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Formation of a Reversible, Intramolecular Main-Group Metal–CO_2 Adduct

Diane A. Dickie,[†] Eric N. Coker,[‡] and Richard A. Kemp*,[†,‡]

[†]Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States
[‡]Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico 87106, United States

Supporting Information

ABSTRACT: The P,P-chelated stannylene $[(i\text{-}Pr_2P)_2N]_2Sn$ takes up 2 equiv of carbon dioxide (CO_2) to form an unusual product in which CO_2 binds to the Sn and P atoms, thus forming a six-membered ring complex. Gentle heating of the solid product releases CO_2, indicating that CO_2 is bound as an adduct to the main-group complex. The groups bound to the CO_2 fragment are not particularly sterically crowded or highly acidic, thus indicating that "frustrated" Lewis acid–base pairs are not required in the binding of CO_2 to main-group elements.

Conversions of carbon dioxide (CO_2) to organic products have been investigated for decades, with transition-metal complexes dominating prior literature. There has recently been increased interest in the interactions of main-group metals with CO_2, particularly those effective at producing polymers using CO_2 and other reagents, e.g., epoxides.[1] Concurrently, there have also been efforts directed toward preparing organic isocyanates and carbodiimides using the direct insertion of CO_2 into divalent main-group metal silylamides, led primarily by Sita et al.[2] Our previous work in this area[3] inspired us to examine whether $-PR_2$ groups could replace silyl groups in these main-group complexes. This investigation has led to the surprising discovery that CO_2 can bind to Sn as an adduct in an unprecedented manner.

The ligand $HN(PPh_2)_2$ is ubiquitous in transition-metal chemistry and is becoming more common in both main-group and lanthanide complexes.[4] As an ambidentate ligand, it is known to coordinate through either nitrogen (Figure 1, mode A) or phosphorus (mode B). We have shown that the main-group complexes $M[N(PPh_2)_2]_2\cdot 3THF$ (M = Ca, Sr; THF = tetrahydrofuran) undergo a very unexpected reaction with CO_2 to form hexanuclear species.[5] The M_6 product $\{M_6[O_2CN(PPh_2)_2]_6[N(CO_2)_3]_2(THF)_7\}$ chemically fixes 12 mol equiv of CO_2, 6 mol as the CO_2-inserted, phosphino-substituted carbamate–$O_2CN(PPh_2)_2$, and 6 mol in two unprecedented $[N(CO_2)_3]^{3-}$ ligands. These trianions are formed via oxidative cleavage of the PPh_2 group from the N atom.

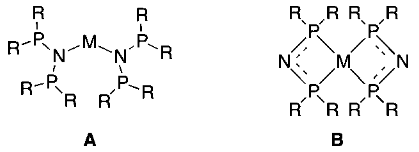

Figure 1. Possible coordination modes (A and B) of $[(R_2P)_2N]^-$ with divalent metals.

Knowing that the behavior of arylphosphines is often quite different from that of alkylphosphines, we have begun to explore the reactivity of main-group complexes of the ligand $HN[P(i\text{-}Pr_2)_2]$ (**1**). Nearly 150 examples of *oxidized* derivatives of **1** can be found in the Cambridge Structural Database,[6] but there is only one structure of a derivative of **1** that is *nonoxidized*. It is a ruthenium carbonyl complex prepared by Woollins et al.,[7] isolated in only 9% yield from the cleavage of $HN[(i\text{-}Pr_2)_2P(S)]_2$. This finding regarding nonoxidized derivatives was a surprise because **1** has been known for decades.

The synthesis and NMR spectra of **1** have been reported elsewhere,[8] but its crystal structure has not been previously described. Details and thermal ellipsoid plots of the structural features of **1** can be found in the Supporting Information. Lithiation of **1** in anhydrous THF followed by the addition of $SnCl_2$ led to the isolation of large red-orange crystals of $[(i\text{-}Pr_2P)_2N]_2Sn$ **2**. Because N-bound stannylenes (type A) are generally reddish in color, it was initially anticipated that the structure of **2** would be N-bound.

The initial characterization of **2** was done by multinuclear NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra were not helpful in determining the coordination mode (N vs P) of **2**. The $^{31}P\{^1H\}$ NMR spectrum showed a downfield shift from 68.0 ppm in **1** to 80.2 ppm in **2**. This singlet exhibited satellites for both ^{117}Sn and ^{119}Sn, with coupling constants of 1128 and 1181 Hz, respectively, indicative of direct Sn–P bonding (type B). The $^{119}Sn\{^1H\}$ NMR spectrum supported this speculation, showing a quintet with a coupling of 1181 Hz at −8.4 ppm.

Confirmation of the structure of **2** was provided by single-crystal X-ray diffraction (Figure 2). As anticipated from the NMR spectroscopic results, each ligand was bound to the Sn atom in a P,P-chelated manner. This coordination mode has been observed by Karsch et al. in the related tin complex $Sn[C(PMe_2)_3]_2$, in which two of the three P atoms in each ligand bind in the bidentate manner B to the Sn.[9] The four P–N bond lengths are equal within experimental error, ranging from 1.623(6) to 1.643(7) Å, and are much shorter than that seen in the free ligand (1.705 Å). This is consistent with the change from true single bonds in **1** to delocalized allylic P–N bonds in **2**. One might expect that the four Sn–P bond lengths would also be equal, but, in fact, they differ markedly.

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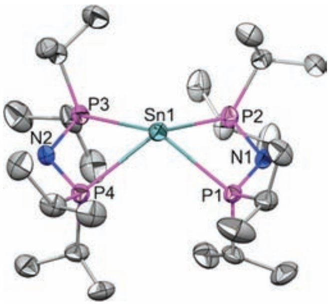
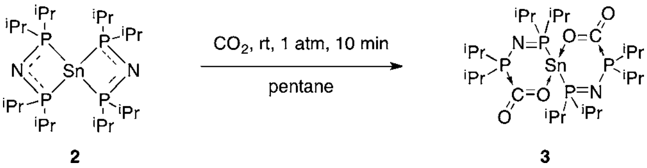


Figure 2. Structure of **2**. Thermal ellipsoids are shown at 50% probability. For clarity, H atoms are not shown.

As with other Sn^{II} centers coordinated to two chelating ligands, the geometry at Sn1 is best described as distorted trigonal bipyramidal rather than square pyramidal.[9,10] The shorter Sn−P bonds [Sn1−P1 = 2.726(2) Å; Sn1−P3 = 2.708(2) Å] are assigned to the equatorial positions, along with the stereochemically active lone pair on Sn1. The longer Sn−P bonds [Sn1−P2 = 2.788(2) Å; Sn1−P4 = 2.769(2) Å] occupy the axial positions. The difference between the axial and equatorial bond lengths, while significant, is much less than that observed by Karsch et al.[9] ($Sn-P_{ax}$ = 2.790(2) and 2.839(2) Å; $Sn-P_{eq}$ = 2.602(2) and 2.598(2) Å. The intraligand P−Sn−P bond angles of **2** are 57.98(6) and 58.29(6)° for P1−Sn1−P2 and P3−Sn1−P4, respectively. These are more acute than those in Karsch et al.'s complex [62.9(1) and 62.8(1)°].[9] Likewise, the axial P2−Sn1−P4 bond in **2** at 131.00(6)° is more distorted from the idealized geometry than that reported by Karsch et al. [142.5(1)°].

CO_2 was bubbled through a pentane solution of **2** at room temperature for 10 min, causing the solution to fade from orange to pale yellow (Scheme 1). Concurrently, a white precipitate formed and was isolated and characterized as **3**. The IR spectrum of **3** showed a very strong absorbance at 1629 cm^{-1}, suggesting that CO_2 had been incorporated into the molecule. The alkyl region of the ^1H and ^{13}C NMR spectra were consistent with lowered molecular symmetry. More informative was a doublet at 168.7 ppm, assigned to a CO_2 fragment bound directly to P. The presence of two distinct, somewhat broadened signals at 26 and 60 ppm in the $^{31}P\{^1H\}$ NMR spectrum was consistent with the unexpected insertion of CO_2 into one of the two Sn−P bonds of each ligand. It was not possible to resolve any P−P or P−C coupling. Finally, the $^{119}Sn\{^1H\}$ signal, which had been a quintet in **2**, appeared as a triplet at −184 ppm in **3** ($^1J_{Sn-P}$ = 2626 Hz).

Scheme 1. Synthesis of 3



2 **3**

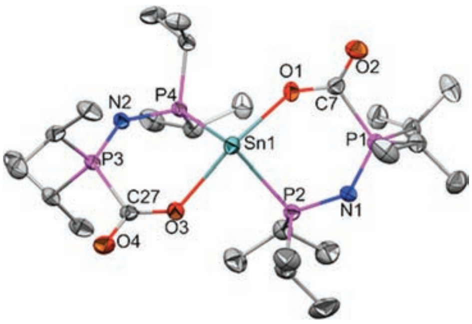
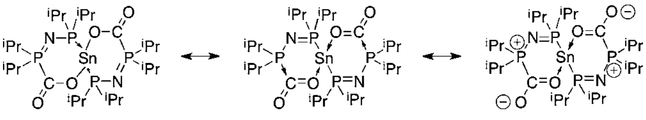


Figure 3. Structure of **3**. Thermal ellipsoids are shown at 50% probability. For clarity, H atoms are not shown.

Single-crystal X-ray diffraction was performed on a sample recrystallized from pentane (Figure 3) revealing that a molecule of CO_2 had inserted into one Sn−P bond of each ligand, consistent with the spectroscopic data. In contrast to **2**, which had equal P−N bond lengths indicative of charge delocalization, **3** contains both short and long P−N bonds. The P atom bound to CO_2 has a shorter P−N bond [P1−N1 = 1.576 (5) Å; P3−N2 = 1.575(5) Å] than the P atom bound to Sn [P2−N1 = 1.623(5) Å; P4−N2 = 1.628(5) Å]. These longer bonds are in the range of the P−N bonds of **2** and are significantly shorter than the indisputable single bonds of **1**. The C−O bonds are also different, with the Sn-bound O only slightly longer [O1−C7 = 1.272(8) Å; O3−C27 = 1.273(8) Å] than the "free, unbound" oxygen [O2−C7 = 1.210(8) Å; O4−C27 = 1.231(7) Å]. In comparison, the C═O bond lengths of gaseous CO_2 measure 1.1600 Å.[11] As with the P−N bonds, the longer C−O bond is significantly shorter than a true single bond (1.366 Å). The Sn−P bonds of 2.6514(18) and 2.6471(18) Å for Sn1−P2 and Sn1−P4, respectively, are shorter than the corresponding bonds in **2**. Lastly, the O−C−O bond angles found in **3** are strongly bent at 126.8(6) and 129.5(6)°, somewhat similar to the 123.9(3)° angle seen earlier by Stephan et al. in a related P−B system.[12]

It is possible to draw at least three formal resonance structures for **3** (Scheme 2). On the basis of the X-ray data, it seems likely that adduct form II dominates, but there are contributions from I and III. Complex **3** is similar in its structural parameters and CO_2 coordination mode to the "frustrated Lewis acid−base" complexes recently reported by Stephan et al.[12,13] In these molecules, a molecule of CO_2 reacts as an electrophile at C to a sterically crowded P or N atom and as a nucleophile at O to a strongly Lewis acidic B atom ligated by fluorinated aromatic groups. We note that in **3** the P atom would not be considered particularly sterically crowded or "frustrated", nor is the Sn atom highly acidic. Two other CO_2 adducts of R_3P with aluminum have also been reported, but two Lewis acidic metals are present so each O atom forms a bond.[14] This has the effect of equalizing the C−O bonds at values roughly intermediate to those seen in **3** and the boron adducts [1.233(8)/1.251(8) Å; 1.248(6)/1.248(6) Å; 1.231(9)/1.243(9) Å].

Scheme 2. Resonance Forms of 3



I **II** **III**

In all of these molecules, including **3**, the P−C bond to CO_2 is significantly longer than the bonds to the alkyl or aryl substituents, suggesting that it is more like a dative bond than a true covalent single bond. We note that the environment around CO_2 in **3** is related to that seen by Stephan et al.; however, the starting reagents used to prepare **3** are quite different and less "frustrated". In fact, the Lewis acidic Sn atom in **3** still possesses a formal lone pair compared to the highly electron-deficient boron acids used previously.

The description of **3** as a CO_2 adduct rather than an inserted, covalently bound molecule is also consistent with stability studies. A thermogravimetric analysis/differential thermal analysis−mass spectrometry (TGA/DTA-MS) experiment on a sample of **3** revealed a two-step endothermic mass loss of 5.6% at 52 and 90 °C followed by an exothermic loss of 5.8% at 126 °C, although the constant mass loss seen in TGA does not indicate a discrete mono-CO_2 decomposition product. The total mass loss of 11.4% is in excellent agreement with the calculated loss of 12.5% for complete CO_2 removal. The MS spectrum confirmed that CO_2 evolved during these mass-loss events (see the Supporting Information). Additional confirmation was provided by simply heating a solid sample under argon to obtain an orange residue whose $^{31}P\{^1H\}$ NMR spectrum was consistent with that of **2**. Finally, a sample of **3** was dissolved in C_6D_6 and exposed to a 5-fold excess of ^{13}C-labeled CO_2 for 1 h. The ^{13}C NMR spectrum showed that the labeled gas was incorporated into the adduct.

A different decomposition process is observed when a sample of **3** is monitored over time. Stored under CO_2 at room temperature or under argon at −25 °C, **3** is stable for several months. Under an argon atmosphere at room temperature, however, **3** decomposes from a white powder into a yellow oil over the course of approximately 1 month. Preliminary evidence (see the Supporting Information) suggests that this oil contains the cyanamide $R_2P(R_2P){=}NC{\equiv}N$ ($R = i\text{-}Pr$), an isomer of the carbodiimide $R_2PN{=}C{=}NPR_2$,[15] but conclusive characterization has not been possible because of difficulties in separating it from the Sn-containing coproduct. Carbodiimides are known products from the reaction of CO_2 with tin amides.[2]

In summary, we have shown that **1** can be used as a ligand toward Sn to form the P,P-chelated stannylene **2**, and this reacts with the addition of 2 equiv of CO_2. This addition reaction results in the reversibly bound CO_2 adduct **3** by the formal insertion of CO_2 into two of the Sn−P bonds, and CO_2 can be easily removed by heating to moderate temperatures. Although over time at ambient temperatures **3** will decompose, we have discovered that under a CO_2 atmosphere **3** is stable for months. The further reaction and reductive chemistry of adduct **3** is currently under study in our group.

■ ASSOCIATED CONTENT

Supporting Information

Detailed synthetic procedures, full characterization data, thermal ellipsoid plot of **1**, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rakemp@unm.edu. Tel: (505) 272-7609.

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