Carbon−Carbon Bond Formation on Reaction of a Copper(I) Stannyl Complex with Carbon Dioxide

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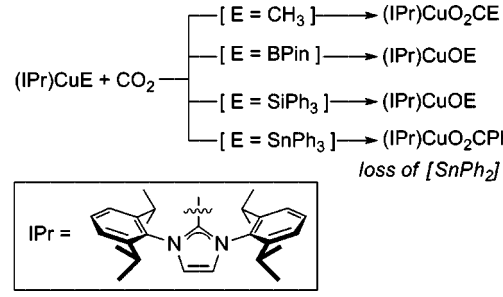
Summary: The reaction of (IPr)CuOt-Bu (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with triphenylstannane forms a stannyl complex, (IPr)CuSnPh$_3$, by deprotonation of the tin−hydrogen bond. This stannyl complex reacts with CO_2 to afford (IPr)CuO$_2$CPh as the sole copper-containing species. A tin−carbon bond in (IPr)CuSnPh$_3$ also undergoes facile cleavage by mild acids such as 2,4-lutidinium chloride.

Carbon dioxide is a benign and readily available source of carbon;[1] however, thermodynamic and kinetic considerations limit its practical use in chemical synthesis.[2] Metal complexes that display unique reactivity toward carbon dioxide hold promise in the development of new catalytic CO_2-fixation reactions.[3,4] The reactivity of organocopper complexes with CO_2 to form copper carboxylates[5,6] encouraged the study of other complexes containing copper−E bonds (E = main-group ligand) (Scheme 1). The N-heterocyclic carbene (NHC) supported copper−boryl species (IPr)CuB(pin) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, B(pin) = boryl pinacolate) reacts with CO_2 to form (IPr)CuOB(pin), with concomitant extrusion of CO.[3] DFT calculations support a nucleophilic Cu−B bond, with initial formation of B−C and Cu−O bonds upon insertion of CO_2.[7] The silyl complex (IPr)CuSiPh$_3$ showed similar net reactivity, reducing CO_2 to CO and forming (IPr)CuOSiPh$_3$.[8] To explore whether and how a copper−tin bond would react with CO_2, we synthesized the stannyl complex (IPr)CuSnPh$_3$ (**1**). To our surprise, treatment of **1** with CO_2 resulted in carbon−carbon bond formation, affording the benzoate complex (IPr)CuO$_2$CPh (**2**).[13]

Scheme 1. (IPr)Cu−E Complexes React Differently with CO_2 Depending on Choice of E



The copper stannyl complex **1** was initially synthesized by the addition of Ph$_3$SnH to [(IPr)CuH]$_2$ in benzene solution (eq 1).[9] Although this reaction proceeded in good yield, the high air-sensitivity and thermal instability of the hydride prompted a search for more synthetically convenient routes to the stannyl complex. Interestingly, the reaction of Ph$_3$SnH with (IPr)CuMe instead produces methyltriphenyltin and [(IPr)CuH]$_2$,[5] as judged by ^{1}H NMR spectroscopy. We later found that (IPr)CuO*t*-Bu is sufficiently basic to deprotonate the stannane, forming **1** and *t*-BuOH (eq 2).[9] Complex **1** was characterized by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction (Figure 1).

$$\tfrac{1}{2}\,[(IPr)CuH]_2 \xrightarrow[C_6H_6,\ 0\ ^\circ C,\ 8\ h]{Ph_3SnH} (IPr)CuSnPh_3\ \mathbf{1} \quad (1)$$
95% conversion

$$(IPr)CuO\textit{t}\text{-}Bu \xrightarrow[C_6H_6,\ r.t.,\ 15\ min]{Ph_3SnH} \mathbf{1} \quad (2)$$
95% conversion
50% yield

Single crystals suitable for X-ray analysis were obtained by slow vapor diffusion of hexanes into a toluene solution of **1** at −40 °C. Complex **1** possesses a Cu−Sn bond length of 2.469(5) Å, similar to that of other copper stannyl complexes (2.45−2.50 Å).[10]

Complex **1** reacts with CO_2 (1.04 atm) to form a single NHC-containing species (eq 3), as determined by ^{1}H NMR spectroscopy. Single crystals of the product were analyzed by X-ray diffraction and identified as the benzoate complex **2** (Figure

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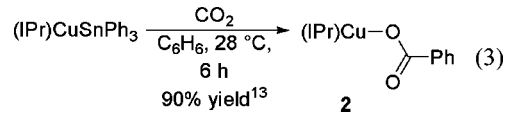


2), resulting from a C−C bond-forming pathway. Another metal triphenylstannyl complex, the anionic $[(OC)_5W(SnPh_3)]^-$ synthesized by Rheingold and co-workers, exhibited no reactivity toward CO_2 even under high pressures.[11] A copper stannyl complex supported by a tridentate phosphine ligand has been shown by Klein and co-workers to react with CS_2, forming the insertion product $L^3CuS_2CSnMe_3$ without loss of tin.[12]

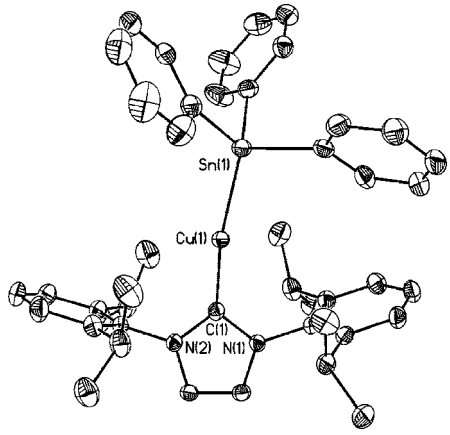


Figure 1. Solid-state structure of **1** shown as 50% ellipsoids. For clarity, hydrogen atoms, disorder, and solvent have been omitted. Select bond lengths (Å) and angles (deg): Sn(1)−Cu(1) = 2.469(5), Cu(1)−C(1) = 1.914(2); Sn(1)−Cu(1)−C(1) = 169.6(8).

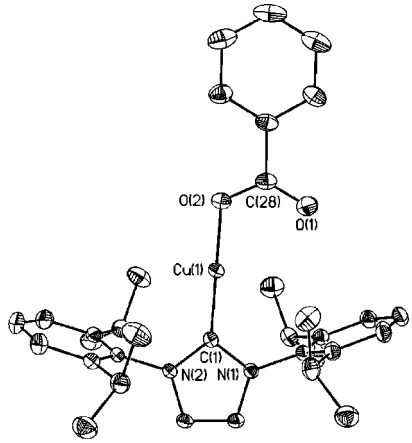
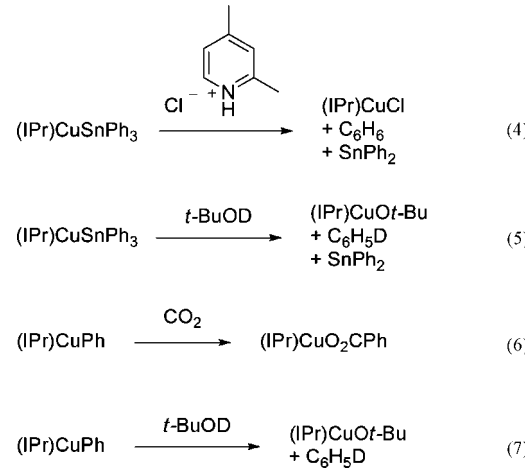


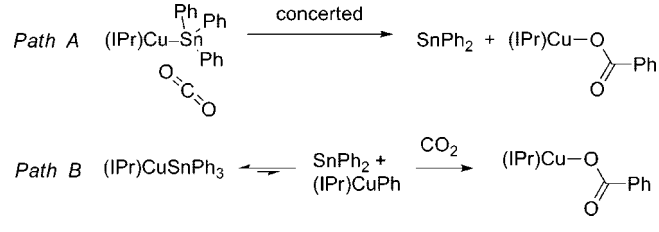
Figure 2. Solid-state structure of **2** shown as 50% ellipsoids. For clarity, hydrogen atoms, disorder, and solvent have been omitted. Select bond lengths (Å) and angles (deg): O(2)−Cu(1) = 1.8504(11), Cu(1)−C(1) = 1.8647(14), O(2)−C(28) = 1.2803(19), O(1)−C(28) = 1.231(2); O(2)−Cu(1)−C(1) = 179.05(6).

The solid-state structure of **2** shows a monodentate carboxylate group, as observed for (IPr)CuOAc.[5] The reaction stoichiometry implies the formation of a diphenyltin-derived byproduct. The best-characterized form of diphenyltin(II) is a six-membered cyclic species, with a ^{119}Sn NMR shift of −208.6 ppm relative to Me_4Sn.[14] In contrast, the tin-containing byproduct formed in this reaction gives rise to a single ^{119}Sn NMR shift of −43.7 ppm. Although this byproduct has eluded definitive identification, ^{1}H and ^{13}C NMR suggest that it contains only phenyl groups (see the Supporting Information). Furthermore, reaction of **1** with $^{13}CO_2$ produces $(IPr)CuO_2{}^{13}CPh$ as the only obviously labeled species. No ^{13}CO was observed in a variable-temperature ^{13}C NMR study, and there was no notable enhancement of any resonances in the ^{13}C NMR spectrum of the isolated tin-containing byproduct. This extrusion of a main-group element, likely made possible by the accessibility of both divalent and tetravalent tin, represents a new mode of reactivity in complexes of the type (NHC)Cu−E.



The copper-bound triphenylstannyl appears to react as a source of the phenyl nucleophile, suggesting the net electrophilic cleavage of a tin−phenyl bond by CO_2. Further evidence for this mode of reactivity is provided in the protonolysis of **1** by 2,4-lutidinium chloride, which formed (IPr)CuCl,[15] benzene, and the tin byproduct (eq 4). The reaction of **1** with *tert*-butyl alcohol-*d* produced (IPr)CuO*t*-Bu, C_6H_5D, and the tin byproduct (eq 5) after heating at 50 °C for 22 h. These electrophilic cleavage reactions might occur through a concerted cleavage with extrusion of $SnPh_2$ (Scheme 2, path A) or via an equilibrium with the copper phenyl species (IPr)CuPh (Scheme 2, path B),[16] which is chemically competent in reactions with CO_2 (eq 6) and *t*-BuOD (eq 7). Such an equilibrium would strongly favor $(IPr)CuSnPh_3$, the only species visible by NMR. Similar equilibria have been observed between $[M]SnR_3$ and $[M]R + SnR_2$ ([M], R = $(R_3P)_2ClPt$, Cl_2; Li, Ph).[17,18]

Scheme 2. Possible Mechanisms for the Conversion of $(IPr)CuSnPh_3$ to $(IPr)CuO_2CPh$



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In conclusion, the NHC-supported copper stannyl complex (IPr)CuSnPh$_3$ was synthesized from (IPr)CuO-*t*-Bu and Ph$_3$SnH. This complex serves as a source of a nucleophilic phenyl group, reacting with CO_2 to form a benzoate species and with mild acids to release benzene. Efforts to elucidate the mechanism of tin−carbon bond cleavage in this complex by DFT calculations are ongoing.

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Supporting Information Available: Text, tables, and figures giving synthetic details, spectroscopic data, and structural parameters and CIF files giving crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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