Communication

Unexpected C–O Bond Cleavage by a Copper–Phosphido Compound

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Abstract: Copper methoxide compound IPrCuOMe was unexpectedly formed in a reaction of IPrCuPPh2 with methyl acrylate. The alkoxide product was identified from the reaction mixture spectroscopically and structurally characterized. This C–O bond cleavage reaction likely depends on nucleophilicity of the Cu–P bond of IPrCuPPh2.

Keywords: copper; NHC; X-ray diffraction; C-O bond cleavage

1. Introduction

N–heterocyclic carbene copper(I) complexes have received significant attention due to their use as catalysts, transfer reagents, and for potential medical applications [1]. In catalysis, NHC-supported copper compounds have been utilized in a wide variety of transformations [2–7]. A convenient feature of these compounds is that they are often monomeric when the supporting NHC ligand contains bulky aryl substituents [8,9]. For this reason, we utilized IPrCuPPh2 (1) in our mechanistic study of copper-photocatalyzed hydrophosphination [10,11]. We hypothesized that alkene insertion into the Cu–P bond was the bond-forming step. We have thus far been unsuccessful in isolating an insertion intermediate. However, during our study, we unexpectedly formed, isolated, and structurally characterized the copper alkoxide compound IPrCuOMe (2), formed from the treatment of 1 with methyl acrylate in a process involving C–O bond cleavage.

Compound 2 has been previously synthesized and characterized spectroscopically [5,8,12]. The related IPrCuOR compounds where R = OH [8], OEt [13], and OPh [13], have been structurally characterized as well. However, to our knowledge, the solid-state molecular structure of 2 has not been determined via X-ray crystallography. Herein, we report the X-ray crystal structure of IPrCuOMe (2) (Figure 1).

Figure 1. The molecular structure of IPrCuOMe (2), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Cu1–O1, 1.8029(13); Cu1–C2, 1.8590(18); O1–C1, 1.391(3); N1–C2, 1.355(2); N1–C3, 1.388(2). Selected bond angles (deg): O1–Cu1–C2, 179.03(7); C1–O1–Cu1, 122.26(14); N1–C2–Cu1, 130.44(13); N2–C2–Cu1, 126.04(13); C2–N1–C17, 125.29(15), C2–N1–C3, 111.30(15); C2–N1–C17, 125.29(15).
2. Results and Discussion

The treatment of a benzene-\textit{d}_6 solution of IPrCuPPh\textsubscript{2} (1) with 1.3 equivalents of methyl acrylate at room temperature resulted in several decomposition products, as determined via \textsuperscript{1}H and \textsuperscript{31}P NMR spectroscopy (Equation (1), see Supplementary Materials for spectra). This reaction was undertaken as an attempt to observe the potential intermediates during hydrophosphination catalysis. Unfortunately, the definitive characterization of all products was not possible from these spectra, but several new signals were observed in the alkyl region of a \textsuperscript{1}H NMR spectrum, as well as several in the range \(\delta = -19\) to \(-15\) in the \textsuperscript{31}P NMR spectrum. In a separate trial with 2.2 equivalents of methyl acrylate, this reaction mixture was allowed to stand overnight, which resulted in the precipitation of large colorless block crystals that were identified as IPrCuOMe (2) upon analysis via X-ray diffraction. The isolated 2 never exceeded 20% of the theoretic yield, and the NMR spectra (Supplementary Materials) show complex mixtures.

![Equation (1)](image)

The solid-state structure of 2 is very similar to IPrCuOEt (3) [13]. The structures of both compounds are monoclinic and crystallize in the space group P2\textsubscript{1}/n. The Cu–O1 bond length of compound 2 is 1.8029(13) Å, which is similar to 1.799(3) Å measured for the corresponding bond in compound 3. Likewise, the Cu1–C2 bond distance of 1.8590(18) Å compares favorably to the 1.863(5) Å distance in compound 3. The C2–Cu1–O1 bond angle of compound 2 is slightly closer to being linear, at 179.03(7)°, compared to 176.9(2)° in compound 3. Finally, the Cu1–O1–C1 bond angle of 2 is slightly smaller than the 128.1(4)° bond angle observed in compound 3, a difference attributed to the presence of the additional carbon in the ethoxide ligand.

While the reaction of 1 with methyl acrylate failed to provide an identifiable product that relates to hydrophosphination reactivity, the study of 1 has been successful in expanding the understanding of photocatalytic hydrophosphinization from early to late metals [11,14,15]. The observed C–O bond cleavage herein was unexpected, but likely relies on the nucleophilicity of the metal–phosphorus bond [16]. Because C–O bond cleavage is an important, but challenging strategy for the conversion of biomass-originated organic precursors of chemical feedstocks [17–19], the direct activation of these bonds with potential heteroatom functionalization is an intriguing possibility for efficient chemical conversions. Further exploration of this kind of unique reactivity is underway.

3. Experimental

3.1. General Considerations

Manipulations were performed under a purified nitrogen atmosphere with dried, deoxygenated solvents in an M. Braun glovebox. Benzene-\textit{d}_6 was degassed and dried over an activated mixture of 3 Å and 4 Å molecular sieves. Compound 1 was prepared by the literature protocol [8,11]. NMR spectra were recorded with a Bruker AXR 500 MHz spectrometer (San Jose, CA, USA). All \textsuperscript{31}P NMR spectra were \textsuperscript{1}H-decoupled and referenced to external 85% H\textsubscript{3}PO\textsubscript{4}. The resonances in \textsuperscript{1}H NMR spectra are referenced to the residual solvent resonance (C\textsubscript{6}D\textsubscript{6} = \(\delta = 7.16\)). The crystals for X-ray analysis were handled and mounted under Paratone–N oil. The X-ray data were collected on a Bruker AXS single-crystal X-ray diffractometer (Billerica, MA, USA) using MoKa radiation and a SMART APEX CCD detector, and analyzed with the Bruker software (Billerica, MA, USA). The CIF was edited with Final CIF [20] and visualization was performed with the Mercury software [21].
3.2. Experimental Details

Trial 1: In an N$_2$-filled glovebox, IPrCuPPh$_2$ (22 mg, 0.0345 mmol) and methyl acrylate (4 mg, 0.046 mmol) were added to ~0.6 mL of benzene-$d_6$ in a J-Young NMR tube with a PTFE cap, and monitored via $^1$H and $^{31}$P NMR spectroscopy.

Trial 2: In an N$_2$-filled glovebox, IPrCuPPh$_2$ (50 mg, 0.783 mmol) and methyl acrylate (15 mg, 0.174 mmol) were added to 2–3 mL of benzene-$d_6$ in a scintillation vial and allowed to stand overnight. The crystals suitable for X-ray crystallography precipitated overnight.

3.3. X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo K$_\alpha$ ($\lambda = 0.71073$ Å), Billerica, MA, USA) at 150(2) K. A suitable colorless block crystal of IPrCuOMe was mounted on a MiTeGen Micromount with Paratone–N cryoprotectant oil. The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F2 by using the Bruker SHELXTL Software Package [22,23]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon were included in the calculated positions and were refined using a riding model.

Crystal Data for C$_{28}$H$_{39}$CuN$_2$O

(M = 483.15 g/mol): monoclinic, space group $P2_1/n$ (14), $a = 12.430(4)$ Å, $b = 16.81(5)$ Å, $c = 14.30(3)$ Å, $\alpha = 90^\circ$, $\beta = 110.24(4)^\circ$, $\gamma = 90^\circ$, $V = 2805.0(16)$ Å$^3$, $Z = 4$, $\rho_{\text{calc}} = 1.144$ g/cm$^3$, 33,207 reflections measured ($3.75^\circ \leq 2\Theta \leq 57.51^\circ$) (0.74 Å), 6889 unique ($R_{int} = 0.0520$, $R_{\text{sigma}} = 0.0422$), which were used in all calculations. The final $R_1$ was 0.0577 (I > 2$\sigma$(I)) and wR$_2$ was 0.1042 (all data). The full crystallographic information (as CIF file) is given in the Supplementary Materials.

Supplementary Materials: The following are available online: $^1$H, $^{31}$P NMR, $^1$H–$^{31}$P HMBC NMR spectra, bond lengths and angles, crystallographic information file (CIF) and CheckCIF report for compound 2.

Author Contributions: Conceptualization, S.G.D. and R.W.; methodology, S.G.D. and R.W.; formal analysis, S.G.D.; investigation, S.G.D. and R.W.; data curation, S.G.D. and R.W.; writing—original draft preparation, S.G.D.; writing—review and editing, R.W.; visualization, S.G.D.; supervision, R.W. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: CCDC-2258630 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, accessed on 25 April 2023, or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk. All other data in this study can be found in Supplementary Materials and original data files at https://www.uvm.edu/~waterman/pubs.html, accessed on 25 April 2023.

Conflicts of Interest: The authors declare no conflict of interest.

References


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