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Reactivity of a Tin(II) (Iminophosphinoyl)(thiophosphinoyl)methanediide Complex toward Isocyanates and Rhodium(I) Chloride

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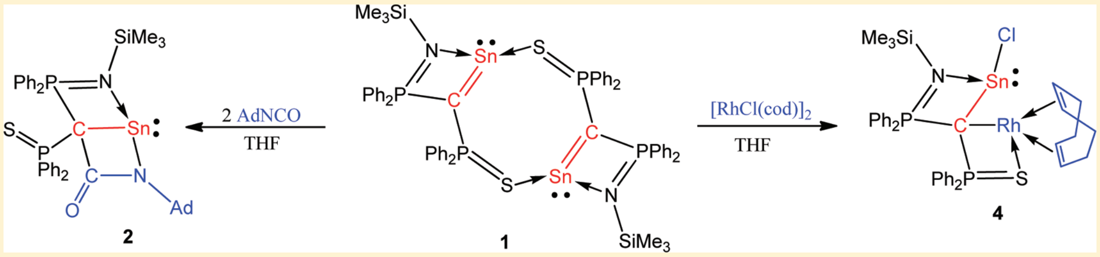
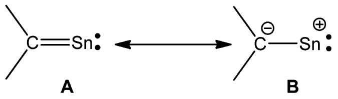
Ⓢ *Supporting Information*



ABSTRACT: The reaction of the tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)CSn:]_2$ (**1**) with AdNCO (Ad = adamantyl), ArNCO (Ar = 2,6-$Pr^i_2C_6H_3$), and $[RhCl(cod)]_2$ in THF afforded $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)\overbrace{C\{C(O)N(Ad)\}Sn}:]$ (**2**), $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)C^-\{C(O)N(Ar)\}Sn^+:]$ (**3**), and $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)C\{Rh(cod)\}(SnCl)]$ (**4**), respectively. Compounds **2**−**4** have been characterized by NMR spectroscopy and X-ray crystallography.

Stable silenes (>Si=C<),[1] germenes (>Ge=C<),[2] and stannenes (>Sn=C<)[3] have attracted much attention in the past 30 years and have been the focus of several reviews.[4] They have been synthesized successfully by incorporating sterically hindered substituents at both carbon and heavier group 14 elements. They are reactive and can undergo 1,2-addition and [2 +*n*] cycloaddition.[5] In contrast, stable heavier group 14 vinylidene analogues (:M=C<) are scarcely known. Because they lack bulky substituents at the low-coordinate metal(II) centers, the M=C bonds are highly reactive and undergo oligomerization more readily. Until now, only two examples of heavier group 14 vinylidene analogues have been reported.[6,8] Leung et al. reported the first example of the bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$, which contains a weak Ge−Ge interaction.[6] The existence of the monomeric germavinylidene intermediate "$(Me_3SiN{=}PPh_2)_2C{=}Ge$:" in solution has been demonstrated by trapping reactions of the bisgermavinylidene with various transition-metal complexes and organic and inorganic substrates.[7] We reported the synthesis of the tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)CSn:]_2$ (**1**), which can be considered as a stannavinylidene derivative.[8] The X-ray structure of **1** implies that the Sn−C bond has some double-bond character. Natural bond orbital (NBO) analysis suggests the existence of a >C=Sn: skeleton in which the electron densities of the σ and π bonds are mostly occupied by the $C_{methanediide}$ atom (85.3% electron density of the σ bond and 96.9% electron density of the π bond). In valence bond terms, the C−Sn bond in **1** can be between the resonance forms **A** and **B** (Scheme 1).

Scheme 1. Resonance Forms A and B



Recently, the [2 + 2] cycloadditions of main-group and transition-metal bis(phosphinoyl)methanediide complexes with AdNCO have been reported to show multiple-bond character in the $C_{methanediide}$−M bonds (M = Ca, Ba, Ge, Zr, Hf).[9] Moreover, the 1,2-addition of $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ with $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) demonstrates the existence of a $C_{methanediide}$−Ge double bond and the nucleophilic character of the $C_{methanediide}$ atom.[7b] In this context, it is highly desirable to explore the reactivity of **1** toward isocyanates and $[RhCl(cod)]_2$ to understand the bonding nature of the $C_{methanediide}$−Sn bond and the electronic properties of the $C_{methanediide}$ atom, respectively.

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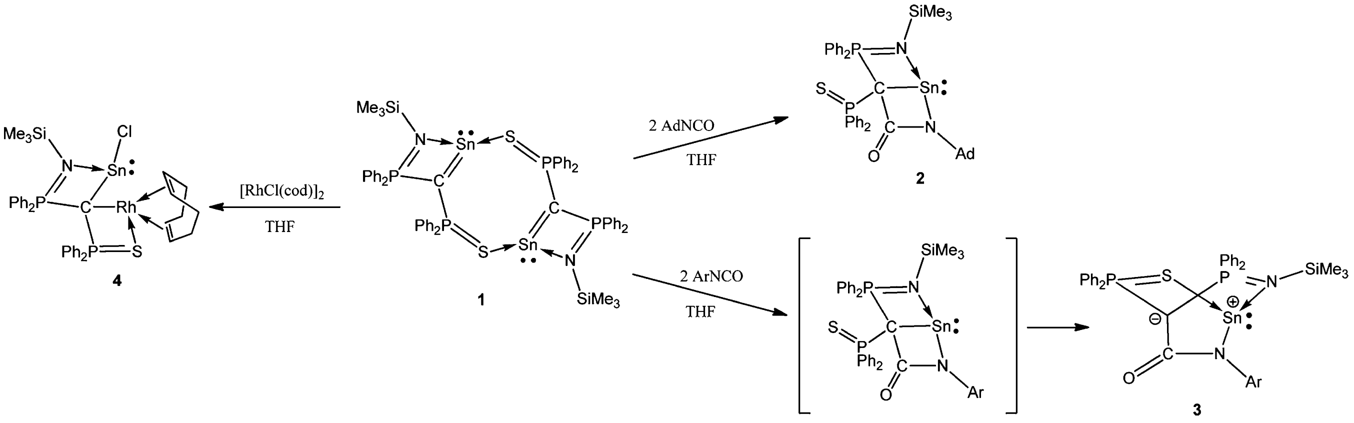
Scheme 2. Synthesis of 2−4



RESULTS AND DISCUSSION

The reaction of compound **1** with 2 equiv of AdNCO (Ad = adamantyl) in THF afforded $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)\overline{C\{C(O)N(Ad)\}Sn}:]$ (**2**, Scheme 2). It is noteworthy that the lone pair electrons at the tin(II) atom do not undergo [1 + 2] cycloaddition. Recently, the [2 + 2] cycloadditions of main-group and transition-metal bis(phosphinoyl)methanediide complexes with AdNCO have been reported by several research groups.[9] For example, the germanium(II),[7d] zirconium, and hafnium bis(phosphinoyl)methanediide complexes underwent a [2 + 2] cycloaddition with the C═N bond of AdNCO,[9a] whereas the calcium and barium bis(phosphinoyl)-methanediide complexes underwent a [2 + 2] cycloaddition with the C═O bond of AdNCO.[9b,c] The results suggest that the reaction of **1** with AdNCO probably proceeds via a [2 + 2] cycloaddition of the >C═Sn: bond or an insertion reaction of the $C^-{-}Sn^+$ bond with the N═C bond of AdNCO. Moreover, the reaction of **1** with 2 equiv of ArNCO (Ar = 2,6-$Pr^i_2C_6H_3$) in THF afforded $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)C^-\{C(O)N(Ar)\}Sn^+:]$ (**3**). It is proposed that the reaction proceeds via a [2 + 2] cycloaddition or an insertion reaction to form an intermediate which contains a four-membered CSnNC ring. Due to the steric hindrance of the Ar group, the $C_{methanide}$−Sn bond in the intermediate is cleaved in order to release the ring strain. The thiophosphinoyl substituent is then coordinated with the tin atom to form **3**. The results imply that the $C_{methanide}$−Sn bond in the intermediate is polar. However, the reactions of **1** with 2 equiv of PhNNPh, PhC≡CPh, $Bu^tN{=}C{=}NBu^t$, Me_3SiCHN_2, Bu^tCN or 1,4-naphthoquinone under various conditions did not afford any cycloaddition product. The ^{31}P NMR spectra of the reaction mixtures show a mixture of $[CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}S)]$ and unreacted **1** only. The results indicate that compound **1** is decomposed during the reactions.

Compounds **2** and **3** were isolated as colorless crystalline solids, which are stable at room temperature in solution and the solid state under an inert atmosphere. They are soluble in Et_2O, toluene, and THF. They have been characterized by NMR spectroscopy and X-ray crystallography. The ^1H NMR spectra of **2** and **3** show a set of signals due to the ligand backbone. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows one doublet of doublets for the $C_{methanide}$ atom at δ 56.70 ppm (J_{P-C} = 56.6 Hz, $J_{P'-C}$ = 70.0 Hz), which shows a downfield shift compared with that of **3** (δ 40.64 ppm (J_{P-C} = 56.6 Hz, $J_{P'-C}$ = 74.3 Hz)). The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets with satellites due to coupling to $^{117/119}Sn$ at δ 22.29 ($^2J_{P-P'}$ = 17.3 Hz, $^2J_{Sn-P}$ = 86.7, 121.4 Hz) and 41.23 ppm ($^2J_{P-P'}$ = 13.0 Hz, $^2J_{Sn-P}$ = 47.7, 73.7 Hz). The $^{119}Sn\{^1H\}$ NMR spectrum of **2** consists of a broad signal at δ −255.15 ppm, which shows an upfield shift in comparison with that of **1** (δ 132.1 ppm). The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two doublets with satellites due to coupling to $^{117/119}Sn$ at δ 27.79 ($^2J_{P-P'}$ = 8.7 Hz, $^2J_{Sn-P}$ = 69.4, 86.7 Hz) and 37.44 ppm ($^2J_{P-P'}$ = 8.7 Hz, $^2J_{Sn-P}$ = 73.7, 134.4 Hz). The $^{119}Sn\{^1H\}$ NMR spectrum of **3** consists of a broad signal at δ −129.25 ppm, which shows a downfield shift compared with that of **2**. The ^{13}C NMR signal for the $C_{methanide}$ atom and the ^{119}Sn NMR signal indicate the presence of zwitterionic $C^-{\cdots}Sn^+$ character in compound **3**.

The molecular structure of compound **2** is shown in Figure 1. Compound **2** has an open book structure with the C(2)−Sn(1) bond lying on the spine. The dihedral angle between the C(2)P(2)N(2)Sn(1) and C(2)C(1)N(1)Sn(1) planes is 76.2°. The iminophosphinoyl substituent is coordinated with the Sn(1) atom, which adopts a distorted-trigonal-pyramidal geometry (sum of bond angles 224.4°). This indicates that the Sn(1) atom possesses a high-s-character lone pair. The C(2)−Sn(1) bond (2.373(4) Å) is significantly longer than the CSn: bond (2.199(4) Å) in **1**.[8] It is similar to that in $[HC(PPh_2{=}NSiMe_3)(PPh_2{=}S)SnN(SiMe_3)_2]$ (2.384(4) Å).[8] The results suggest that the C−Sn bond in **2** has no multiple-bond character. Moreover, the C(1)−N(1) (1.372(13) Å) and C(1)−O(1) bonds (1.233(4) Å) in **2** are single and double bonds, respectively.

The molecular structure of compound **3** is shown in Figure 2. Compound **3** has a propeller structure, in which the N and S donors adopt a tripodal rearrangement. Both the iminophosphinoyl and thiophosphinoyl substituents are coordinated with the Sn(1) atom, which adopts a distorted-trigonal-pyramidal geometry (sum of bond angles 282.2°). This indicates that the Sn(1) atom possesses a high-s-character lone pair. The C(25)···Sn(1) distance (3.211(1) Å) is significantly longer than the C−Sn bond in base-stabilized stannylenes such as $[\{C_5H_4N\text{-}2\text{-}C(SiMe_3)_2\}Sn\{N(SiMe_3)_2\}]$ (2.356(8) Å)[10] and $[\{2,6\text{-}(CH_2NMe_2)_2C_6H_3\}SnCl]$ (2.158(8) Å),[11] but it is shorter than the sum of van der Waals radii (ca. 3.87 Å). The results suggest that there is a weak interaction between the $C_{methanide}$ and Sn(1) atoms. The Sn(1)−S(1) bond (2.6418(4) Å) is longer than the terminal Sn−S σ bond in $[:Sn(SAr')_2]$ (Ar′ = C_6H_2-2,4,6-Bu^t_3) (2.435(1) Å),[12] but it is comparable with that of the aryltin(II) dithiocarboxylate $[:Sn(Ar')\{S_2CAr'\}]$ (average 2.659 Å).[13] The Sn(1)−N(1)

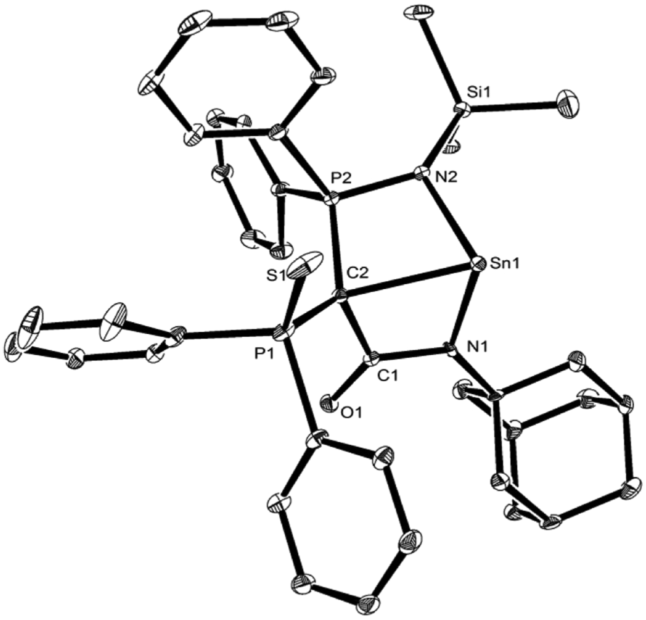


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. The disordered phenyl substituent at the P(2) atom, the $NSiMe_3$ substituent, the NAd substituent, and the Sn(1A) atom are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−N(1) = 2.146(8), Sn(1)−N(2) = 2.235(8), Sn(1)−C(2) = 2.373(4), C(1)−C(2) = 1.550(5), C(1)−O(1) = 1.233(4), C(1)−N(1) = 1.372(13), C(2)−P(1) = 1.783(4), C(2)−P(2) = 1.785(4), P(2)−N(2) = 1.628(11), P(1)−S(1) = 1.9599(15); C(2)−Sn(1)−N(1) = 64.1(3), C(2)−Sn(1)−N(2) = 71.5(3), N(1)−Sn(1)−N(2) = 88.8(4), Sn(1)−N(2)−P(2) = 94.4(4), N(2)−P(2)−C(2) = 104.2(3), P(2)−C(2)−Sn(1) = 85.89(16), Sn(1)−C(2)−C(1) = 85.1(2), C(2)−C(1)−N(1) = 110.8(4), C(1)−N(1)−Sn(1) = 99.0(5), P(1)−C(2)−P(2) = 123.7(2).

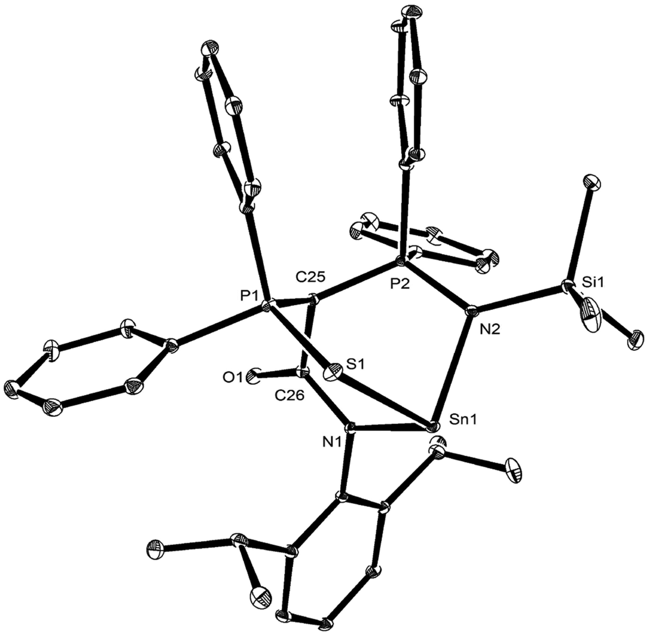


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)−S(1) = 2.6418(4), Sn(1)−N(2) = 2.1913(12), Sn(1)−N(1) = 2.1477(12), N(1)−C(26) = 1.3649(18), C(26)−O(1) = 1.2279(17), C(25)−C(26) = 1.524(2), C(25)−P(1) = 1.7244(15), C(25)−P(2) = 1.7367(15), P(1)−S(1) = 2.0545(5), P(2)−N(2) = 1.6329(12); S(1)−Sn(1)−N(1) = 96.50(4), S(1)−Sn(1)−N(2) = 94.02(4), N(1)−Sn(1)−N(2) = 91.69(5), Sn(1)−N(1)−C(26) = 123.58(10), N(1)−C(26)−C(25) = 114.36(12), C(26)−C(25)−P(1) = 112.77(10), C(26)−C(25)−P(2) = 113.31(10), P(1)−C(25)−P(2) = 119.22(8), C(25)−P(1)−S(1) = 113.78(5), P(1)−S(1)−Sn(1) = 95.755(18), C(25)−P(2)−N(2) = 114.10(7), P(2)−N(2)−Sn(1) = 112.14(7).

(2.1477(12) Å) and Sn(1)−N(2) (2.1913(12) Å) bonds in **3** are comparable to those in **2**. Moreover, the C(26)−N(1) (1.3649(18) Å) and C(26)−O(1) bonds (1.2279(17) Å) are single and double bonds, respectively.

The reaction of compound **1** with 1 equiv of $[RhCl(cod)]_2$ in THF afforded $[(PPh_2{=}NSiMe_3)(PPh_2{=}S)C\{Rh(cod)\}(SnCl)]$ (**4**), in which RhCl(cod) underwent a 1,2-addition with the >CSn: bond in **1**. The addition also illustrates the nucleophilic character of the $C_{methanediide}$ atom in **1**. The tin(II) atom in **1** did not act as a Lewis base or undergo an insertion reaction toward RhCl(cod).[14] The results are comparable with the 1,2-addition of $[RhCl(cod)]_2$ with the bisgermavinylidene to form $[(PPh_2{=}NSiMe_3)_2C\{Rh(cod)\}(GeCl)]$.[7b] Compound **4** is a heterobimetallic methanediide complex. Other examples of heterobimetallic methanediide complexes such as $[(PPh_2{=}NSiMe_3)_2C(M)\{Rh(cod)\}]$ (M = Li, Pd(allyl)) and $[\{(C_6H_4N\text{-}2)(PPr^i_2{=}NSiMe_3)C\}_2(Sn)(Pb)]$ have been reported.[15]

Compound **4** was isolated as a red crystalline solid, which is stable at room temperature in solution and the solid state under an inert atmosphere. It is soluble in THF and CH_2Cl_2. It has been characterized by NMR spectroscopy and X-ray crystallography. The ^1H NMR spectrum of **4** shows a set of signals due to the $SiMe_3$, cod and phenyl protons. Similar to the case for compound **1**, a $^{13}C\{^1H\}$ NMR signal for the $C_{methanediide}$ atom is not observed. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at δ 28.36 ppm ($^2J_{P-P'}$ = 26.0 Hz) and a doublet of doublets at δ 37.86 ppm ($^2J_{P-P'}$ = 26.0 Hz, $^2J_{P-Rh}$ = 13.0 Hz) due to two nonequivalent phosphorus nuclei. The $^{119}Sn\{^1H\}$ NMR spectrum shows a multiplet at δ 110.74 ppm. The results indicate that compound **4** retains its solid-state structure in solution.

The molecular structure of compound **4** is shown in Figure 3. The C(1) atom is bonded to the Rh(1) and Sn(1) atoms. Moreover, it is spirocyclic, with the thiophosphinoyl substituent coordinated to the Rh(1) atom and the iminophosphinoyl substituent coordinated to the Sn(1) atom. This indicates that the C(1) atom is chiral. However, compound **4** is racemic, and the *R* and *S* enantiomers are present in the unit cell. This is because compound **4** was prepared from optically inactive reactants. The C(1)−Sn(1) bond (2.3617(16) Å) is comparable with that in **2**. The results indicate that the C−Sn bond in compound **4** does not have any multiple-bond character. The Sn(1) atom adopts a distorted-trigonal-pyramidal geometry (sum of bond angles 265.38°), which indicates that the Sn(1) atom possesses a high-s-character lone pair. The Sn(1)···Rh(1) distance (2.8155(2) Å) is significantly longer than the Sn−Rh bonds in the rhodium−stannylene complex *cis*-$[Rh\{Sn(NBu^t)_2SiMe_2\}_2(PPh_3)_2Cl]$ (2.571(2), 2.577(2) Å) and $[Rh(\eta\text{-}C_6H_5Me)(\eta\text{-}C_8H_{14})\{SnCl(NR_2)_2\}]$ (R = $SiMe_3$, 2.554(1) Å).[14a,b] However, it is shorter than the sum of van der Waals radii (ca. 4.0 Å). The results show that there is a weak interaction between the Sn(1) and Rh(1) atoms. The Rh(1)−C(1) bond (2.1715(16) Å) is comparable with the Rh−$C_{methanediide}$ bonds in $[(PPh_2{=}NSiMe_3)_2C\{Rh(cod)\}$-

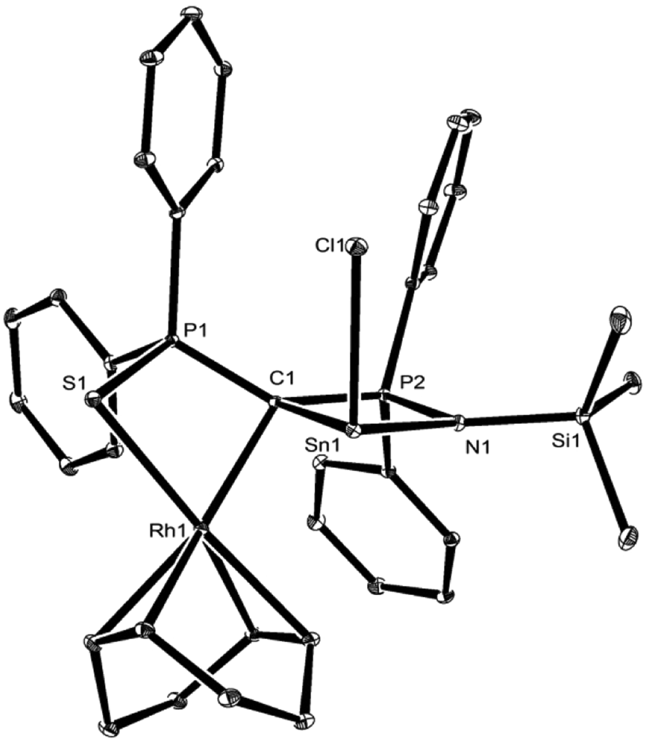


Figure 3. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Disordered CH_2Cl_2 molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−C(1) = 2.3617(16), Sn(1)−Cl(1) = 2.5311(4), Sn(1)−N(1) = 2.2535(13), P(2)−N(1) = 1.6060(14), P(1)−S(1) = 2.0256(6), C(1)−P(2) = 1.7370(15), C(1)−P(1) = 1.7233(15), Rh(1)−C(1) = 2.1715(16), Rh(1)−S(1) = 2.4005(4); C(1)−Sn(1)−N(1) = 68.42(5), C(1)−Sn(1)−Cl(1) = 96.79(4), N(1)−Sn(1)−Cl(1) = 100.17(4), Sn(1)−N(1)−P(2) = 98.34(6), N(1)−P(2)−C(1) = 101.84(7), P(2)−C(1)−Sn(1) = 90.79(6), Sn(1)−C(1)−Rh(1) = 76.66(5), C(1)−Rh(1)−S(1) = 77.67(4), Rh(1)−S(1)−P(1) = 78.247(17), S(1)−P(1)−C(1) = 99.71(6), P(1)−C(1)−Rh(1) = 91.53(7), P(1)−C(1)−P(2) = 134.23(10).

(GeCl)][7b] (2.204(3) Å) and [(PPh$_2$=NSiMe$_3$)$_2$C{Rh(cod)}$_2$] (2.148(2), 2.168(2) Å).[15d]

In conclusion, the formation of [(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)$\overline{\mathrm{C\{C(O)N(Ad)\}Sn}}$:] (**2**) and [(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)C$^-${C(O)N(Ar)}Sn$^+$:] (**3**) illustrate that the reactions of **1** with isocyanates probably proceed via a [2 + 2] cycloaddition of the >C=Sn: bond or an insertion reaction of the C$^-$—Sn$^+$ bond with the N=C bond of RNCO (R = Ad, Ar). Moreover, the formation of [(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)C{Rh(cod)}(SnCl)] (**4**) underlines the nucleophilic character of the $C_{\mathrm{methanediide}}$ atom in **1**. Furthermore, X-ray crystal structures show that the C−Sn bonds in **2**−**4** are lengthened in comparison with that in **1**. These results are consistent with the X-ray crystal structure and NBO analyses of **1**, which show that the Sn−$C_{\mathrm{methanediide}}$ bond has some double-bond character and the electron densities are mostly occupied by the $C_{\mathrm{methanediide}}$ atom. Thus, compound **1** could be between the resonance forms [(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)C=Sn:]$_2$ and [(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)C$^-$—Sn:$^+$]$_2$.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an inert atmosphere of nitrogen gas using standard Schlenk techniques. THF and toluene were dried over and distilled over Na/K alloy prior to use. CH_2Cl_2 was dried over and distilled over CaH_2 prior to use. **1** was prepared as described in the literature.[8] AdNCO (Ad = admantyl), ArNCO (Ar = 2,6-Pr$^i_2$C$_6$H$_3$), and [RhCl(cod)]$_2$ were purchased from Sigma-Aldrich Co. The ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe$_4$ for ^{1}H and ^{13}C, to SnMe$_4$ for ^{119}Sn, and to H$_3$PO$_4$ for ^{31}P. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)$\overline{\mathrm{C\{C(O)N(Ad)\}Sn}}$:] (2). A solution of AdNCO (0.041 g, 0.23 mmol) in THF (5 mL) was added dropwise to **1** (0.14 g, 0.11 mmol) in THF (5 mL) at 0 °C. The yellow suspension was stirred at room temperature and turned clear gradually. After it was stirred for 34 h, the reaction mixture was a pale yellow clear solution. Volatiles were removed in vacuo, and the residue was extracted with toluene. After filtration and concentration of the filtrate, **2** was obtained as colorless crystals. Yield: 0.068 g (38.8%). Mp 217 °C dec. Anal. Calcd for $C_{39}H_{44}N_2OP_2SSiSn$: C, 58.72; H, 5.56; N, 3.51. Found: C, 58.50; H, 5.47; N, 3.14. ^{1}H NMR (399.5 MHz, 25 °C, C_6D_6): δ −0.043 (s, 9H, SiMe$_3$), 1.59−1.66 (m, 6H, Ad), 1.87−1.89 (d, 3H, Ad), 1.96−2.00 (m, 6H, Ad), 6.99−7.03 (m, 12H, Ph), 7.35−7.40 (m, 2H, Ph), 8.15−8.18 (m, 4H, Ph), 8.80−8.86 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.5 MHz, 25 °C, C_6D_6): δ 2.37 (SiMe$_3$), 30.57, 37.52, 43.51 (Ad), 56.70 (dd, J_{P-C} = 56.6 Hz, $J_{P'-C}$ = 70.0 Hz, PCP), 127.11, 127.24, 128.22, 130.26, 130.28, 130.85, 130.88, 131.69, 131.72 (CH of Ph), 132.64 (dd, J_{P-C} = 57.3 Hz, $^3J_{P'-C}$ = 10.5 Hz, C_{ipso} of Ph), 134.46 (dd, J_{P-C} = 57.3 Hz, $^3J_{P'-C}$ = 11.5 Hz, C_{ipso} of Ph), 165.16 ppm (C=O). ^{31}P{^{1}H} NMR (161.7 MHz, 25 °C, C_6D_6): δ 22.29 (d, $^2J_{P-P'}$ = 17.3 Hz, $^2J_{Sn-P}$ = 86.7, 121.4 Hz), 41.23 ppm (d, $^2J_{P-P'}$ = 13.0 Hz, $^2J_{Sn-P}$ = 47.7, 73.7 Hz). ^{119}Sn{^{1}H} NMR (147.6 MHz, 25 °C, C_6D_6): δ −255.15 ppm (br).

[(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)C$^-${C(O)N(Ar)}Sn$^+$:] (3). A solution of ArNCO (0.05 mL, 0.23 mmol) in THF (5 mL) was added dropwise to **1** (0.14 g, 0.11 mmol) in THF (5 mL) at 0 °C. The yellow suspension was stirred at room temperature and turned clear gradually. After it was stirred for 15 h, the reaction mixture was a pale yellow clear solution. Volatiles were removed in vacuo, and the residue was extracted with toluene. After filtration and concentration of the filtrate, **3** was obtained as colorless crystals. Yield: 0.066 g (36.5%). Mp 185 °C dec. Anal. Calcd for $C_{41}H_{46}N_2OP_2SSiSn$: C, 59.78; H, 5.63; N, 3.40. Found: C, 59.53; H, 5.57; N, 3.32. ^{1}H NMR (399.5 MHz, 22 °C, C_6D_6): δ 0.21 (s, 9H, SiMe$_3$), 0.51 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 0.67 (d, $^3J_{H-H}$ = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.20 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.37 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 2.26 (sept, $^3J_{H-H}$ = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.03 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 6.40−6.45 (m, 2H, Ph), 6.51−6.57 (m, 4H, Ph), 6.83−6.87 (m, 1H, Ph), 7.03−7.16 (m, 4H, Ph), 7.23−7.27 (m, 1H, Ph), 7.33−7.38 (m, 5H, Ph), 7.83 − 7.89 (m, 2H, Ph), 8.60−8.70 (m, 4H, Ph). ^{13}C{^{1}H} NMR (100.5 MHz, 25 °C, C_6D_6): δ 4.73 (SiMe$_3$), 24.29, 24.70, 25.99, 26.64 (CH(CH$_3$)$_2$), 28.87, 29.13 (CH(CH$_3$)$_2$), 40.64 (dd, J_{P-C} = 56.6 Hz, $J_{P'-C}$ = 74.3 Hz, PCP), 123.86, 124.18, 126.72, (Ar) 127.78, 127.91, 128.84, 128.87, 128.98, 129.00, 130.56, 130.59, 131.36, 131.39 (CH of Ph), 132.22 (dd, J_{P-C} = 79.4 Hz, $^3J_{P'-C}$ = 11.5 Hz, C_{ipso} of Ph), 134.20 (dd, J_{P-C} = 75.8 Hz, $^3J_{P'-C}$ = 10.5 Hz, C_{ipso} of Ph), 140.56, 146.58, 146.77 (Ar), 166.82 ppm (C=O). ^{31}P{^{1}H} NMR (161.7 MHz, 22 °C, C_6D_6): δ 27.79 (d, $^2J_{P-P'}$ = 8.7 Hz, $^2J_{Sn-P}$ = 69.4, 86.7 Hz), 37.44 ppm (d, $^2J_{P-P'}$ = 8.7 Hz, $^2J_{Sn-P}$ = 73.7, 134.4 Hz). ^{119}Sn{^{1}H} NMR (149.0 MHz, 22 °C, C_6D_6): δ −129.25 ppm (br).

[(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)C{Rh(cod)}(SnCl)] (4). A solution of [RhCl(cod)]$_2$ (0.079 g, 0.16 mmol) in THF (8.4 mL) was added dropwise to a solution of **1** (0.20 g, 0.16 mmol) in THF (8.4 mL) at 0 °C. The yellow suspension was then stirred at room temperature and turned clear and red gradually. After it was stirred for 5 h, the reaction mixture became a red suspension with yellow solid. Volatiles were removed in vacuo, and the residue was extracted with CH_2Cl_2. After filtration and concentration of the filtrate, **4** was obtained as red crystals. Yield: 0.18 g (55.4%). Mp 140 °C dec. Anal. Calcd for $C_{36}H_{41}ClNP_2RhSSiSn$: C, 49.87; H, 4.77; N, 1.62. Found: C, 49.63; H,

Table 1. Crystallographic Data for Compounds 2−4

	2	3	4
formula	$C_{39}H_{44}N_2OP_2SSiSn$	$C_{41}H_{46}N_2OP_2SSiSn$	$C_{37.5}H_{47}Cl_4NP_2RhSSiSn$
M_r	797.54	823.58	997.5
color	colorless	colorless	red
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$P2_1/n$
a/Å	30.8813(11)	9.4127(3)	11.7899(2)
b/Å	11.1580(4)	21.5662(6)	16.7568(3)
c/Å	22.3386(8)	19.0244(5)	20.4015(3)
α/deg	90	90	90
β/deg	104.853(2)	95.3480(10)	97.5720
γ/deg	90	90	90
V/Å^3	7440.1(5)	3845.07(19)	3995.39(11)
Z	8	4	4
d_{calcd}/g cm^{-3}	1.424	1.423	1.658
μ/mm^{-1}	0.895	0.868	1.497
F(000)	3280	1696	2008
cryst size/mm	0.34 × 0.28 × 0.26	0.34 × 0.30 × 0.16	0.40 × 0.34 × 0.30
index range	$-44 \leq h \leq 44$	$-15 \leq h \leq 15$	$-19 \leq h \leq 17$
	$-16 \leq k \leq 13$	$-32 \leq k \leq 34$	$-27 \leq k \leq 27$
	$-32 \leq l \leq 32$	$-30 \leq l \leq 29$	$-32 \leq l \leq 32$
no. of rflns collected	76 461	73 823	74 292
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0612, 0.1625	0.0333, 0.0779	0.0290, 0.0657
$R1$, $wR2$ (all data)	0.0948, 0.1916	0.0507, 0.0928	0.0412, 0.0704
goodness of fit, F^2	1.351	1.082	1.045
no. of data/restraints/params	11 810/623/639	17 312/0/449	17 658/3/457
largest diff peak, hole/e Å^{-3}	0.665, −1.421	0.831, −0.750	1.436, −1.100

4.64; N, 1.43. ^{1}H NMR (399.5 MHz, 25 °C, THF-d_8): δ 0.065 (s, 9H, SiMe$_3$), 1.57−2.61 (m, 8H cod), 3.21 (m, 1H, cod), 4.14 (m, 1H, cod), 4.43 (m, 1H, cod), 4.91 (m, 1H, cod), 7.06−7.15 (m, 4H, Ph), 7.21−7.37 (m, 9H, Ph), 7.45−7.56 (m, 3H, Ph), 7.72−7.77 (m, 2H, Ph), 8.04−8.09 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.5 MHz, 25 °C, THF-d_8): δ 3.43 (SiMe$_3$), 29.04, 30.40, 32.89, 34.15 (sp^3 C of cod), 77.41 (d, J_{C-Rh} = 11.1 Hz, sp^2 C of cod), 81.68 (d, J_{C-Rh} = 12.1 Hz, sp^2 C of cod), 85.23 (d, J_{C-Rh} = 10.1 Hz, sp^2 C of cod), 87.11 (d, J_{C-Rh} = 8.0 Hz, sp^2 C of cod), 128.12, 128.23, 128.68, 128.81, 129.00, 129.13, 129.20, 129.31, 131.53, 132.12 (CH of Ph), 132.59 (dd, J_{P-C} = 57.3 Hz, $^3J_{P'-C}$ = 12.5 Hz, C$_{ipso}$ of Ph), 133.91 (dd, J_{P-C} = 57.3 Hz, $^3J_{P'-C}$ = 11.5 Hz, C$_{ipso}$ of Ph). ^{31}P{^{1}H} NMR (161.7 MHz, 25 °C, THF-d_8): δ 28.36 (d, $^2J_{P-P'}$ = 26.0 Hz), 37.86 ppm (dd, $^2J_{P-P'}$ = 26.0 Hz, $^2J_{P-Rh}$ = 13.0 Hz). ^{119}Sn{^{1}H} NMR (149.0 MHz, 25 °C, THF-d_8): δ 110.74 ppm (m).

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2**−**4** were collected using a Bruker APEX II diffractometer. The crystals of **2**−**4** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2.[16] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure factor calculations. Selected X-ray crystallography data of **2**−**4** are summarized in Table 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving X-ray data for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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