), 200.4 ($\mathrm{CO_{eq}}$, $^1J(^{13}\mathrm{C}-^{183}\mathrm{W})$ = 134 Hz). ^{19}F NMR ($\mathrm{CDCl_3}$, 111.92 MHz): δ = −78.1 ppm, ^{119}Sn NMR ($\mathrm{CDCl_3}$, 111.92 MHz): δ = −34 (bs), −430 ppm.

*Synthesis of [L^1SnOTf][OTf] (**7**).* Compound **3** (0.35 g, 0.28 mmol) in toluene (30 mL) was added with stirring to AgOTf (288 mg, 1.12 mmol) at room temperature. The reaction mixture was stirred for an additional 24 h. The solution was filtered, and the filtrate was concentrated to a volume of ∼15 mL. Storage of the saturated toluene solution at room temperature for 2 d gave yellow crystals of **7**$\cdot\mathrm{C_7H_8}$ (yield 0.15 g, 59%). mp 167−170 °C. Anal. Calcd for $\mathrm{C_{35}H_{43}F_6N_3O_6S_2Sn\cdot C_7H_8}$ (MW = 990.66): C, 50.8; H, 5.15; Found: C, 51.1; H 5.4%. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.13 MHz): δ = 1.12 (bs, 24H, $\mathrm{CH}(CH_3)_2$), 2.50 (bs, 6H, $(CH_3)\mathrm{C{=}N}$), 3.03 (bs, 4H, $CH(\mathrm{CH_3})_2$), 7.19−7.27 (m, 6H, ArH), 8.41 (bs, 3H, ArH). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.5 MHz): δ = 19.3$(CH_3)\mathrm{C{=}N}$, 24.3 $\mathrm{CH}(CH_3)_2$, 25.0 $\mathrm{CH}(CH_3)_2$, 27.6 $CH(\mathrm{CH_3})_2$, 120.1 (CF_3, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 316 Hz), 124.9, 125.3, 128.1, 137.2, 137.8, 141.2, 151.8, 171.6 $(\mathrm{CH_3})C\mathrm{{=}N}$. ^{19}F NMR ($\mathrm{CDCl_3}$, 300.13 MHz): δ = −77.5 ppm. ^{119}Sn NMR ($\mathrm{CDCl_3}$, 111.92 MHz): δ = −447 ppm.

*Synthesis of [L^2Sn(OTf)$_2$] (**8**).* $\mathrm{L^2}$ powder (0.55 g, 1.77 mmol) in toluene (30 mL) was added with stirring to $\mathrm{Sn(OTf)_2}$ (0.74 mg, 1.77 mmol) at room temperature. The reaction mixture was stirred for an additional 24 h, and the suspension was filtered. The remaining solid was dissolved in $\mathrm{CH_2Cl_2}$ (10 mL). Storage of this saturated $\mathrm{CH_2Cl_2}$ solution at room temperature gave orange crystals of **8** (yield 1.09 g, 85%). mp 159.2 °C dec. Anal. Calcd for $\mathrm{C_{22}H_{26}F_6N_2O_7S_2Sn}$ (MW = 727.27): C, 36.3; H, 3.6; Found: C, 36.5; H, 3.61%. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.13 MHz): δ = 1.07 (d, 6H, $\mathrm{CH(CH_3)_2}$), 1.20 (d, 6H, $\mathrm{CH(CH_3)_2}$), 2.30 (s, 3H, $\mathrm{(CH_3)C{=}N}$), 2.81 (h, 2H, $\mathrm{CH(CH_3)_2}$), 4.24 (s, 3H, $\mathrm{OCH_3}$), 7.28−7.48 (m, 3H, ArH), 7.48 (d, 1H, ArH), 7.77 (d, 1H, ArH), 8.33 ppm (t, 1H, ArH). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.5 MHz): δ = 19.5$(CH_3)\mathrm{C{=}N}$, 23.6 $\mathrm{CH}(CH_3)_2$, 24.0 $\mathrm{CH}(CH_3)_2$, 29.1 $CH(\mathrm{CH_3})_2$, 58.1 $\mathrm{OCH_3}$, 114.3, 119.7 ((CF_3, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 322 Hz) 121.3, 124.8, 129.4, 130.2, 142.1, 143.3, 147.4, 164.5, 178.7 $(\mathrm{CH_3})C\mathrm{{=}N}$. ^{19}F NMR ($\mathrm{CDCl_3}$, 300.13 MHz): δ = −77.9 ppm. ^{119}Sn NMR ($\mathrm{CDCl_3}$, 111.92 MHz): $\delta\delta$ = −165 ppm.

Computational Details. The DFT calculations were performed with Gaussian09[22] by using the pure BP68[23] functional and the wB97xD[24] functional, which includes dispersive interactions. The split valence basis set def2-TZVP[25] was used for the tin atom and contains the effective core potentials on tin.[25] For all other atoms the Popel basis set 6-31g(d)[27] was employed. After geometry optimization, stationary points were verified by frequency analysis (no imaginary frequencies for local minima). The NBO analysis was performed by the NBO program version 3.1[28] as implemented in the Gaussian09 program.

Crystallography. Intensity data for the crystals (**3**$\cdot 1.5\mathrm{C_7H_8}$, **5**$\cdot\mathrm{CH_2Cl_2}$) were collected on a XcaliburS CCD diffractometer (Oxford Diffraction) using Mo Kα radiation at 110 K. The X-ray data for the crystals of **7**$\cdot\mathrm{C_7H_8}$ and **8** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å), a graphite monochromator, and the ϕ and χ scan modes. The structures were solved with direct methods using SHELXS-97.[29] Refinements were performed against F^2 by using SHELXL-2014/6 (**3**$\cdot 0.5\mathrm{C_7H_8}$, **5**$\cdot\mathrm{CH_2Cl_2}$) and SHELXL-2014/7 (**7**$\cdot\mathrm{C_7H_8}$, **8**).[30] The C−H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters. The severely disordered electron densities of noncoordinating solvent molecules of compounds **3**$\cdot 1.5\mathrm{C_7H_8}$ and **7**$\cdot\mathrm{C_7H_8}$ were modeled by the SQUEEZE routine of the program Platon[31] to improve the main part of the structure. Additional crystallographic information is available in the Supporting Information. For decimal rounding of numerical parameters and su values the rules of IUCr have been employed.[32]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data and structure refinement, NBO charges, and synthesis and characterization. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00678. CCDC-1050001 (**3**·1.5C_7H_8), CCDC-1050002 (**5**·CH_2Cl_2), CCDC-1027223 (**7**·C_7H_8) and CCDC- 1027224 (**8**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

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