Inorganic Chemistry
Communication
pubs.acs.org/IC

Synthesis and Structural Characterization of a Tin Analogue of Allene

Wing-Por Leung,* Yuk-Chi Chan, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Supporting Information

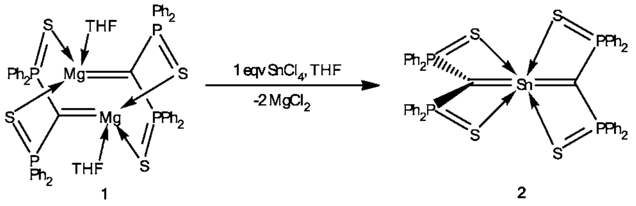
ABSTRACT: The reaction of $[MgC(PPh_2{=}S)_2(THF)]_2$ (**1**; THF = tetrahydrofuran) with 1 equiv of $SnCl_4$ in THF afforded a novel tin analogue of allene $[Sn\{C(PPh_2{=}S)_2\}_2]$ (**2**). The structure of compound **2** has been characterized by X-ray crystallography and NMR spectroscopy.

Compounds containing a double bond between carbon and a heavier group 14 element >C=M< (M = Si, Ge, and Sn) have attracted much attention in the past 2 decades.[1a−e] Moreover, group 14 compounds containing two metal−carbon double bonds are scarcely found.[2] These types of compounds can be considered as the heavier group 14 metal analogues of allene. These analogues include 1-metallaallene (>C=C=M<) and 2-metallaallene (>C=M=C<). It was believed that the thermal stability of M=C is intrinsically low, and it easily undergoes oligomerization. However, compounds containing the M=C bond can be kinetically stabilized by incorporating bulky substituents to both carbon and the heavier group 14 metal. Stable silylene >C=Si<,[3a,b] germene >C=Ge<,[4a,b] and stannene >C=Sn<[5a−e] have been successfully synthesized and characterized. Recently, So and co-workers reported the synthesis of a germanium bis(methanediide) complex, which can be considered as a derivative of 2-germaallene.[6] However, the heavier 1-stannaallene and 2-stannaallene still remain unknown. Previously, Escudié and co-workers reported the synthesis of a stable distannirane in which it was proposed to undergo salt elimination to produce a 1-stannaallene intermediate and [2 + 1] cycloaddition between 1-stannaallene and stannylene.[7] Until now, there is no stable 1-stannallene or 2-stannaallene that can be isolated and characterized successfully.

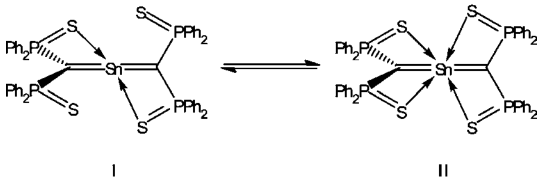
In this Communication, we report the synthesis and characterization of a novel tin bis(methanediide) complex **2**, which is the first example of 2-stannaallene.

Our group recently reported the synthesis of a magnesium methanediide complex from the reaction of neutral bis(diphenylthiophosphinoyl)methane and $^{n}Bu_2Mg$, which can be used as a ligand-transfer reagent to synthesize some group 13 methanediide complexes.[8] The reaction of **1** with 1 equiv of $SnCl_4$ afforded tin bis(methanediide) complex $[Sn\{C(PPh_2{=}S)_2\}_2]$ (**2**; Scheme 1).

Scheme 1



Compound **2** was isolated as yellow crystals, and it is soluble in tetrahydrofuran (THF), CH_2Cl_2, and toluene. It has been characterized by X-ray crystallography, NMR spectroscopy, and elemental analysis. The ^{1}H and ^{13}C NMR spectra of **2** displayed signals due to the phenyl groups. Though there is no ^{13}C NMR signal for the carbenic carbon, the absence of methylenic protons was confirmed by ^{1}H NMR. The absence of a ^{13}C NMR signal for the carbenic carbon was commonly found in bis(diphenyliminophosphinoyl)- and bis(diphenylthiophosphinoyl)metal carbene complexes. Similar results have been reported in $[(PPh_2{=}S)_2C{=}Pd(PPh_3)]$[9] and $[(PPh_2{=}S)_2C{=}Ge{=}C(PPh_2{=}S)_2]$.[6] The ^{31}P NMR spectrum at room temperature displayed one signal at δ 28.1 with tin satellites ($^{2}J_{P-Sn}{}^{119}$ = 30.0 Hz), which is consistent with the solid-state structure. However, the ^{31}P NMR spectrum of **2** at −80 °C displayed three signals at δ27.0, 31.2, and 37.0. It is suggested that **2** undergoes some fluxional behavior in the solution state. We proposed that the structures **I** and **II** may exist in equilibrium in the solution state.



At room temperature (25 °C), the singlet at δ 28.1 is due to the rapid interconversion between structures **I** and **II**. At −80 °C, the fast interconversion between structures **I** and **II** slowed down, and both structures exist. A similar result for structure **I** has been found in the germanium bis(methanediide) complex, in which two ligands are bound to the germanium center in a spirocyclic fashion.[6] In the ^{31}P NMR spectrum of **2** at −80 °C, the signals at δ 27.0 and 31.2 correspond to the two different phosphorus nuclei in structure **I**, while the signal at δ 37.0 corresponds to the four equivalent phosphorus nuclei in structure **II**, which is slightly downfield from that in **I**. Integration of the ^{31}P NMR spectrum indicates that the signals are in a 1.0:1.0:1.0 ratio, which suggests that structures **I** and **II** are in a 2:1 equilibrium. The ^{119}Sn NMR spectrum of **2** at room temperature showed only one broad signal at δ −401 ($\nu_{1/2}$ = 165 Hz); no resolvable tin−phosphorus coupling could be

Received: August 29, 2011
Published: October 14, 2011

dx.doi.org/10.1021/ic201888d | *Inorg. Chem.* 2011, 50, 10517−10518

observed. The ^{119}Sn NMR spectrum of **2** at −80 °C displayed two signals at δ −192 and −445, which indicates that there are two different tin environments present and it is consistent with the low-temperature ^{31}P NMR spectrum. In the ^{119}Sn NMR spectrum, the signal at δ −192 corresponds to structure **I**, while the signal at δ −445 corresponds to the more shielded tin atom in structure **II**. The ^{119}Sn NMR signal of **2** at δ −401 is comparable to that in 1,3-distannacyclobutane in $[2\text{-}\{Sn\{C(^{i}Pr_2P{=}NSiMe_3)\}\}\text{-}6\text{-}\{Sn\{CH(^{i}Pr_2P{=}NSiMe_3)\}Cl\}C_5H_3N]_2$ (δ −11.0),[10] 6-stannapentafulvene $[(Tbt)(Mes)Sn{=}CR_2]$ (Tbt = 2,4,6-$\{CH(SiMe_3)_2\}_2C_6H_2$, Mes = 2,4,6-$Me_3C_6H_2$, and CR_2 = fluoroenylidene) (δ 270),[11] and $[Sn{=}C(PPh_2{=}NSiMe_3)(PPh_2{=}S)]_2$ (δ 132.1),[12] which suggests that compound **2** exists as a tin(IV) bis(thiophosphinoyl)methanediide complex and does not undergo oligomerization in the solution state. The relatively upfield ^{119}Sn NMR signal indicates that the two carbon atoms may have some carbenic character.

The molecular structure of compound **2** is shown in Figure 1. There are two bidentate bis(thiophosphinoyl)methanediide ligands bound to the tin center. The four sulfur atoms from the two bis(thiophosphinoyl)methanediide ligands coordinate to the tin center, and the tin center is hexacoordinate. The C1−Sn1 bond distance of 2.063(2) Å is slightly longer than that in the theoretical calculation of the Sn−C distance of 1.999−2.005 Å for $[CH_2{=}Sn{=}CH_2]$.[13] It is comparable to the distance of 2.0245(4) Å for stannaethane $[\{(Me_3Si)_2CH\}_2Sn{=}C\{(B^{t}Bu)_2C(SiMe_3)_2\}]$[4a] and 2.016(5) Å for 6-stannapentafulvene $[(Tbt)(Mes)Sn{=}CR_2]$.[10] The P−S and C−P bond distances in **2** suggest delocalization of π electrons from the conjugation of P=S and C=Sn, which slightly lengthens the Sn=C double-bond distance. Therefore, the Sn1−S1 [2.8882(6) Å] and Sn1−S2 [2.7212(6) Å] bonds show different bond distances. The C1−Sn1−C1#1 angle of 171.12(11)° is much larger than those in the theoretical studies of $[CH_2{=}Sn{=}CH_2]$ (134.3−142.0°) because there are two thiophosphinoyl substituents that coordinate to Sn1 at distances of 2.7216(6) and 2.8882(6) Å. The Sn1 center is hexacoordinate, which makes the C1−Sn1−C1#1 angle almost linear. The sum of the angles at C1 in **2** is 354.6°, which is very close to those in the theoretical studies of $[CH_2{=}Sn{=}CH_2]$ (348.5−353.1°).[12]

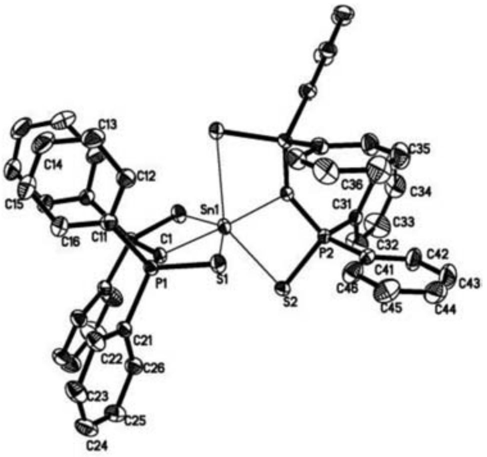


Figure 1. Molecular structure of **2** (30% ellipsoid probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C1−Sn1 2.063(2), C1−P1 1.735(2), C1#1−P2 1.724(2), P1−S1 1.999(8), P2−S2 2.021(8), Sn1−S1 2.888(6), Sn1−S2 2.721(6); C1−Sn1−C1#1 171.1(1), S1−Sn1−S1#1 85.41(2), S2−Sn1−S2#1 95.77(3), C1−Sn1−S1 70.51(6), C1−Sn1−S2#1 73.51(6), S1−Sn1−S2 100.208(18), P1−C1−Sn1 108.13(10), P2#1−C1−Sn1 105.94(10), P2#1−C1−P1 140.58(13).

In conclusion, the first example of a tin analogue of allene compound **2** has been synthesized by the reaction of **1** with 1 equiv of $SnCl_4$ in THF.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format and detailed experimental procedures for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kevinleung@cuhk.edu.hk. Fax: +852 2603 5057.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from The Chinese University of Hong Kong (Direct Grant, Project ID 2060324).

■ REFERENCES

(1) (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem. Rev.* **1996**, *39*, 71. (b) Escudié, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178*, 565. (c) Chaubon, M. A.; Ranaivonjatovo, H.; Escudié, J.; Satgé, J. *Main Group Met. Chem.* **1996**, *19*, 145. (d) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (e) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283.

(2) Escudié, J.; Ranaivonjatovo, H. *Organometallics* **2007**, *26*, 1542.

(3) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (b) Wiberg, N.; Kim, C.-K. *Chem. Ber.* **1986**, *119*, 2966.

(4) (a) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798. (b) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828.

(5) (a) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546. (b) Anselme, G.; Declercq, J.-P.; Dubourg, A.; Ranaivonjatovo, H.; Escudié, J.; Couret, C. *J. Organomet. Chem.* **1993**, *458*, 49. (c) Weidenbruch, M.; Kilian, H.; Stürmann, M.; Pohl, S.; Saak, W.; Marsmann, H.; Steiner, D.; Berndt, A. *J. Organomet. Chem.* **1997**, *530*, 255. (d) Mizuhata, Y.; Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1050. (e) Ghereg, D.; Ranaivonjatovo, H.; Saffon, N.; Gornitzka, H.; Escudié, J. *Organometallics* **2009**, *28*, 2294.

(6) Foo, C.; Lau, K.-C.; Yang, Y.-F.; So, C.-W. *Chem. Commun.* **2009**, 6816.

(7) Baiget, L.; Ranaivonjatovo, H.; Escudié, J.; Gornitzka, H. *J. Am. Chem. Soc.* **2004**, *126*, 11792.

(8) Leung, W.-P.; Wan, C.-L.; Mak, T. C. W. *Organometallics* **2010**, *29*, 1622.

(9) Cantat, T.; Mézailles, N.; Ricard, L.; Jean, L.; Le Floch, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 6382.

(10) Leung, W.-P.; Ip, Q. W.-Y.; Wong, S.-Y.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4604.

(11) Mizuhata, Y.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Chem. Commun.* **2005**, 5876.

(12) Guo, J.; Lau, K.-C.; Xi, H.-W.; Lim, K.-H.; So, C.-W. *Chem. Commun.* **2010**, 1929.

(13) Sigal, N.; Apeloig, Y. *Organometallics* **2002**, *21*, 5486.