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Synthesis, Structure, and CO_2 Reactivity of a Two-Coordinate (Carbene)copper(I) Methyl Complex

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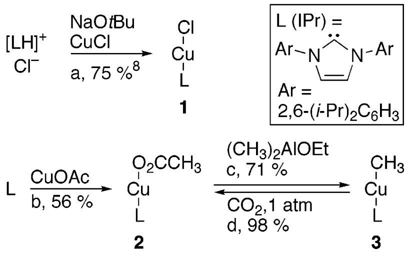
Summary: Two-coordinate copper(I) acetate and copper(I) methyl complexes, bearing an N-heterocyclic carbene (NHC) supporting ligand, have been synthesized and structurally characterized, and the stability of the monodentate acetate has been examined by DFT calculations. The methyl complex readily inserts carbon dioxide at ambient temperature and pressure, regenerating the acetate in near-quantitative yield.

The catalytic formation of carbon−carbon bonds from carbon dioxide presents an ongoing challenge in organometallic chemistry.[1] With the goal of developing new catalytic reactions, we have been interested in the insertion of CO_2 into alkyl complexes of late transition metals, particularly Cu.[2] Many copper(I) alkyls are quite unstable, but those complexes supported by bulky, electron-rich phosphines[2b−e] are notably robust, and several phosphine-ligated copper(I) alkyls have been reported to undergo CO_2 insertion.[2e−h] To avoid potential side reactions involving binuclear reaction pathways, we have sought supporting ligands that would disfavor ligand redistribution[3a] or bridged-oligomer formation.[3b−f]

Since their discovery by Arduengo and co-workers,[4] N-heterocyclic carbenes have become versatile and prolific ligands in catalysis,[5] often supplanting sterically demanding, electron-rich phosphines. Their use as ligands for copper complexes, however, remains relatively rare.[6] Herein we report the structural characterization of a carbene-ligated copper(I) chloride, the synthesis and structure of a two-coordinate (carbene)copper(I) acetate, a computational comparison of monodentate and bidentate acetates, and the synthesis and structure of a linear (carbene)copper(I) methyl, which reacts readily with CO_2.

Scheme 1[a]



[a] Solvents and conditions: (a) THF, room temperature; (b) $PhCH_3$, room temperature; (c) Et_2O, −45 °C; (d) C_6H_6, room temperature.

The synthetic routes to (carbene)copper(I) complexes **1**−**3** are shown in Scheme 1.[7] Chloride complex **1** was synthesized as reported previously;[8] its crystal structure (Figure 1) displays a monomeric, two-coordinate geometry, with a Cu−Cl bond distance of 2.106(2) Å.[9] Related (NHC)copper(I) halides, prepared by N-methylation of (azolyl)chlorocuprates, display very similar geometries and bond lengths.[6d]

Attempts to replace the chloro ligand in **1** with a methyl group, using a variety of methyl nucleophiles, did not give clean reactions. (Phosphine)copper(I) methyl complexes are often synthesized by addition of Me_2AlOR (R = Et, *i*Pr) to $Cu(acac)_2$ in the presence of free phosphine;[2] however, the analogous reaction using the free ligand IPr afforded a yellow powder that defla-

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[1] Selected references: (a) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188−15189. (b) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2002**, *124*, 10008−10009. (c) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27−59.

[2] (a) Coan, P. S.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1989**, *8*, 2724−2728. (b) Pasynkiewicz, S.; Pikul, S.; Poplawska, J. *J. Organomet. Chem.* **1985**, *293*, 125−130. (c) Pasynkiewicz, S.; Poplawska, J. *J. Organomet. Chem.* **1985**, *282*, 427−434. (d) Miyashita, A.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1102−1108. (e) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1974**, *72*, 145−151. (f) Marsich, N.; Camus, A.; Nardin, G. *J. Organomet. Chem.* **1982**, *239*, 429−437. (g) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *113*, 187−199. (h) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* **1973**, *49*, C57−C58.

[3] (a) Dempsey, D. F.; Girolami, G. S. *Organometallics* **1988**, *7*, 1208−1213. (b) Koenig, T. M.; Daeuble, J. F.; Bretensky, D. M.; Stryker, J. M. *Tetrahedron Lett.* **1990**, *31*, 3237−3240. (c) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354−7355. (d) Beguin, B.; Denise, B.; Sneeden, R. P. A. *J. Organomet. Chem.* **1981**, *208*, C18−C20. (e) Goel, R. G.; Beauchamp, A. L. *Inorg. Chem.* **1983**, *22*, 395−400. (f) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1975**, 637−643.

[4] Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

[5] See for example: (a) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194−16195. (b) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558. (c) Muehlhofer, M.; Strassner, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1745−1747. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

[6] (a) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 12237−12245. (b) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340−2341. (c) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027−2031. (d) Raubenheimer, H. G.; Cronje, S.; Olivier, P. J. *J. Chem. Soc., Dalton Trans.* **1995**, 313−316. (e) Arduengo, A. J., III; Rasika Dias, H. V.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405−3409.

[7] For complete synthetic, computational, spectroscopic, and crystallographic details, see the Supporting Information.

[8] Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2417−2420.

[9] Crystal data for $C_{29}H_{40}N_2Cl_5Cu$ ($\mathbf{1}\cdot 2CH_2Cl_2$): monoclinic, space group $P2_1/m$, $a = 9.5298(8)$ Å, $b = 16.3972(14)$ Å, $c = 11.1057(10)$ Å, $\beta = 103.348(1)°$, $V = 1688.5(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.293$ g/cm^3, $F(000) = 684$, $T = 194(2)$ K. Least-squares refinement converged normally with residuals of R1 (based on F) = 0.0655, wR2 (based on F^2) = 0.1651, and GOF = 1.058 based on $I > 2\sigma(I)$.

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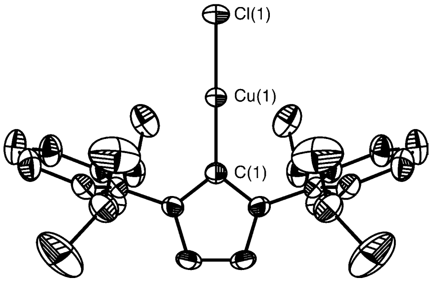

Figure 1. Representation of **1**, shown as 50% ellipsoids. Hydrogen atoms (calculated) and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(1) = 1.881(7), Cu(1)−Cl(1) = 2.106(2); C(1)−Cu(1)−Cl(1) = 176.7(2).

grated when touched, probably $[CuMe]_4$.[10] Prior coordination of the carbene ligand to copper thus appears necessary.

Reaction of free IPr with copper(I) acetate in benzene affords $(IPr)CuO_2CCH_3$ (**2**).[11] The carbonyl resonance in the ^{13}C NMR spectrum (128.9 ppm) is well upfield of other copper(I) acetate carbonyl resonances.[12] Complex **2** crystallizes with two molecules in the asymmetric unit, and slightly different bond distances and angles are obtained for each. In both molecules, the crystal structure[13] reveals a monodentate acetate ligand.[14] This binding mode is noteworthy, as monodentate copper(I) carboxylates are relatively rare.[15]

In the molecule shown in Figure 2, the Cu−O bond distance (1.850(3) Å) is quite close to that of the linear bis(acetato)cuprate(I) anion (1.821(8) Å)[16] and shorter than the Cu^I−O bond distances in three- or four-coordinate monodentate carboxylates.[15] In the other form of **2** (Figure S5),[7] the acetate is somewhat closer to a κ^2-binding mode, with a distortion from linearity about the copper center and a smaller difference between the two copper−oxygen distances. However, the distance from the metal to the proximal oxygen atom (1.924(5) Å) is shorter, and that to the distal oxygen atom (2.673(7) Å) considerably longer, than the corresponding distances in the bidentate acetate $(Ph_3P)_2CuO_2CCH_3$ (2.166(3) and 2.228(3) Å).[17]

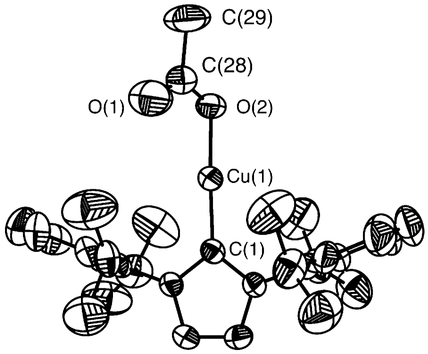

Figure 2. Representation of **2**, shown as 50% ellipsoids. For clarity, hydrogens and solvent are omitted, and only one of the two molecules in the asymmetric unit is shown.[7] Selected interatomic distances (Å) and angles (deg) [corresponding values for the other molecule]: Cu(1)−O(2) = 1.850(3) [1.924(5)], Cu(1)−O(1) = 2.868(4) [2.673(7)], Cu(1)−C(1) = 1.854(4) [1.850(5)], O(1)−C(28) = 1.166(6) [1.157(8)], O(2)−C(28) = 1.280(6) [1.228(8)]; O(2)−Cu(1)−C(1) = 177.19(18) [166.0(2)], O(1)−C(28)−O(2) = 126.2(5) [120.2(8)].

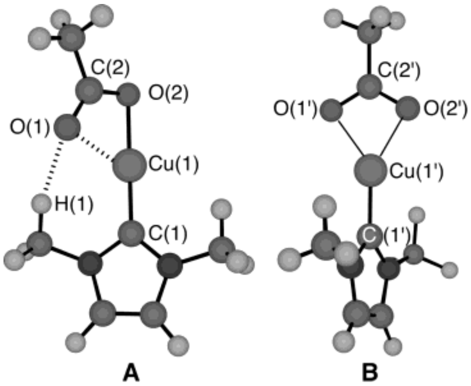

Figure 3. Optimized structures calculated for κ^1- (**A**) and κ^2-acetate (**B**) model complexes. Selected interatomic distances (Å): for **A**, Cu(1)−O(2) = 1.901, Cu(1)−O(1) = 2.251, Cu(1)−C(1) = 1.821, O(1)−H(1) = 2.435, O(1)−C(2) = 1.251, O(2)−C(2) = 1.286; for **B**, Cu(1′)−O(2′) = 2.014, Cu(1′)−O(1′) = 2.039, Cu(1′)−C(1′) = 1.825, O(1′)−C(2′) = 1.268, O(2′)−C(2′) = 1.269.

The relative stabilities of the κ^1- and κ^2-acetate binding modes were explored through DFT calculations on model complexes,[7] in which *N*-methyl groups have replaced the *N*-(2,6-diisopropylphenyl) groups of the carbene ligand in **2**. Figure 3 depicts the optimized geometries of the κ^1complex **A** and κ^2 complex **B**; bonding distances calculated for **A** agree favorably with those determined crystallographically for **2**.[18] Chelated isomer **B** is calculated to be more stable than **A** by 1.1 kcal/mol, but this difference is smaller than the uncertainty of ±5 kcal/mol estimated for the calculation.[19]

In the κ^1 complex **A**, the calculated distance between copper and the distal oxygen atom is 2.251 Å, which is

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[10] (a) Thiele, K.-H.; Koehler, J. *J. Organomet. Chem.* **1968**, *12*, 225−229. See also ref 2c.

[11] Copper(I) acetate (1.06 g, 2.74 mmol) and IPr (0.336 g, 2.74 mmol) were stirred in toluene (25 mL) for 11 h. The resulting solution was filtered through Celite and then concentrated. The crude product was triturated with hexanes (3 × 20 mL) and then dried in vacuo, affording **2** as a white powder; yield 0.777 g (56%).

[12] Taqui Khan, M. M.; Paul, P.; Venkatasubramanian, K.; Purohit, S. *Inorg. Chim. Acta* **1991**, *183*, 229−237. See also ref 15c.

[13] Two molecules of **2** and one benzene molecule were present in the crystallographic asymmetric unit. See Figure S5 in the Supporting Information for the other molecule. Crystal data for $C_{32}H_{42}N_2O_2Cu$ ($\mathbf{2}\cdot 0.5C_6H_6$): monoclinic, space group $P2_1/c$, $a = 17.6693(16)$ Å, $b = 23.498(2)$ Å, $c = 16.4406(15)$ Å, $\beta = 115.716(2)°$, $V = 6150.0(10)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.189$ g/cm^3, $F(000) = 2344$, $T = 193(2)$. Least-squares refinement converged normally with residuals of R1 (based on F) = 0.0628, wR2 (based on F^2) = 0.1408, and GOF = 1.029 based on $I > 2\sigma(I)$.

[14] We are at present uncertain whether this binding mode is preferred in solution. A comparison of asymmetric and symmetric stretching frequencies for the carboxylate moiety in **2** is precluded by strong vibrations arising from the IPr ligand, in the 1400−1500 cm^{-1} region, which mask the peaks calculated for the symmetric vibration in both model complexes **A** and **B**. We thank a reviewer for raising this point.

[15] (a) Darensbourg, D. J.; Larkins, D. L.; Reibenspies, J. H. *Inorg. Chem.* **1998**, *37*, 6125−6128. (b) Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Reibenspies, J. H. *Inorg. Chem.* **1994**, *33*, 531−537. (c) Darensbourg, D. J.; Longridge, E. M.; Holtcamp, M. W.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 8839−8840. (d) Speier, G.; Szabo, L.; Fulop, V. *J. Organomet. Chem.* **1993**, *462*, 375−378.

[16] Darensbourg, D. J.; Longridge, E. M.; Atnip, E. V.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 3951−3955.

[17] Darensbourg, D. J.; Holtcamp, M. W.; Longridge, E. M.; Klausmeyer, K. M.; Reibenspies, J. H. *Inorg. Chim. Acta* **1994**, *227*, 223−232.

[18] All calculated vibrational frequencies for **A** and **B** are real, indicating that both forms represent stable minima.

[19] Himo, F.; Siegbahn, P. E. M. *Chem. Rev.* **2003**, *103*, 2421−2456.

shorter than those found crystallographically for **2** (2.868(4) and 2.673(7) Å). An atoms-in-molecules analysis[20] finds bond critical points between copper and both oxygen atoms in **A**, indicating a bonding interaction between the metal and the distal oxygen, O(1). The same analysis also finds a bond critical point connecting O(1) with a methyl hydrogen 2.435 Å away. No such interaction within the molecule is observed for **2**; however, the extended crystal structure of **2** (Figure S7)[7] shows a 2.238-Å approach (2.347 Å, for the other molecule in the asymmetric unit) of a distal oxygen atom to the calculated position of a carbene backbone hydrogen in an adjacent molecule.[7] The preferential crystallization of the κ^1isomer could conceivably result from this intermolecular stabilization.[21] Vibrational animation finds that a hinging motion of the κ^1-acetate corresponds to a 40.7 cm^{-1} torsional mode, implying that a slight energy input elicits a large distortion.

Addition of Me$_2$AlOEt to **2** in diethyl ether led to clean formation of the two-coordinate methyl complex **3** (Figure 4).[22,23] The Cu−C$_{\mathrm{methyl}}$ distance, 1.913(6) Å, is similar to that found in dimethylcuprates (ca. 1.94 Å),[3a,24] slightly shorter than that of [η^5-(C$_5$H$_4$SiMe$_3$)$_2$-Ti(CCSiMe$_3$)$_2$]CuCH$_3$ (1.966(2) Å),[25] and appreciably shorter than that of (Ph$_3$P)$_3$CuCH$_3$ (2.043(12) Å).[2a]

Exposure of a benzene solution of **3** to ca. 1 atm of CO$_2$ at room temperature afforded (IPr)CuO$_2$CCH$_3$ (**2**) in near-quantitative yield.[26,27] The ^{1}H NMR spectrum of **2** prepared in this manner is identical with that of authentic **2** prepared from IPr and copper(I) acetate.

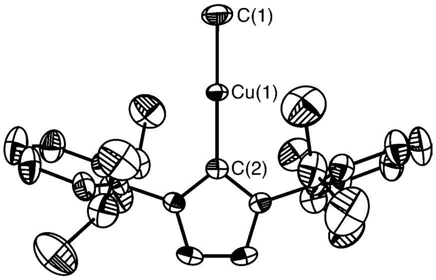

Figure 4. Representation of **3**, shown as 50% ellipsoids; hydrogens and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu−C(1) = 1.913(6), Cu−C(2) = 1.887(5); C(2)−Cu−C(1) = 180.000(1).

In conclusion, an N-heterocyclic carbene ligand supports monomeric, linear complexes of copper(I), including the chloride and the new acetate and methyl complexes. Calculations suggest that the monodentate and bidentate binding modes of acetate are of very similar energies. The neutral, two-coordinate methyl complex **3** reacts readily and cleanly with CO$_2$ to form the acetate. The potential of (NHC)copper(I) complexes to catalyze new carboxylation processes is currently being explored.

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Supporting Information Available: Text, tables, and figures giving synthetic and computational details, spectroscopic data, ^{1}H and ^{13}C NMR spectra for **3**, additional crystal structures, and structural parameters for **1**−**3**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893−928.

[21] We cannot rule out a steric contribution to the monodentate binding of the acetate in crystalline **2**. However, the close approaches of the pendant oxygen atoms to C-bonded hydrogen atoms (see Figure S7 in the Supporting Information), despite being able to rotate away from them, indicate that the observed interactions are attractive, not repulsive. Moreover, using a crude model derived from the crystal structure of **2**, we estimate that the intramolecular approaches of the acetate oxygen atoms to the ligand alkyl groups would be closer in an alternative κ^2-bound form but longer than the intermolecular approaches in the actual structure. We thank a reviewer for raising this point.

[22] Dimethylaluminum ethoxide, generated in situ from trimethylaluminum (2.0 mmol) and ethanol (0.117 mL, 2.0 mmol) in toluene/diethyl ether solution (1:1, 2 mL), was transferred by cannula to a −45 °C suspension of **2** (0.396 g, 0.776 mmol) in diethyl ether (3 mL). The reaction mixture was warmed gradually to room temperature with stirring over 4 h and then concentrated to afford a crude yellow solid. This solid was taken up in hexanes (5 mL), and the precipitate was collected by filtration and washed repeatedly with hexanes. Yield: 0.256 g (71%).

[23] Crystal data for C$_{33}$H$_{39}$N$_2$Cu (**3**·C$_5$H$_{12}$ (pentane hydrogens not calculated)): monoclinic, space group $C2/c$, a = 22.561(3) Å, b = 9.4266(12) Å, c = 16.890(2) Å, β = 116.117(2)°, V = 3225.3(7) Å^3, Z = 4, ρ_{calcd} = 1.086 g/cm^3, F(000) = 1120, T = 193(2). Least-squares refinement converged normally with residuals of R1 (based on F) = 0.0869, wR2 (based on F^2) = 0.1758, and GOF = 1.158 based on $I > 2\sigma(I)$.

[24] Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337−4338.

[25] Janssen, M. D.; Kohler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817−4829.

[26] A solution of **3** (0.0683 g, 0.147 mmol) in benzene (4 mL) was frozen at −78 °C in the dark. The reaction vessel was evacuated and back-filled with carbon dioxide (ca. 1 atm). The reaction mixture was then thawed, warmed to room temperature, and stirred for 18 h. Concentration in vacuo afforded a tan powder; yield 72.1 mg (96%).

[27] The carboxylation of **3** was also monitored by ^{1}H NMR (in C$_6$D$_6$ solution at ambient temperature, under 1 atm of CO$_2$) and judged to be 50% complete after 65 min and 95% complete after 2.5 h.