Communication

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

Steven G. Dannenberg and Rory Waterman*

Department of Chemistry, University of Vermont, Burlington, Vermont 05405-0125, United States.
* Correspondence Rory.Waterman@UVM.edu; Tel.: +1 (802) 656-0278

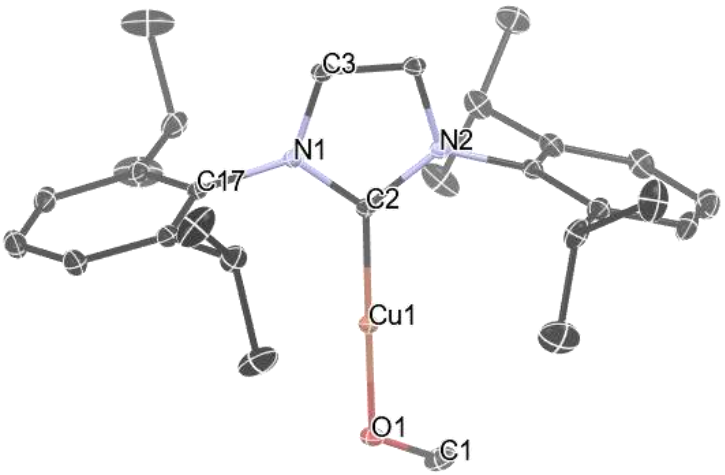
Abstract: Copper methoxide compound IPrCuOMe was unexpectedly formed in a reaction of IPrCuPPh$_2$ with methyl acrylate. The alkoxide product was identified from the reaction mixture spectroscopically and structurally characterized. This C–O bond cleavage reaction likely depends on nucleophilicity of the Cu–P bond of IPrCuPPh$_2$.

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 IPrCuPPh$_2$ (**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 copper alkoxide compound IPrCuOMe (**2**) formed from 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]. 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 determined by X-ray crystallography. Herein we report the X-ray crystal structure of IPrCuOMe (**2**) [Figure 1].



Citation: To be added by editorial staff during production.

Academic Editor: Firstname Lastname

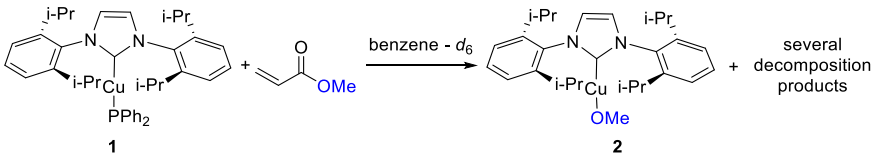
Received: date
Revised: date
Accepted: date
Published: date

Copyright: © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Figure 1. Molecular structure of IPrCuOMe (**2**) with thermal ellipsoids drawn at the 10% 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

Treatment of a benzene-d_6 solution of IPrCuPPh$_2$ (**1**) with 1.3 equivalents of methyl acrylate at room temperature resulted in several decomposition products as determined by ^{1}H and ^{31}P NMR spectroscopy (Eqn. 1, see SI for spectra). This reaction was undertaken as an attempt to observe potential intermediates in hydrophosphination catalysis. Unfortunately, definitive characterization of all products was not possible from these spectra, but several new signals were observed in the alkyl region of a ^{1}H NMR spectrum as well as several in the range $\delta = -19$ to -15 in the ^{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 by X-ray diffraction.



(Eqn. 1)

The solid-state structure of **2** is very similar to IPrCuOEt (**3**)[13]. The structures of both compounds are monoclinic and crystalize in space group P21/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 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 understanding of photocatalytic hydrophosphination 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:

General Considerations

Manipulations were performed under a purified nitrogen atmosphere with dried, deoxygenated solvents in an M. Braun glovebox. Benzene-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. All ^{31}P NMR spectra were ^{1}H decoupled and referenced to external 85% H_3PO_4. Resonances in ^{1}H NMR spectra are referenced to the residual solvent resonance ($C_6D_6 = \delta$

7.16). 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 using MoKα radiation and a SMART APEX CCD detector and analyzed with Bruker software. The CIF was edited with Final CIF [20] and visualization was performed with Mercury software [21].

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 PTFE cap and monitored by ^{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. Crystals suitable for X-ray crystallography precipitated overnight.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα (λ = 0.71073 Å)) 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. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model.

Crystal Data for $C_{28}H_{39}CuN_2O$:

(M = 483.15 g/mol): monoclinic, space group $P2_1/n$ (14), a = 12.430(4) Å, b = 16.815(5) Å, c = 14.303(5) Å, α = 90°, β = 110.238(4)°, γ = 90°, V = 2805.0(16) Å^3, Z = 4, ρ_{calc} = 1.144 g/cm^3, 33207 reflections measured (3.75° ≤ 2Θ ≤ 57.51°) (0.74 Å), 6,889 unique (R_{int} = 0.0520, R_{sigma} = 0.0422), which were used in all calculations. The final R_1 was 0.0577 (I > 2σ(I)) and wR_2 was 0.1042 (all data). 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.; resources, 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.

Funding: This research was supported by the U. S. National Science Foundation through CHE-2101766 (to R.W.), a graduate research fellowship for S.G.D. funded by the Vermont Space Grant Consortium under NASA Cooperative Agreement NNX15AP86H and 80NSSC20M0122, and Japan Society for the Promotion of Science (Fellowship to R.W.).

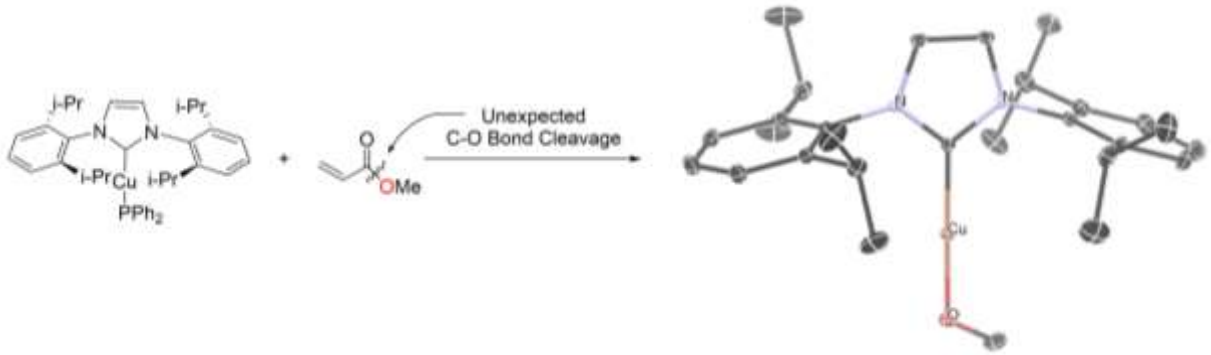
Data Availability Statement: CCDC-2258630 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via **http://www.ccdc.cam.ac.uk/conts/retrieving.html**, accessed on 25 April 2023, (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 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

1. Danopoulos, A. A.; Simler, T.; Braunstein, P., N-Heterocyclic Carbene Complexes of Copper, Nickel, and Cobalt. *Chem. Rev.* **2019,** *119* (6), 3730-3961.

2. Lazreg, F.; Nahra, F.; Cazin, C. S. J., Copper–NHC complexes in catalysis. *Coord. Chem. Rev.* **2015,** *293-294*, 48-79.
3. Horsley Downie, T. M.; Hall, J. W.; Collier Finn, T. P.; Liptrot, D. J.; Lowe, J. P.; Mahon, M. F.; McMullin, C. L.; Whittlesey, M. K., The first ring-expanded NHC–copper(i) phosphides as catalysts in the highly selective hydrophosphination of isocyanates. *ChemComm* **2020,** *56* (87), 13359-13362.
4. Zhang, L.; Cheng, J.; Hou, Z., Highly efficient catalytic hydrosilylation of carbon dioxide by an N-heterocyclic carbene copper catalyst. *Chem. Commun.* **2013,** *49* (42), 4782-4784.
5. Bonet, A.; Lillo, V.; Ramírez, J.; Díaz-Requejo, M. M.; Fernández, E., The selective catalytic formation of β-boryl aldehydes through a base-free approach. *Org. Biomol. Chem* **2009,** *7* (8), 1533-1535.
6. Nayal, O. S.; Hong, J.; Yang, Y.; Mo, F., Cu-Catalysed carboxylation of aryl boronic acids with CO_2. *Org. Chem. Front.* **2019,** *6* (21), 3673-3677.
7. Hall, J. W.; Unson, D. M. L.; Brunel, P.; Collins, L. R.; Cybulski, M. K.; Mahon, M. F.; Whittlesey, M. K., Copper-NHC-Mediated Semihydrogenation and Hydroboration of Alkynes: Enhanced Catalytic Activity Using Ring-Expanded Carbenes. *Organometallics* **2018,** *37* (18), 3102-3110.
8. Fortman, G. C.; Slawin, A. M. Z.; Nolan, S. P., A Versatile Cuprous Synthon: [Cu(IPr)(OH)] (IPr = 1,3 bis(diisopropylphenyl)imidazol-2-ylidene). *Organometallics* **2010,** *29* (17), 3966-3972.
9. Coyle, J. P.; Sirianni, E. R.; Korobkov, I.; Yap, G. P. A.; Dey, G.; Barry, S. T., Study of Monomeric Copper Complexes Supported by N-Heterocyclic and Acyclic Diamino Carbenes. *Organometallics* **2017,** *36* (15), 2800-2810.
10. Dannenberg, S. G.; Waterman, R., A bench-stable copper photocatalyst for the rapid hydrophosphination of activated and unactivated alkenes. *Chem. Commun.* **2020,** *56* (91), 14219-14222.
11. Dannenberg, S. G.; Seth, D. M., Jr.; Finfer, E. J.; Waterman, R., Divergent Mechanistic Pathways for Copper(I) Hydrophosphination Catalysis: Understanding That Allows for Diastereoselective Hydrophosphination of a Tri-substituted Styrene. *ACS Catal.* **2023,** *13* (1), 550-562.
12. Ohishi, T.; Zhang, L.; Nishiura, M.; Hou, Z., Carboxylation of Alkylboranes by N-Heterocyclic Carbene Copper Catalysts: Synthesis of Carboxylic Acids from Terminal Alkenes and Carbon Dioxide. *Angew. Chem. Int. Ed.* **2011,** *50* (35), 8114-8117.
13. Goj, L. A.; Blue, E. D.; Munro-Leighton, C.; Gunnoe, T. B.; Petersen, J. L., Cleavage of X−H Bonds (X = N, O, or C) by Copper(I) Alkyl Complexes To Form Monomeric Two-Coordinate Copper(I) Systems. *Inorg. Chem.* **2005,** *44* (24), 8647-8649.
14. Waterman, R., Triamidoamine-Supported Zirconium Compounds in Main Group Bond-Formation Catalysis. *Acc. Chem. Res.* **2019,** *52* (8), 2361-2369.
15. Reuter, M. B.; Seth, D. M.; Javier-Jiménez, D. R.; Finfer, E. J.; Beretta, E. A.; Waterman, R., Recent advances in catalytic pnictogen bond forming reactions via dehydrocoupling and hydrofunctionalization. *Chem. Commun.* **2023,** *59* (10), 1258-1273.
16. Glueck, D. S., Metal-catalyzed nucleophilic carbon–heteroatom (C–X) bond formation: the role of M–X intermediates. *Dalton Trans.* **2008,** (39), 5276-5286.
17. Son, S.; Toste, F. D., Non-Oxidative Vanadium-Catalyzed C⊚O Bond Cleavage: Application to Degradation of Lignin Model Compounds. *Angew. Chem., Int. Ed.* **2010,** *49* (22), 3791-3794.
18. Wan, W.; Ammal, S. C.; Lin, Z.; You, K.-E.; Heyden, A.; Chen, J. G., Controlling reaction pathways of selective C–O bond cleavage of glycerol. *Nat. Commun.* **2018,** *9* (1), 4612.
19. Oyeyemi, V. B.; Keith, J. A.; Carter, E. A., Trends in Bond Dissociation Energies of Alcohols and Aldehydes Computed with Multireference Averaged Coupled-Pair Functional Theory. *J. Phys. Chem.* **2014,** *118* (17), 3039-3050.
20. Kratzert, D. *FinalCif*, V118, https://dkratzert.de/finalcif.html.
21. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A., Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Crystallogr.* **2020,** *53* (1), 226-235.
22. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallogr. C.* **2015,** *71* (1), 3-8.
23. Sheldrick, G., A short history of SHELX. *Acta Crystallogr. A.* **2008,** *64* (1), 112-122.


i-Pr
i-Pr
N
N
i-Pr
Cu
i-Pr
PPh2
O
OMe
Unexpected
C-O Bond Cleavage
Cu
O

175