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 $(IPr)CuO_2CPh$ 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 CO₂-fixation reactions.^{3,4} The reactivity of organocopper complexes with CO₂ 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 CO₂ 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 CO₂.⁷ The silvl complex (IPr)CuSiPh₃ showed similar net reactivity, reducing CO₂ to CO and forming (IPr)CuOSiPh₃.⁸ To explore whether and how a copper-tin bond would react with CO₂, we synthesized the stannyl complex (IPr)CuSnPh₃ (1). To our surprise, treatment of 1 with CO_2

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resulted in carbon–carbon bond formation, affording the benzoate complex (IPr)CuO₂CPh (2).¹³

The copper stannyl complex **1** was initially synthesized by the addition of Ph₃SnH 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 Ph₃SnH with (IPr)CuMe instead produces methyltriphenyltin and [(IPr)CuH]₂,⁵ as judged by ¹H 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 ¹H NMR spectroscopy and single-crystal X-ray diffraction (Figure 1).

$$\frac{1/2 \left[(|Pr)CuH]_2 \xrightarrow{Ph_3SnH} (|Pr)CuSnPh_3}{C_6H_6, 0 \ ^\circ C, 8 h} \underbrace{1 \qquad (1)}_{1}$$

$$(|Pr)CuOt-Bu \xrightarrow{Ph_3SnH} (1)$$

$$\frac{Ph_3SnH}{C_6H_6, r.t., 15 \min} \underbrace{1 \qquad (2)}_{50\% \ vield}$$

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 NHCcontaining species (eq 3), as determined by ¹H 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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$$(IPr)CuSnPh_3 \xrightarrow[C_6H_6, 28 °C,]{} (IPr)Cu-O$$

$$6 h$$

$$90\% \text{ yield}^{13} 2 (IPr)Cu-O$$

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 CO₂ 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 CS₂, forming the insertion product L³CuS₂CSnMe₃ 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 ¹¹⁹Sn NMR shift of -208.6 ppm relative to Me₄Sn.¹⁴ In contrast, the tin-containing byproduct formed in this reaction gives rise to a single ¹¹⁹Sn NMR shift of -43.7 ppm. Although this byproduct has eluded definitive identification, ¹H and ¹³C NMR suggest that it contains only phenyl groups (see the Supporting Information). Furthermore, reaction of **1** with ¹³CO₂ produces (IPr)CuO₂¹³CPh as the only obviously labeled species. No ¹³CO was observed in a variable-temperature ¹³C NMR study, and there was no notable enhancement of any resonances in the ¹³C NMR spectrum of the isolated tincontaining 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 CO2. 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)CuOt-Bu, C₆H₅D, 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 SnPh₂ (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 CO₂ (eq 6) and t-BuOD (eq 7). Such an equilibrium would strongly favor (IPr)CuSnPh₃, the only species visible by NMR. Similar equilibria have been observed between [M]SnR3 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)CuSnPh₃ to (IPr)CuO₂CPh



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In conclusion, the NHC-supported copper stannyl complex (IPr)CuSnPh₃ was synthesized from (IPr)CuO-*t*-Bu and Ph₃SnH. 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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