

Amidines as Effective Ancillary Ligands in Copper-catalyzed Hydrogenation of Carbon Dioxide

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Mononuclear Cu(II) complexes bearing a bidentate bisamidinate ligand were newly synthesized and characterized. The catalytic activity was evaluated in the hydrogenation of carbon dioxide to formate salts. A substantial enhancement of the catalyst turnover number was achieved by the imidazoline-based complex, indicating that amidines serve as effective ancillary ligands for homogeneous copper catalysis.

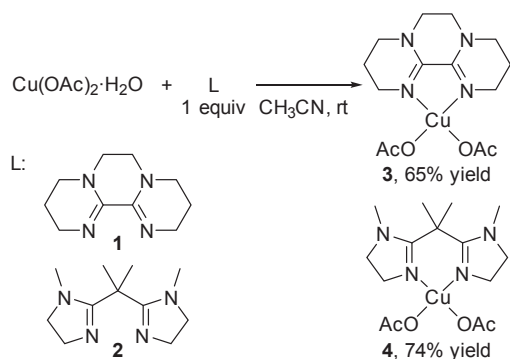
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Carbon dioxide (CO₂) utilization driven by redundant renewable energy sources has drawn increasing attention to attaining net zero carbon emissions in the near future.¹ Hydrogenation of CO₂ is one of the most promising and significant ways directed toward large-scale applications.² Recently, earth abundant first-row transition metals, such as Mn, Fe, Co, Ni, and Cu, have emerged as alternatives to the well-established hydrogenation catalysts based on precious metals.³ For example, the rational design of Fe catalysts contributed to achieve excellent turnover number (TON) of 58990 in the hydrogenation of CO₂ to formate salts.⁴

In this context, we have disclosed the potential of homogeneous copper catalysts to promote the hydrogenation of CO₂.⁵ Among the base additives tested, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) specifically assisted to exert the catalytic function, even though homogeneous copper catalysts were considered to be less effective for the CO₂ hydrogenation than other 3d metals.⁶ The combined use of Cu(OAc)₂ and DBU with a molar ratio of 1:500 led to a satisfactory TON up to 167. Aside from a primary role in trapping the formic acid product as its salt, we conceived that DBU can behave as a supporting ligand to form a DBU-Cu species. Actually, we identified the first DBU-ligated copper complex, (dbu)₂CuI, which showed a decent activity for the CO₂ hydrogenation. In the subsequent studies, analogous marked enhancement by addition of DBU was observed in the CO₂ hydrogenation with phosphine- and cyclic (alkyl)(amino)-carbene (CAAC)-Cu complexes. Appel and co-workers reported that a tridentate phosphine-Cu complex, [(triphos)Cu(CH₃CN)]-[PF₆] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane), effectively catalyzed the formate synthesis with TONs up to 500.⁷ The roles of DBU were proposed to promote heterolytic cleavage of H₂ and to suppress the formation of catalytically inactive dinuclear copper species by its reversible coordination.⁸ Bertrand's group achieved the best catalytic activity in the Cu-catalyzed hydrogenation by combination of a CAAC-Cu complex and tris(pentafluorophenyl)borane (TON = 1881).⁹ A frustrated Lewis pair-like activation of H₂ by DBU and the borane was considered to be conducive to the formation of copper hydrides and formates.¹⁰

The involvement of DBU-coordinated copper species in the hydrogenation step was not postulated in either system; however, the catalytic activity of copper hydrides is possibly evoked by coordination of the amidine structure, as studied previously in the heterogeneous C=O bond hydrogenation using copper nanoparticles supported by polystyrene-bound DBU.¹¹ Considering that amidines have rarely been utilized as competent ligands in transition metal catalysis,¹² we envisioned that molecules containing proximal amidine units will behave as rigid and viable ligands suited for Cu-based catalysis. In this context, Iwasawa and co-workers reported the oxidative coupling of CO₂ with alkynes or allenes using a stoichiometric amount of bisamidinate-Ni(0) species.¹³ Recently, Onishi, Himeda, and co-workers demonstrated that the catalytic hydrogenation of CO₂ was accelerated by a Cp*Ir complex bearing a bisimidazoline, 4,4',5,5'-tetrahydro-1*H*,1'*H*-2,2'-biimidazole.¹⁴ Herein, we report the synthesis of novel copper complexes with a bidentate bisamidinate ligand and their catalytic activities in the CO₂ hydrogenation.

We targeted bisamidines (Scheme 1), which are accessible in a single step from commercially available materials. In a reported work by Weisman and Wong,¹⁵ the tricyclic bisamidinate (**1**) derived from dithiooxamide and *N,N'*-bis(3-aminopropyl)-1,2-ethylenediamine reacted with Cu(ClO₄)₂, to form dicationic bis- and tris-chelate complexes with an appropriate bite angle. A propylidene-linked bis(1-methylimidazoline)¹³ (**2**) was conveniently obtained from dimethylmalononitrile with 2 equiv of a monotosylate salt of *N*-methylethylenediamine with modification of the reported procedure for synthesis of polymethyl-ene-linked bisimidazolines (see the Supporting Information).¹⁶ Treatment of an acetonitrile solution of Cu(OAc)₂·H₂O with 1 equiv of the bisamidinate followed by crystallization from CH₂Cl₂/Et₂O gave blue crystals of the expected mononuclear



Scheme 1. Synthesis of bis(acetato)copper(II) complexes bearing a bidentate bisamidinate ligand.

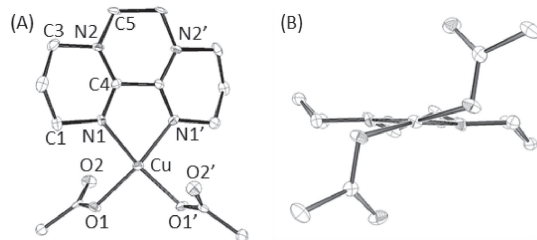


Figure 1. ORTEP drawings of the Cu complex **3** (A: top view, B: front view). The asymmetric unit contains only one-half of the molecule. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Cu–N1, 1.974(5); Cu–O1, 1.961(4); N1–Cu–N1', 81.3(2); O1–Cu–O1', 93.96(15); N1–Cu–O1, 93.71(18); N1–Cu–O1', 166.15(10); Cu–N1–C1, 126.4(3); Cu–N1–C4, 115.0(5); C1–N1–C4, 118.3(4); C3–N2–C4, 119.8(4); C3–N2–C5, 116.8(4); C4–N2–C5, 119.8(5).

Cu(II) complexes (**3** and **4**) in reasonable yields of 65% and 74%, respectively.

The isolated complexes were characterized by elemental analysis or high-resolution mass spectroscopy as well as X-ray crystallography.¹⁷ As shown in Figures 1 and 2, the crystal structures revealed that these Cu(II) complexes adopt a slightly twisted square-planar geometry around the metal bonded to two neutral imine nitrogen atoms of the cyclic amidines and two oxygen atoms of the acetato group in a κ^1 -coordination mode. Sums of the angles around the Cu atom are 362.7° for **3** and 365.0° for **4**, displaying a moderate distortion from planarity. Comparison of the four-coordinate geometry index τ_4 , which can range from an ideal square planar arrangement ($\tau_4 = 0$) to a tetrahedral structure ($\tau_4 = 1$),¹⁸ indicates that **4** ($\tau_4 = 0.25$) has a more distorted geometry, compared to **3** ($\tau_4 = 0.20$). The complex **3** crystallized in the space group $C2$ and contains half of the molecule in the asymmetric unit. The structure of **3** exhibits a C_2 symmetry represented by an enantiomerically pure conformer, as seen in the front view of Figure 1(B). The near coplanarity of bonds at the coordinating nitrogen atoms for **3** was indicated by the sum of the bond angles being 359.7°, whereas **4** showed a bent structure, as seen in the side view of Figure 2(B). The average sum of the bond angles around the sp^2 nitrogen atoms is 357.3°, that is in accord with the pyramidalized configuration. The non-conjugated bisamidine ligand in **4** possibly offers a stronger σ -donation to the Cu atom.

The isolated complexes were applied to the hydrogenation of CO₂ to formate salts in the presence of a base, as summarized in Table 1. We initially examined the effect of bisamidine ligands on the catalytic activities by comparison with the hydrogenation using Cu(OAc)₂·H₂O (Entry 1). Both complexes catalyzed the formate production using a 2.0 M solution of DBU in 1,4-dioxane with a DBU/catalyst ratio of 500 at 100 °C under a mixture of CO₂ (30 atm) and H₂ (30 atm) for 21 h (Entries 2 and 3). The TON for **3** and the yield of formate based on the added DBU were 81 and 16%, respectively, displaying a lower catalytic activity than that of Cu(OAc)₂·H₂O (TON = 163 and 32% yield).⁵ In contrast, the hydrogenation was surely enhanced in the presence of **4** to attain the TON of 210 (Entry 3). Presumably, the relatively strong electron-donating ability of the

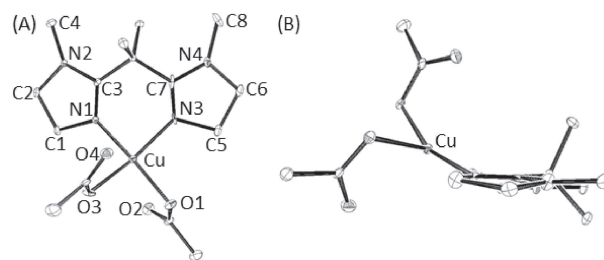


Figure 2. ORTEP drawings of the Cu complex **4** (A: top view, B: side view). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Cu–N1, 1.944(4); Cu–N3, 1.963(5); Cu–O1, 1.967(4); Cu–O3, 1.977(4); N1–Cu–N3, 87.74(19); O1–Cu–O3, 90.35(19); N1–Cu–O3, 92.50(19); N3–Cu–O1, 94.42(19); N1–Cu–O1, 165.5(2); N3–Cu–O3, 159.9(2); Cu–N1–C1, 123.2(4); Cu–N1–C3, 127.5(3); C1–N1–C3, 108.1(4); Cu–N3–C5, 120.3(4); Cu–N3–C7, 127.2(4); C5–N3–C7, 108.3(5); C2–N2–C3, 109.3(5); C2–N2–C4, 117.9(4); C3–N2–C4, 132.2(5); C6–N4–C7, 109.3(5); C6–N4–C8, 118.3(5); C7–N4–C8, 132.5(6).

Table 1. Cu-catalyzed hydrogenation of CO₂ to formate.^a

CO ₂ + H ₂ + base $\xrightarrow[1,4\text{-dioxane, 21 h}]{\text{Cu cat}}$ [base-H] ⁺ [HCO ₂] ⁻							
Entry	Cat	Base	Base/Cat	<i>P</i> [atm] ^b	<i>T</i> [°C]	Yield [%] ^c	TON
1	Cu(OAc) ₂ ·H ₂ O	DBU	500	30/30	100	32	163
2	3	DBU	500	30/30	100	16	81
3	4	DBU	500	30/30	100	41	210
4	4	DBU	500	30/30	80	12	65
5	4	DBU	500	20/40	100	46	239
6	4	DBU	500	10/50	100	39	212
7	4	NEt ₃	500	20/40	100	<1	<1
8	4	BTMG	500	20/40	100	<1	<1
9	4	TBD	500	20/40	100	19	95
10 ^d	4	KO ^t Bu	250	20/40	100	5	27
11	4	DBU	40000	20/40	100	4	1660

^aReaction conditions: base (10 mmol), 1,4-dioxane (5.0 mL), 21 h. ^b $P(\text{CO}_2)/P(\text{H}_2)$. ^cMolar ratios of the product/initial DBU determined by ¹H NMR. ^dKO^tBu (5 mmol).

non-conjugated bisamidine contributed to the superior formate productivity.¹⁹ Although the hydrogenation at a lower reaction temperature of 80 °C decreased the yield to 12% (Entry 4), reduction of the CO₂ partial pressure had a positive influence on the catalytic performance of **4**. Among the reactions under a total pressure of 60 atm, a $P(\text{CO}_2)/P(\text{H}_2)$ ratio of 20/40 provided an optimal TON of 239 (Entry 5).

Changing the additive base from DBU to triethylamine and a sterically hindered guanidine, 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (BTMG), hampered the formate synthesis and resulted in formation of copper precipitates after the hydrogenation (Entries 7 and 8). The use of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was effective for the formate synthesis, affording a moderate TON of 95 (Entry 9). A strong solid base, KO^tBu, did not exhibit promotional effects (Entry 10), possibly due to a

rapid formation of KOCO_2^tBu from CO_2 . Further optimization of the hydrogenation catalyzed by **4** at low catalyst concentration with a DBU/Cu ratio of 40000 reached a maximum TON of 1660 (Entry 11), which is comparable to the Bertrand system comprised of CAAC-Cu species and tris(pentafluorophenyl)borane.⁹ Although the beneficial effect of DBU underlies the CO_2 hydrogenation in analogy with Appel's⁷ and our⁵ previous systems, the marked catalytic performance of **4** surpassing the original DBU-Cu catalysts clearly indicates that the amidines play a pivotal role as the supporting ligand during the H_2 and CO_2 activation processes.

In conclusion, we have developed novel mononuclear copper complexes bearing a bidentate amidine ligand as catalyst precursors for CO_2 hydrogenation using DBU. The complex **4** with a non-conjugated bis(1-methylimidazoline) chelate showed a satisfactory activity and achieved the optimal TON of 1660, due to the relatively strong σ -donating ability of the amidine unit to enhance the hydricity of catalytic species. This work opens up the potential applications of bidentate amidine ligands to extensive Cu-promoted reactions. Further studies on the rational design of multidentate amidines compatible with transition metal catalysts are in progress in our laboratory.

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Supporting Information is available on <https://doi.org/10.1246/cl.190873>.

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