

Low-Valent Cobalt(I) CNC Pincer Complexes as Catalysts for Light-Driven Carbon Dioxide Reduction

Chance M. Boudreaux, Dinesh Nugegoda, Wenzhi Yao, Nghia Le, Nathan C. Frey, Qing Li, Fengrui Qu, Matthias Zeller, Charles Edwin Webster,* Jared H. Delcamp,* and Elizabeth T. Papish*



Cite This: *ACS Catal.* 2022, 12, 8718–8728



Read Online

ACCESS |



Metrics & More



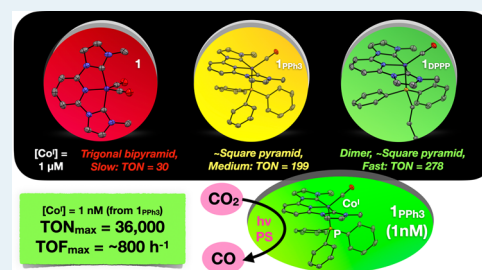
Article Recommendations



Supporting Information

ABSTRACT: Durable catalysts based on abundant metals are needed for the photocatalytic CO₂ reduction reaction (PCO₂RR). Thus, we synthesized a series of low-valent cobalt(I) complexes, [(CNC)Co(CO)₂]⁺[Co(CO)₄][−], with H (1_{C6}) or OMe (2_{C6}) in the 4-position of the pyridyl N donor group (where CNC = L1 and L2 from double deprotonation of the [CNC]²⁺ preligands L1(HOTf)₂ = 1,1'-(pyridine-2,6-diyl)bis(3-methyl-1H-imidazol-3-ium) ditriflate and L2-(HOTf)₂ = 1,1'-(4-methoxypyridine-2,6-diyl)bis(3-methyl-1H-imidazol-3-ium) ditriflate). Anion exchange for [BARF₂₄][−] (tetrakis(3,5-trifluoromethyl)phenyl)borate) produced 1 and 2 and phosphine substitution produced 1_{PMe3}, 1_{PPh3}, and 2_{PPh3} complexes with the structure [(CNC)Co(CO)(PR'₃)]⁺[BARF₂₄][−]. In 1_{DPPP}, the DPPP ligand bridges two Co(I) centers (DPPP = 1,3-bis(diphenylphosphino)propane). All complexes were fully characterized, and electrochemical measurements suggest that for most of the phosphine complexes, CO₂ binding by the complex occurs prior to reduction due to a vacant coordination site. Intriguingly, the introduction of a phosphine ligand resulted in a geometry change from trigonal bipyramidal to square pyramidal which correlates to preassociation of CO₂ to the complex and higher reactivity in the PCO₂RR. Complexes 1, 1_{PMe3}, 1_{PPh3}, 1_{DPPP}, 2, 2_{PPh3}, and Na[Co(CO)₄] are PCO₂RR catalysts with a methoxy substituent deactivating and a phosphine ligand activating. With monodentate phosphines, catalyst 1_{PPh3} (1 μM) had the highest turnover frequency (TOF_M = 3.9 h^{−1}) and turnover number (TON = 199). The dinuclear 1_{DPPP} complex was the most active and robust catalyst with TON = 278 and TOF = 21.1 h^{−1} at 1 μM loading. Under dilute conditions (1 nM), 1_{PPh3} produced up to 36,000 TON with TOF = ~800 h^{−1} over 6 days, which shows that this is a durable molecular catalyst acting with fast rates in the PCO₂RR. Thus, stabilizing low-valent cobalt can offer a unique entry point to highly active PCO₂RR catalysts. While cobalt(I) has been proposed as a catalytic species, catalysts that start from Co(I) have not been made previously and the use of phosphine co-ligands has allowed these catalysts to achieve high activity.

KEYWORDS: photocatalysis, cobalt, pincer ligands, carbon dioxide reduction, phosphine ligands, N-heterocyclic carbenes, organometallic compounds

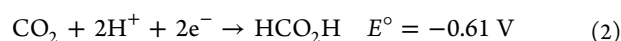
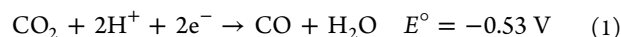


INTRODUCTION

Fossil fuels are a nonrenewable source of energy, and replacing these fuels with solar fuels will require catalysis.¹ The reduction of carbon dioxide (CO₂) could allow for the use of our current fuel infrastructure in a renewable carbon neutral cycle.² A key piece of such a process is the source of energy to power the reduction. The photocatalytic CO₂ reduction reaction (PCO₂RR) is a potential key reaction for obtaining a carbon neutral cycle. The supply of solar energy is vastly greater than our world's current consumption and can provide a sustainable energy source.

The direct one-electron reduction of CO₂ is very energy-intensive, at −1.9 V vs normal hydrogen electrode (NHE).^{3,4} Therefore, the reduction of CO₂ usually occurs by proton coupled electron transfer (PCET) due to the decreased energy requirement of this pathway.^{2,5–8} With both protons and electrons available, the reduction potential for CO₂ conversion

to CO is −0.53 V (eq 1) and −0.61 V for HCO₂H formation (eq 2) (both potentials are vs NHE).⁹

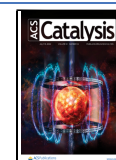


Proton reduction to form H₂ (E° = −0.414 V) is often competitive with these processes.^{2,10} Thus, product selectivity among these commonly formed products (CO, HCO₂H, and H₂) is an important consideration.^{11–26} Homogeneous catalysis can often address this selectivity challenge by precise

Received: March 14, 2022

Revised: June 8, 2022

Published: July 6, 2022



control of the catalyst structure and uniform control of reaction conditions.²⁷ Targeting CO can lead to a viable solution for fuel production via the well-established Fischer–Tropsch process (FTP) and allows for simple gas phase separation of the CO product from the reduction reaction solution.^{2,28}

In 1993, Fujita and co-workers were the first to demonstrate that cobalt(III) cyclam complexes have activity in PCO₂RR with selective reduction of CO₂ to CO.^{15,29} This discovery initiated a focus on cobalt by many research groups (Figure 1).^{12,19,30–37} Notably, a pentadentate N₅ donor in Lit-1

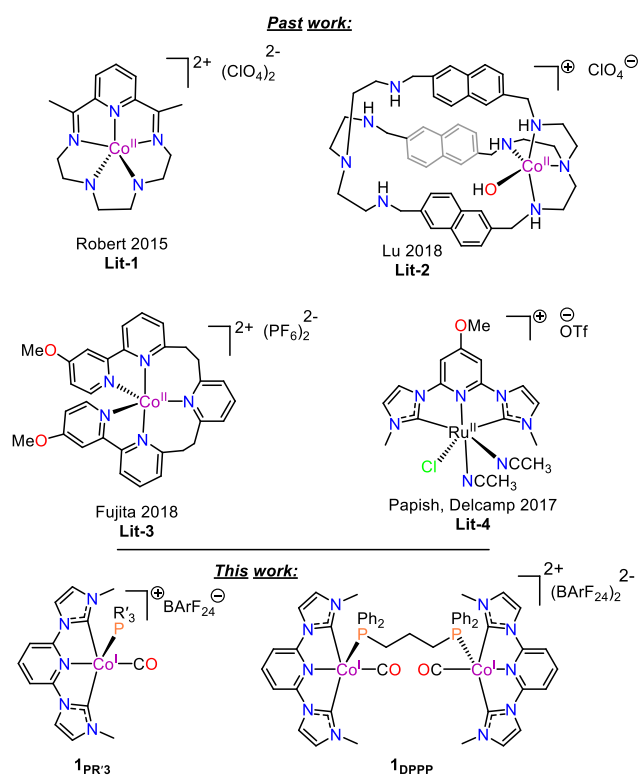


Figure 1. Selected literature catalysts for photocatalytic CO₂ reduction featuring Co(II) and Ru(II). In this work, we use Co(I) catalysts shown above, with the best catalysts including phosphine ligands.

supports the formation of CO (TON = 270) with cobalt(II).⁶ Likewise, a cobalt(II) cryptate complex (Lit-2) is highly robust in the PCO₂RR to give CO (TON as high as 51,392).³¹ Catalyst Lit-3 with a pentadentate N₅ donor ligand chelating Co(II) demonstrates that methoxy substituents (relative to the H analogues) serve to increase CO production.³⁷ Similarly, in Ru(II) CNC pincer complexes methoxy groups led to substantial improvements in PCO₂RR with catalyst Lit-4 relative to the analogue bearing an H in place of methoxy (TON = 1006 vs 120, respectively).^{17,18,26,27} These differences were attributed to more favorable reduction potentials with methoxy groups for electron transfer from the reduced photosensitizer (PS) to the catalyst.¹⁷ The strong donor properties of the NHC rings^{38,39} combined with an electronically tunable pyridine ring presents a unique opportunity for catalysis with cobalt.^{40,41}

However, the use of Co(II) or Co(III) with CNC pincer ligands leads to the formation of bis ligand complexes (e.g., [(CNC)₂Co]³⁺).⁴² There are two basic strategies to prevent

the formation of bis(ligand) complexes. The first strategy is to rely on steric bulk (typically via mesityl or 2,6-diisopropylphenyl wingtip substituents on the NHC) to form 1:1 complexes between CNC or CCC ligands and Co(II) or Co(III).^{43–45} The second strategy, which is used herein, relies upon a low-valent Co(I) to favor a lower coordination number. There is precedence in the literature for taking the latter approach, and Co(I) tends to favor four- and five-coordinate complexes.^{37,44,46–49} Furthermore, the catalytic cycle for CO₂ reduction is believed to access Co(I) intermediates,^{50,51} and access to a Co(I) species during catalysis is proposed to influence product selectivity.⁵² However, the impact of choosing a ligand set which stabilizes Co(I) has not been explored in the PCO₂RR because most, if not all, cobalt catalysts used in this reaction feature Co(II) or Co(III).^{15,29} To the best of our knowledge, Co(I) starting materials have been used for stoichiometric but not catalytic CO₂ reduction.⁵³

In this report, a series of Co(I) CNC pincer complexes were synthesized and studied for the activation of CO₂ (Figure 2). The Co(I) complexes are all five-coordinate with a tridentate pincer ligand and two supporting monodentate ligands. Complex 1 is the parent complex [(CNC)Co(CO)₂]⁺ and phosphine substitution of one of the CO groups gives two derivatives (1_{PPh₃}, 1_{PMe₃}) (Table 1). Herein, phosphine substitution is used to easily achieve a range of complexes with more electron donating (PMe₃) compared to less electron donating (PPh₃) phosphines. We note that a wide range of phosphines can rapidly be explored with this ligand manifold. A bidentate phosphine, 1,3-bis(diphenylphosphino)propane (DPPP), leads to a dicobalt(I) complex with DPPP bridging two metal centers in 1_{DPPP}. Methoxy substitution on the CNC pyridine ring gives complex 2 as a derivative of 1. Phosphine substitution of a CO on 2 leads to 2_{PPh₃}. These modifications have allowed us to study structure–function relationships in the PCO₂RR starting from Co(I) as a unique way to access the catalytic cycle through Co(I) complexes that are more similar to the active catalyst species than has been done in the literature.

RESULTS AND DISCUSSION

Synthesis. The synthesis of the cobalt(I) complexes starts with the deprotonation of the previously synthesized bis imidazolium salts (L1(HOTf)₂ and L2(HOTf)₂)^{17,18} with triethylamine (TEA) as the base in the presence of Co₂(CO)₈ (Figure 3). The cobalt(0) source undergoes a disproportionation reaction in ~50% yield producing a CNC pincer bound Co(I) cation and a Co¹⁻ anion as [Co(CO)₄]⁻, which is observed by FTIR.^{54,55} Thus, 1_{Co-} and 2_{Co-} are formulated as [(L1)Co(CO)₂][Co(CO)₄]⁻ and [(L2)Co(CO)₂][Co(CO)₄]⁻ (for L1: R = H and for L2: R = OMe), respectively, and their structures have been confirmed crystallographically. To avoid the presence of two unique cobalt ions in the PCO₂RR, salt metathesis was performed with the sodium salt of Kobayashi's anion, tetrakis(3,5-trifluoromethyl)phenylborate (BARF₂₄)⁻, producing complexes 1 and 2. To further modulate the activity of these complexes, one carbonyl was substituted with PPh₃ or PMe₃. The ligand substitution was achieved in nearly quantitative yields by introducing the Co(I) pincer complex to excess PR'₃ in dichloromethane producing complexes 1_{PMe₃}, 1_{PPh₃}, and 2_{PPh₃}. The bisphosphine DPPP was added to complex 1, leading to DPPP bridging two Co(I) centers rather than displacing two carbonyl ligands on a single cobalt(I) center regardless of the ratio of DPPP to 1 employed.

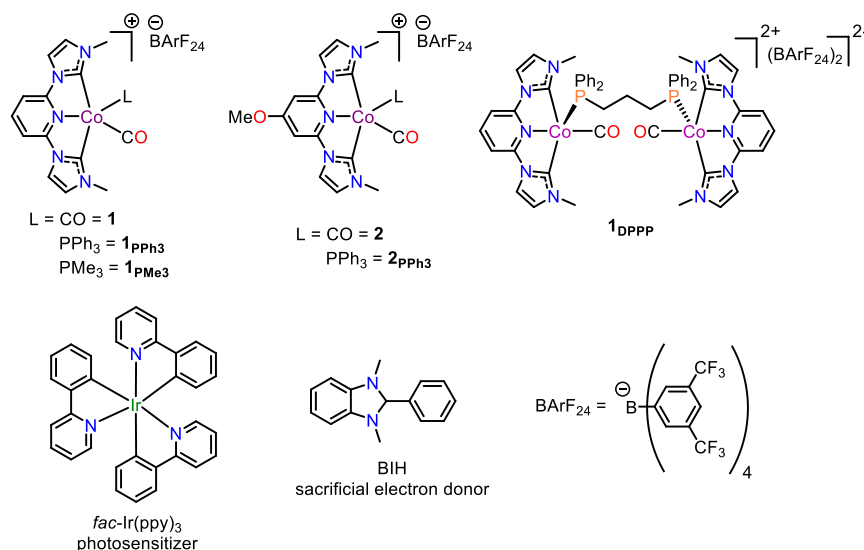


Figure 2. Structures of the six new Co(I) complexes used herein, the photosensitizer (tris(2-phenylpyridine)iridium(III) = *fac*-(Ir(ppy)₃)), and the sacrificial donor (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]-imidazole = BIH).

Table 1. Cobalt(I) Complexes Designated Labeling Scheme^a

compound designation	R	co-ligands	anion
1 _{Co-}	H	CO, CO	[Co(CO) ₄] ⁻
2 _{Co-}	OMe	CO, CO	[Co(CO) ₄] ⁻
1	H	CO, CO	[BArF ₂₄] ⁻
2	OMe	CO, CO	[BArF ₂₄] ⁻
1PPh ₃	H	CO, PPh ₃	[BArF ₂₄] ⁻
1PMe ₃	H	CO, PMe ₃	[BArF ₂₄] ⁻
1DPPP	H	CO, PPh ₂ (CH ₂) ₃ PPh ₂	[BArF ₂₄] ⁻
2PPh ₃	OMe	CO, PPh ₃	[BArF ₂₄] ⁻

^aAll reported complexes are monomers with the structure below (left), except 1DPPP, which is a phosphine bridged dimer (right).

Single Crystal X-ray Diffraction. Crystals suitable for X-ray diffraction were grown by evaporation of CH₂Cl₂ (for 1_{Co-} and 2_{Co-} in the SI as Figure S36), by evaporation of diethyl ether (for 1 and 2), or from a concentrated solution of diethyl ether layered with hexanes (for 1PPh₃, 1PMe₃, 2PPh₃, and 1DPPP). The latter six structures are shown in Figure 4. In each structure, the Co(I) center is five-coordinate with a tridentate CNC pincer and two monodentate ligands. Addison's τ_5 parameter is used to measure geometric distortion with extreme values of 0 = square pyramid and 1 = trigonal bipyramid.⁵⁶ The τ_5 values for complexes 1_{Co-}, 2_{Co-}, 1, and 2 are ~0.53–0.55, which results from a distorted trigonal bipyramid geometry with the pincer ligand restricting the C1–Co1–C11 angle to ~159° (see Table 2, Figure 4, and the SI). However, the geometric distortion is not toward a square pyramid, because neither carbonyl ligand lies in or near the plane of the pincer ligand. Upon PPh₃ substitution for a CO ligand, the geometry changes to a distorted square pyramid for 1PPh₃ and 2PPh₃ with the phosphine apical and τ_5 ~ 0.3. Herein,

the N3–Co1–C14 angle (~139–142°) is larger than in 1 and 2, and the CO ligand is nearly coplanar with the pincer ligand. The steric bulk of the PPh₃ ligand seems to prevent an idealized square pyramidal geometry. The bis(phosphine) complex, 1DPPP, is also a distorted square pyramidal structure with a τ_5 of 0.301. Complex 1PMe₃ is nearly square pyramidal with τ_5 = 0.127 and N3–Co1–C14 angle of 151.20(6)°.

The bond distances and angles are similar for 1, 2, and their cobaltate analogues 1_{Co-} and 2_{Co-}, which shows that the cobalt anion in the latter structures does not alter the structure of the cobalt cations. The bond distances around cobalt shown in Table 2 show that phosphine substitution for CO results in shorter Co–C and Co–N distances. For complexes 2_{Co-}, 2, and 2PPh₃, the average C6–O bond length is ~1.35 Å, indicating a structure with significant double bond character due to π donation from the methoxy substituent. The effects of the methoxy groups are also observed in the slightly elongated averaged C6–C5 and C6–C7 bonds (1.381(6) Å in 1 vs 1.404(4) Å in 2). These trends reflect partial dearomatization of the pyridyl ring as seen in other Ru(II) pincer complexes with oxygenated substituents.^{17,18} The carbonyl ligands of 1 and 2 have Co–C and C–O average bond lengths of 1.775(4) and 1.145(4) Å, respectively, which reflects a high degree of π -backbonding.⁵⁷ This observation is expected due to the electron-rich nature of Co(I) and the highly electron donating carbenes in the pincer. Within the phosphine ligated complexes, the carbonyl C14–O1 bond lengthens and there is a noticeable contraction of the Co1–C14 bond showing an increase in π -backbonding from the metal center as compared to the dicarbonyl series.

Vibrational Spectroscopy. FTIR spectroscopy confirms the presence of the [Co(CO)₄]⁻ anion in complexes 1_{Co-} and 2_{Co-} (Table 3). The IR spectra of the anion displays a large and broad peak between 1844 and 1870 cm⁻¹ (see Figures S3 and S25 in the SI).^{54,55,58} The dicarbonyl ligand stretches of the Co(I) complexes were also observed as sharper peaks at higher energy (e.g., 2001 and 1952 cm⁻¹ for 1_{Co-} and typically falling from 1944 to 2025 cm⁻¹ for 1, 2, and 2_{Co-}). These Co(I) cations have C_{2v} symmetry, and the peak at 2000–2025 cm⁻¹ is of lower intensity and has been tentatively assigned as an A₁ symmetric stretch while the peak at 1944–1968 cm⁻¹ is of

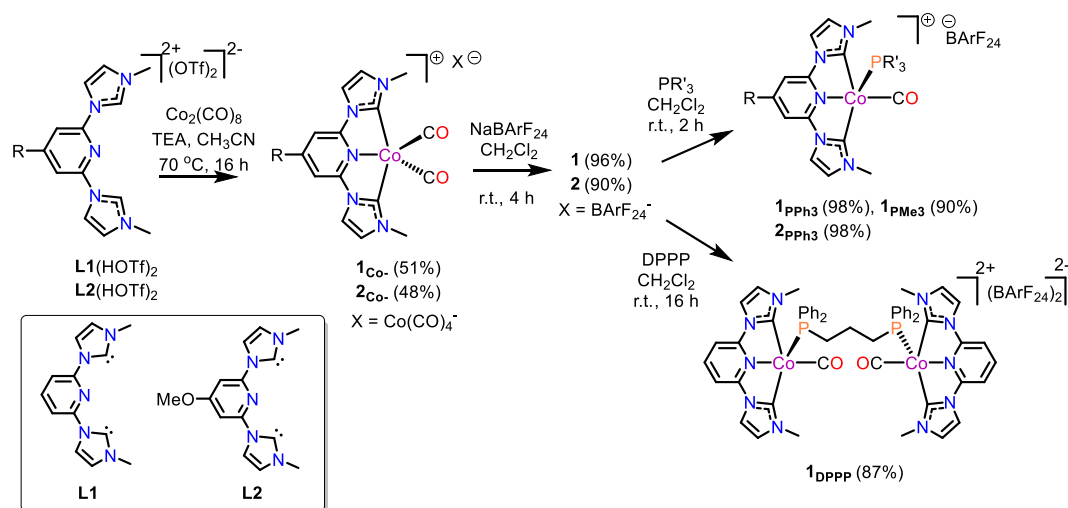


Figure 3. Synthetic scheme for the formation of the cobalt(I) complexes reported herein. Complexes of type **1** use $\text{R} = \text{H}$ on the pyridine ring of the CNC ligand (**L1**) and complexes of type **2** use $\text{R} = \text{OMe}$ in this position (**L2**). Preligands **L1** and **L2** were previously reported, and detailed procedures can be found in the [Supporting Information](#).^{17,18}

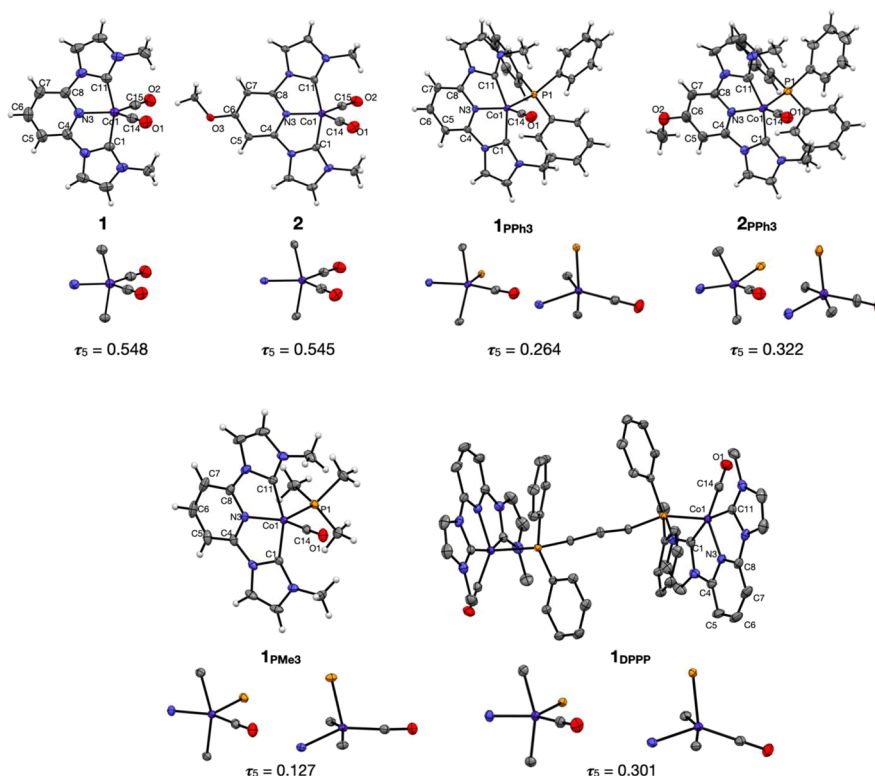


Figure 4. Molecular diagram of the cobalt(I) complexes based on crystallographic data with solvent molecules (for **1PMe₃**), hydrogen atoms (for **1DPPP**), and the BARF_{24} anions removed in all cases for clarity. Coordination sphere views are also shown along with the τ_s parameter. Thermal ellipsoids are drawn at the 50% probability level.

greater intensity and assigned as a B_2 asymmetric stretch.⁵⁹ These peaks shift to higher energy upon exchange of the cobaltate anion for the BARF_{24} anion. Complex **2** shows that the OMe group on the pincer leads to slightly weaker carbonyl stretches (cf. **1**) due to increased d to π^* -back-donation and weakening of the C–O bond due to the higher electron density at the metal in **2** vs **1**. In the phosphine series, the Co(I) cation has approximate C_s symmetry, and the observed carbonyl stretch is from an A' vibrational mode. The A' stretches are also quite intense, like the B_2 vibrational modes

since the motion leads to a strong change in dipole moment. The A' stretch occurs at a significantly lower frequency (cf. A_1 and B_2) because the remaining carbonyl is the only π -acceptor. Complexes **1PPh₃** and **1DPPP** show the same CO stretching frequency, indicating that any electronic changes are minimal. However, the electron donating phosphine (PMe_3) produces a CO stretch of 1932 cm^{-1} indicating increased electron density at the metal center in **1PMe₃**. Similarly, **2PPh₃** shows the impact of the methoxy group on the pincer for increasing the electron density at the metal center via π donation with a CO stretch of

Table 2. Selected Bond Lengths, Angles, and τ_5 Parameter for Co(I) complexes^a

designation	1	1 _{PPh3}	1 _{PMe3}	1 _{DPPP}	2	2 _{PPh3}
bond angles (°)						
N3–Co1–C _{NHC} -avg	79.4(1)	79.70(8)	79.90(8)	79.85(7)	79.3(1)	79.7(3)
N3–Co1–C _{CO} -avg	125.4(1)	142.48(6)	151.20(6)	141.26(5)	125.2(1)	139.3(2)
N3–Co1–P1		105.42(4)	101.42(4)	102.15(3)		106.7(1)
C14–Co1–L ^b	109.2(2)	112.08(5)	107.38(5)	116.57(5)	109.7(1)	114.0(2)
C1–Co1–C11	158.8(1)	158.30(6)	158.79(6)	159.34(5)	158.6(1)	158.6(2)
τ_5	0.548	0.264	0.127	0.301	0.545	0.322
bond lengths (Å)						
Co1–C _{NHC} -avg	1.922(4)	1.909(2)	1.892(1)	1.897(1)	1.914(3)	1.899(6)
Co1–N3	1.916(3)	1.900(1)	1.892(1)	1.9014(9)	1.918(2)	1.914(4)
Co1–C _{CO} -avg	1.775(4)	1.741(1)	1.739(2)	1.740(1)	1.775(4)	1.727(4)
Co1–P1		2.2428(5)	2.2150(5)	2.2173(7)		2.248(1)
C–O _{CO} -avg	1.145(6)	1.153(2)	1.154(2)	1.154(1)	1.144(6)	1.164(6)

^aAverages are used when applicable. ^bL = C15 or P1 depending on respective metal bounded atom.

Table 3. Carbonyl Stretching Frequencies Collected via FTIR-ATR for Co(I) Complexes and [Co(CO)₄]^{–a}

complex	cation carbonyl frequencies [cm ^{–1}]	anion carbonyl frequencies [cm ^{–1}]	computed CO frequency [cm ^{–1}]
1 _{Co}	2001 (A ₁), 1952 (B ₂)	1852	
1	2025 (A ₁), 1968 (B ₂)		2086, 2037
1 _{PPh3}	1942 (A')		2003
1 _{PMe3}	1932 (A')		2000
1 _{DPPP}	1942 (A')		2003
2 _{Co}	2005 (A ₁), 1944 (B ₂)	1870	
2	2011 (A ₁), 1958 (B ₂)		2083, 2032
2 _{PPh3}	1927 (A')		1996
Na[Co(CO) ₄]		1844	

^aComputed CO stretching frequencies are also tabulated (see Figure S52).

1927 cm^{–1}. For selected examples, computed stretching frequencies have been generated, and these show good agreement with the experimental values (Figure S52).

Electrochemical Studies. Electrochemical studies were performed on complexes 1, 1_{PPh3}, 1_{PMe3}, 1_{DPPP}, 2, 2_{PPh3}, and Na[Co(CO)₄] for comparison purposes in acetonitrile. Cyclic voltammetry (CV) experiments with each complex under N₂, under CO₂, and CO₂ after a rinse test for homogeneity were conducted (Figures S37–S43). Changes in the current passed under each atmosphere were analyzed as a ratio (i_{cat}/i_p) where the current of the reduction peak under CO₂ is divided by the current of the reduction peak under N₂.²⁶ Each cobalt complex studied herein had a reduction peak more positive than *fac*-Ir(ppy)₃ (–2.61 V vs Fc⁺/Fc) indicating thermodynamically downhill electron transfer from the reduced photosensitizer to the catalyst (Table 4 and Figure 5).²⁷ Assuming a pK_a value of 18.5 for protonated triethylamine (the strongest acid in the photocatalysis conditions below) in acetonitrile^{60,61} and a standard reduction potential of CO₂ in MeCN at –0.12 V vs Fc⁺/Fc (ferrocenium/ferrocene),⁶² then the reduction potential of CO₂ under the photocatalysis conditions is –1.21 V vs Fc⁺/Fc (Figure 5).^{62,63} The electron transfer from a reduced Co complex to CO₂ is favorable for each complex at even the least negative onset potential (–2.00 V for 1) by 0.79 V. The first reduction potential onset values under CO₂ are all within 300 mV between the complexes. Only 1_{PMe3} exhibited an observable second potential within the electrochemical window of these studies. Complex 1 has both the highest

Table 4. Electrochemical Data Collected via CV for CO₂ Reduction with Various Co(I) Complexes and [Co(CO)₄]^{–a}

catalyst	E_{RED} peak _{N₂/CO₂} [V]	E_{RED} onset _{N₂/CO₂} [V]	overpotential [V]	i_{cat}/i_p
1	–2.11/–2.25	–2.00/–2.00	0.79	4.8
1 _{PPh3}	–2.31/–2.34	–2.20/–2.14	0.93	1.7
1 _{PMe3}	–2.45/–2.26 ^b	–2.35/–2.13	0.92	1.1
1 _{DPPP}	–2.32/–2.85	–2.15/–2.15	0.94	4.6
2	–2.19/–2.30	–2.07/–2.10	0.89	3.7
2 _{PPh3}	–2.43/–2.45	–2.29/–2.20	0.99	1.8
Na[Co(CO) ₄]	–2.73/–2.78	–2.44/–2.44	1.23	2.1

^aElectrochemical experiments were conducted with 1 mM analyte and 100 mM potassium hexafluorophosphate in acetonitrile with a scan rate of 100 mV/s. The electrochemical study used a three electrodes setup: glassy carbon (working), Pt⁰ (counter), and Ag⁰ wire (reference). Potentials are reported vs Fc⁺/Fc. ^bA second reduction wave is observed at –2.51 V vs NHE.

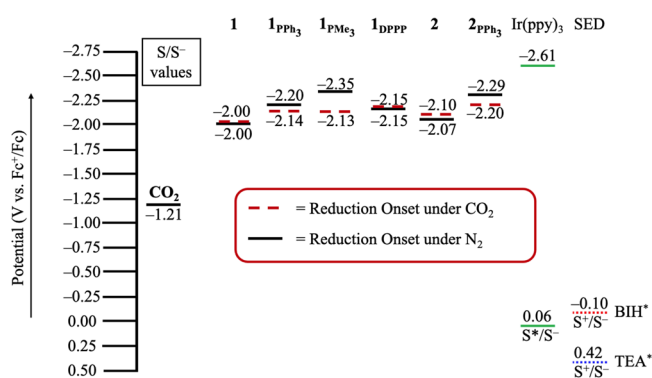


Figure 5. Energy level diagrams based on cyclic voltammetry of the catalyst, PS (CV and optical data), and sacrificial electron donors (SEDs) in acetonitrile. Solid lines are estimated reduction onset potentials under inert atmosphere, dashed are the reduction onset potentials under CO₂, and short dashes are oxidation potentials. TEA is triethylamine. *BIH and TEA are onset values.²⁷

i_{cat}/i_p (4.8) and the lowest overpotential of 0.79 V. The overpotential for 1_{PPh3}, 0.93 V, is slightly higher and the i_{cat}/i_p is significantly lower at 1.7. These general trends are also observed in the series utilizing L2 (2 and 2_{PPh3}), although the complexes reduce at more negative potentials upon the addition of a methoxy substituent. Interestingly, the first

reduction potential onset of $\mathbf{1_{PMe_3}}$, $\mathbf{1_{PPh_3}}$, and $\mathbf{2_{PPh_3}}$ under CO_2 is less negative than that under N_2 by up to 190 mV from peak-to-peak measurements. This result suggests that the complexes undergo a chemical change in a CO_2 atmosphere prior to reduction, which likely involves CO_2 binding. The crystallographic studies show that these phosphine complexes ($\mathbf{1_{PMe_3}}$, $\mathbf{1_{PPh_3}}$, and $\mathbf{2_{PPh_3}}$) have a distorted square pyramidal geometry with a vacant coordination site in contrast to $\mathbf{1}$ and $\mathbf{2}$. Therefore, associative CO_2 binding or an associative interchange mechanism should be more facile for the phosphine complexes than the bis-CO complexes. A shift in the reduction potential toward more positive values under CO_2 is not observed for $\mathbf{1_{DPPP}}$ suggesting that it reduces CO_2 through a different mechanism than that of the other phosphine complexes. The salt, $\text{Na}[\text{Co}(\text{CO})_4]$, is reduced at the most negative potential (-2.73 V) which is expected due to the oxidation state of the cobalt center although the reduction is still feasible due to the stabilization imparted by the carbonyls (Figure S43). Upon rinsing the working electrode after CV studies under CO_2 and collecting CV data in a catalyst-free fresh electrolyte solution, no signal is observed for the catalyst which is consistent with the catalysts being homogenous rather than heterogenized on the electrode surface.

Photocatalytic CO_2 Reduction. PCO_2RR studies were conducted using neutral white light LEDs as the photon source set to 1 Sun intensity from 400 to 700 nm (~ 64 mW/cm^2). The photoreactions were undertaken in acetonitrile solutions saturated with CO_2 containing catalyst (1×10^{-6} M), *fac*-Ir(ppy) $_3$ as the photosensitizer (PS, 1×10^{-4} M), BIH as the sacrificial electron donor (SED, 1×10^{-2} M), and triethylamine (TEA, 0.36 M) as a base to deprotonate the BIH cation after electron transfer to the excited PS which drives the irreversible electron transfer from BIH to the PS (Figures 2 and 5).^{64,65} The PS (*fac*-Ir(ppy) $_3$) has a 160 mV downhill electron transfer from BIH when photoexcited and a minimum of a 410 mV downhill electron transfer driving force to the Co catalysts under CO_2 from the reduced PS. Aliquots of the headspace of the photocatalysis reaction were collected and analyzed by gas chromatography (GC) for the formation of products. The resulting solution after irradiation was also analyzed for formate as well by ^1H NMR. Only CO was observed with no appreciable CH_4 , H_2 , or HCO_2^- observed. Isotopic labeling experiments with $^{13}\text{CO}_2$ confirmed by both GC-MS and ^{13}C NMR methods that external CO_2 is the source of CO generated (Figures S50–S51; S56–S57). The catalytic performances are reported as turnover numbers (TON, where $\text{TON} = \text{moles of CO}/\text{moles of Co catalyst}$). This study primarily focuses on the TON at 72 h as a practical stopping point; however, it is worth noting that the catalysts are still active past 72 h in many cases. The turnover frequency (TOF, where $\text{TOF} = \text{TON}/\text{h}$) for each complex was calculated at 1 and 72 h which represents the initial (TOF_i) and last measured turnover frequencies (TOF_{72}), respectively. A turnover frequency max (TOF_M) was also calculated to determine the highest obtained rate throughout the duration of each experiment. These values are used to distinguish the activity and durability of the active catalytic species.

In every case, the cobalt(I) complexes were 100% selective for the reduction of CO_2 to CO in the PCO_2RR . This selectivity for photoreduction of CO_2 to CO is also observed for sodium tetracarbonyl cobaltate. These complexes show exceptionally robust activity, and this continuous activity is

important for the development of an enduring CO_2 reduction process (Figure 6). Among the dicarbonyl series, complexes $\mathbf{1}$

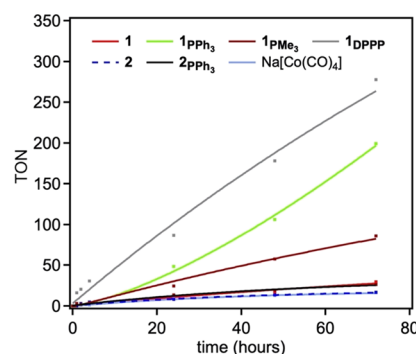


Figure 6. CO TON vs time plot of the PCO_2RRs . The fit lines are simple exponential fits only to help track the data points except $\mathbf{1_{PPh_3}}$, which uses a power fit due to an induction period.

and $\mathbf{2}$ had similar TON values of 30 and 17, respectively (Table 5). The substitution of a carbonyl for a phosphine ligand universally improves photocatalysis. For example, complex $\mathbf{1_{PPh_3}}$ is nearly an order of magnitude more active over 72 h ($\text{TON} = 199$) than complex $\mathbf{1}$ ($\text{TON} = 30$) without a phosphine ligand. Thus, phosphine is highly activating. Better TON values are achieved with the phosphine precoordinated; for example, catalyst $\mathbf{1}$ with 1 equiv of PPh_3 as an additive achieves a TON of 96 (Figure S47). In contrast to L1 complexes, the methoxy derivative with PPh_3 coordinated L2 complex ($\mathbf{2_{PPh_3}}$) showed significantly less CO production ($\text{TON} = 26$) vs the unsubstituted analogue $\mathbf{1_{PPh_3}}$ ($\text{TON} = 199$). Thus, the methoxy group is deactivating for these Co(I) complexes which is in contrast to the catalytic trends for these same ligands bound to Ru(II) or with pendentate Co(II) complexes (e.g., Lit-4 and Lit-3, respectively, Figure 1, $\text{TON: OMe} > \text{H}$).^{17,18,26,27,37} This suggests different ligand design trends may be necessary for optimal low-valent Co(I) catalysts in the PCO_2RR .

Having established that $\mathbf{1_{PR_3}}$ complexes appear to be optimal for the PCO_2RR , we set out to investigate other phosphine derivatives. Catalyst $\mathbf{1_{PMe_3}}$ also led to a large (~ 3 -fold) increase in activity relative to $\mathbf{1}$ with $\text{TON} = 86$ at 72 h. However, the dinuclear catalyst $\mathbf{1_{DPPP}}$ (at 0.5 μM to provide the same number of Co(I) centers as $\mathbf{1_{PMe_3}}$ and $\mathbf{1_{PPh_3}}$ at 1 μM) was the most active catalyst with $\text{TON} = 278$. Future work will aim to elucidate the origins of the high activity for $\mathbf{1_{DPPP}}$, which may include cooperation between two cobalt centers or unique electronic and steric factors present from the DPPP ligand. Overall, the order of activity with phosphine ligands is $\mathbf{1_{PMe_3}} < \mathbf{1_{PPh_3}} < \mathbf{1_{DPPP}}$ (at 1 μM Co(I)) based upon TON values.

Complex $\mathbf{1_{PPh_3}}$ was then subjected to Maitlis' test to probe homogeneous vs heterogeneous catalysis pathways being present (Figure S45).⁶⁶ The test was performed by irradiating a catalytic solution under typical conditions until catalysis is observed for 4 h. The solution was then subjected to in-line filtration through Celite under an inert atmosphere, and the collected solution was degassed with CO_2 followed by irradiation for the remaining time to reach 72 h. The filtration is meant to remove any formed nanoparticles. The test results in modest changes in TON (from 199 to 155) and suggest that the active catalyst is homogeneous. Early time points after the filtration reveal very similar catalytic behavior compared with

Table 5. CO Production Data of Photocatalytic Reductions with Co(I) Complexes and $[\text{Co}(\text{CO})_4]^-$ ^a

complex	change	TON	TOF _i [h ⁻¹]	TOF _M [h ⁻¹] ^b	TOF ₇₂ [h ⁻¹]
1	none	30 ± 2	^c	0.7 ± 0.5	0.5 ± 0.1
1 _{PPh3}	none	199 ± 18	^c	3.9 ± 0.0 ^d	3.9 ± 0.0
1 _{PMe3}	none	86 ± 6	1.5 ± 0.1	1.5 ± 0.1	1.2 ± 0.1
1 _{DPPP}	none	278 ± 25	21.1 ± 9.9	21.1 ± 9.9	4.1 ± 1.2
2	none	17 ± 5	^c	1.5 ± 1.0	0.1 ± 0.2
2 _{PPh3}	none	26 ± 7	4.3 ± 0.2	4.3 ± 0.2	0.3 ± 0.1
Na[Co(CO) ₄]	none	16 ± 5	0.4 ± 0.6	0.7 ± 0.3	0.1 ± 0.1
1 _{PPh3}	1 nM catalyst	36,000 ± 6100	^c	796 ± 185	19.4 ± 3.4
1 _{PMe3}	1 nM catalyst	20,000 ± 5700	^c	423 ± 72	10.8 ± 2.8
1	+1.0 PPh ₃ at 0 h	96 ± 5	5.8 ± 2.6	5.8 ± 2.6	1.8 ± 0.2
1	+0.2 PPh ₃ at 0 h	43 ± 3	3.7 ± 0.9	3.7 ± 0.9 (10.7 ± 0.1) ^e	0.3 ± 0.0
1	+1.0 PPh ₃ at 0 & 10 h	253 ± 46	5.1 ± 1.0	5.7 ± 1.2 (8.7 ± 2.9) ^f	3.4 ± 1.1

^aTONs are reported at a maximum of 72 h and are the average of at least three experiments. TOFs calculated at 1 h for initial and 72 h for final, respectively. TOF_M calculated at the maximum rate recorded. ^bMaximum values reported between 1 and 72 h unless otherwise noted. ^cValue below the limit of detection. ^dInduction period observed via change in TOF over time. ^eValue at 0.5 h. ^fValue at 0.12 h.

the standard reaction. Maitlis' test was also performed on the Na[Co(CO)₄] complex (Figure S46). In this test, the complex had a 7× increase in TON, from 16 to 114. This is likely due to the removal of a poison which could be NaOH which is a common impurity in the simple salt, Na[Co(CO)₄], as reported in the literature synthetic procedure.^{58,67,68} The activity exhibited by this simple salt is extraordinary due to the ease of access and low cost for producing this compound. Notably, no evidence of heterogeneous catalysis was found via Maitlis' test.

Na[Co(CO)₄] was further tested for nanoparticle formation by the addition of Hg⁰ after 4 h of irradiation (Figure S46).^{69,70} While it is apparent from the literature that Co metal has limited solubility in Hg⁰, some solubility seems likely based on literature reports.^{71,72} Thus, if any Co metal nanoparticles are forming it is possible that added Hg⁰ would result in decreased catalytic rates as the Co metal dissolves into the Hg out of the active catalytic layer. The trials were continued in the presence of Hg⁰ for a cumulative 40 h without a significant reduction in TON. These tests have not provided evidence for a heterogeneous catalyst, and the active photocatalytic species present for both 1_{PPh3} and Na[Co(CO)₄] appears to be homogenous.

The rates of the photocatalytic reaction were quantified through TOF_i, TOF₇₂, and TOF_M (Table 5). By taking all three variables into consideration, inferences can be made about the nature of the Co complexes in the catalytic cycles. Catalysts 1_{PMe3}, 2_{PPh3}, and 1_{DPPP} all produce CO initially and thus the active catalytic species is rapidly formed. Complex 1_{PMe3} (TOF_M = 1.5 h⁻¹), shows a nearly constant catalytic output and maintains a catalytic activity from the first hour and throughout the entire 72 h experiment. Complex 2_{PPh3} reaches its TOF_M within the first hour (TOF_M = TOF_i = 4.3 h⁻¹ for 2_{PPh3}) but then declines in activity. Complex 1_{DPPP} is the most active catalyst with TOF_M = TOF_i = 21.1 h⁻¹ at 0.5 μM, and while it does decline in activity over 72 h (TOF₇₂ = 4.1 h⁻¹), the catalyst remains active for over 3 days and thus is a robust catalyst.

All the other complexes (1, 1_{PPh3}, and 2) are more slowly activated precatalysts as they undergo a transformation to enter the catalytic cycle and over time the rate increases as the active catalyst is formed, which is denoted by the difference between TOF_M and TOF_i. Comparing TOF_M to TOF₇₂ gives a sense of the stability of the active catalytic species. In this comparison,

1_{PPh3} maintains 100% of its TOF_M after 72 h (TOF_M = 3.9 h⁻¹, TOF₇₂ = 3.9 h⁻¹). Therefore, 1_{PPh3} has struck a balance between both reactivity and stability of the active catalytic species leading to a relatively high TON of 199. Interestingly, in all cases the mononuclear phosphine complexes show increased reactivity in the PCO₂RR relative to the bis-carbonyl complexes. This observation correlates to the change in geometry from trigonal bipyramidal to square pyramidal when phosphine ligands are introduced and the observation of binding of CO₂ prior to reduction of the complex in the electrochemical studies above. This prebinding of CO₂ induced by a geometry change with a strongly donating *trans* phosphine ligand to the open coordination site could be beneficial for increasing the rate and durability of the phosphine ligated complexes in a range of catalytic reactions.

Reducing the catalyst loading has been reported by several teams to result in increased photocatalyst TOF and TON values.^{18,73–76} Thus, to probe the maximum observable TON values from the most active catalysts rather than a practically time limited analysis, a photoreaction with 1.0 nM concentration of 1_{PPh3} was irradiated for 6 days. Under these conditions, catalysis ceases after 4 days with 36,000 turnovers being observed (Figure 7). A maximum TOF of 796 h⁻¹ is observed during this time period. After 3 days, catalysis had slowed to 19.4 h⁻¹. The robust and rapid nature of this catalyst is exceptional. Similarly, 1_{PMe3} at 1.0 nM gives a TON of

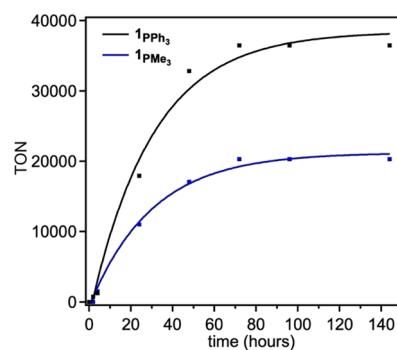


Figure 7. CO TON vs time plot of the PCO₂RRs conducted at 1 nM concentration for 6 days. The fit lines are simple exponential fits only to help track the data points.

20,000 a TOF_M of 423 h⁻¹. These TON and TOF values are exceptional in the homogeneous photocatalysis field.

The difference in behavior of **1** and **1**_{PPh₃} in the PCO₂RR prompted us to examine the influence of added phosphine ligand in the reaction. Interestingly, the addition of 1 equivalent of PPh₃ with respect to **1** to the PCO₂RR results in a reaction showing no detectable induction period, which indicates the active catalyst is rapidly obtained (Figure S47). Furthermore, **1** with added PPh₃ shows a higher TOF_i and TOF_M relative to **1**_{PPh₃} with the PPh₃ precomplexed (e.g., TOF_M of 5.8 vs 3.9, Table 5). Reducing the amount of PPh₃ from 1 equivalent to 0.2 equivalents or using 1 equivalent of DPPP gave a TOF of ~4 h⁻¹ at 1 h; however, when earlier times were evaluated a TOF of 10.7 h⁻¹ is observed at 0.5 h for the added PPh₃ experiment (Figures S47 and S48). Phosphines are believed to reversibly bind to CO₂ in a manner similar to carbenes and electron-rich imine-type nitrogens.^{77–80} This reversible binding could serve to bend the CO₂ molecule into a more reactive geometry than the linear form which would allow PPh₃ to serve the role of a catalytic CO₂ activator operating at a rate faster than the Co(I) catalyst in the PCO₂RR.⁸¹

Notably, the addition of PPh₃ to **1** leads to a lower TON than with **1**_{PPh₃} (96 vs 199) despite a much higher TOF_i. To elucidate whether the lower TON was due to decomposition of **1** or decomposition of PPh₃, 1 additional equivalent of PPh₃ was added at 10 h and reactivity was observed to increase to near the original rate and a TON near that of **1**_{PPh₃} was obtained (253 vs 199; Figure S49). This clearly indicates that the active catalyst was still present in similar amounts to the start of the reaction and that the PPh₃ had been consumed. Attempting to make sense of the reactivity of **1**_{PR₃} complexes, it appears that their robust nature with sluggish activation relates to stabilizing PR₃ and releasing it slowly during the reaction.

The importance of added free PPh₃ may also explain the induction period observed with **1**_{PPh₃} where the role of the phosphine ligand in increasing the reaction rate is to first dissociate and activate CO₂. The dissociation of CO or phosphine could be photochemically initiated because there is antibonding character between the cobalt center and the ligands corresponding to the excitations computed at λ = 354 nm for **1** and 356 nm for **1**_{PPh₃} (see Figures S53–S54). Initial computational studies also suggest that PPh₃ is the most labile ligand on the **1**_{PPh₃} complex (Figure S55, see also Tables S3 and S4). However, NMR studies on **1**_{PMe₃} suggests that CO loss to some small extent is also possible upon irradiation in the presence of free phosphine (Figure S58), but other experiments suggest that both CO and phosphine ligands (in **1**_{PPh₃}) are mostly stable upon irradiation (Figures S59–S60). However, a small amount of dissociation of either CO or phosphine to generate the active catalyst cannot be ruled out, and in fact this mechanism invoking reduction followed by ligand loss (Figure S55) is plausible given that the starting complexes are 18 electron complexes that lack a free site for CO₂ binding.

CONCLUSIONS

We have reported a new synthetic method for the isolation of Co(I) CNC pincer complexes. These pincer complexes have been used as catalysts for the photochemical CO₂ reduction reaction, and to the best of our knowledge this is the first study of CO₂ reduction to use Co(I) photocatalysts directly. Co(II)

and Co(III) catalysts have been used in the past, and it has been proposed that they form Co(I) catalytic species in situ.^{15,29} This study examined the advantages of stabilizing Co(I) and using it for catalysis. Several interesting observations about these catalysts can be made. Unlike our results for octahedral Ru(II) pincer complexes (e.g., **Lit-4**) wherein a methoxy substituent was activating, herein a methoxy substituent was deactivating and better catalytic output was observed with the **L1** complexes having a hydrogen in place of the methoxy. Phosphine ligands were highly activating, with the most robust catalysts (based on TON) being **1**_{DPPP} at 0.5 μM and **1**_{PPh₃} at 1 nM. The latter catalyst produced 36,000 TON with TOF_M = ~800 h⁻¹. Interestingly, the geometry change induced by the introduction of a phosphine ligand to the complexes is correlated to binding of CO₂ prior to electrochemical reduction and higher reactivity in the PCO₂RR among the mononuclear complexes. However, the role of the phosphine ligands proved multifaceted with added external phosphine accelerating the reaction and several roles being possible. We propose that free phosphine plays a catalytic role and serves to activate CO₂. Further mechanistic studies clarifying the role of phosphine and the active Co(I) catalytic species are currently in progress.

Given the ease of synthetic access to new low-valent Co complexes (including Co(I) and Co(–I) as explored herein), this study has opened the door to a new area of exploration within photocatalytic CO₂ reduction as well as potentially other catalytic reactions. These results suggest that the exploration of low-valent metal complexes in varied geometries is an attractive path forward in designing more active and durable catalysts in the PCO₂RR and in other reductive catalytic manifolds. There appear to be advantages to stabilizing Co(I) and using it directly rather than attempting to access the proposed intermediates in situ.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.2c01281>.

Experimental details on synthesis and characterization, single crystal X-ray diffraction, photocatalysis, and computations (PDF)

Computational structures (XYZ)

Crystallographic information (CIF)

Accession Codes

CCDC 2129284–2129291 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Charles Edwin Webster – Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States; orcid.org/0000-0002-6917-2957; Email: ewebster@chemistry.msstate.edu

Jared H. Delcamp – Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States; orcid.org/0000-0001-5313-4078; Email: delcamp@olemiss.edu

Elizabeth T. Papish – Department of Chemistry and Biochemistry, University of Alabama, Tuscaloosa, Alabama 35487, United States; orcid.org/0000-0002-7937-8019; Email: etpapish@ua.edu

Authors

Chance M. Boudreaux – Department of Chemistry and Biochemistry, University of Alabama, Tuscaloosa, Alabama 35487, United States; orcid.org/0000-0003-1322-9878

Dinesh Nugegoda – Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States; orcid.org/0000-0002-5456-8940

Wenzhi Yao – Department of Chemistry and Biochemistry, University of Alabama, Tuscaloosa, Alabama 35487, United States; orcid.org/0000-0002-4874-0169

Nghia Le – Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States

Nathan C. Frey – Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States

Qing Li – Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States; orcid.org/0000-0001-6723-5195

Fengrui Qu – Department of Chemistry and Biochemistry, University of Alabama, Tuscaloosa, Alabama 35487, United States; orcid.org/0000-0002-9975-2573

Matthias Zeller – Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-2084, United States; orcid.org/0000-0002-3305-852X

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acscatal.2c01281>

Notes

The authors declare the following competing financial interest(s): E.T.P. and J.H.D. have filed a patent application related to this chemistry.

ACKNOWLEDGMENTS

The authors thank the NSF (CHE-1800281, 1800214, 1800201, 2102416, 2102511, and 2102552) for funding this research. We thank NSF CHE MRI 1828078 and UA for the purchase of the SC XRD instrument. We thank NSF CHE MRI 1919906 and UA for the purchase of an NMR spectrometer. We thank Dr. Ken Belmore for assistance with the NMR experiments. We thank NSF MRI program (CHE 1726812, PI Cassady) and UA for the purchase of a MALDI TOF/TOF MS and Dr. Qiaoli Liang for MS experimental work. The computational work was completed with resources provided by the Mississippi State University High Performance Computing Collaboratory and the Mississippi Center for Supercomputing Research. C.M.B. thanks GAANN and AL EPSCoR for partial support. Q.L. thanks the University of Mississippi Sally McDonnell Barksdale Honors College for support. N.C.F. thanks NSF S-STEM 1458449 for funding.

REFERENCES

- (1) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels. *Chem. Soc. Rev.* **2009**, *38*, 89–99.
- (2) Kunene, T.; Xiong, L.; Rosenthal, J. Solar-powered synthesis of hydrocarbons from carbon dioxide and water. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 9693–9695.
- (3) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO₂ Fixation. *Chem. Rev.* **2013**, *113*, 6621–6658.
- (4) Frese, K. W., Jr. *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*; Elsevier: New York, 1993; p 299.
- (5) Morris, A. J.; Meyer, G. J.; Fujita, E. Molecular Approaches to the Photocatalytic Reduction of Carbon Dioxide for Solar Fuels. *Acc. Chem. Res.* **2009**, *42*, 1983–1994.
- (6) Chen, L.; Guo, Z.; Wei, X.-G.; Gallenkamp, C.; Bonin, J.; Anxolabéhère-Mallart, E.; Lau, K.-C.; Lau, T.-C.; Robert, M. Molecular Catalysis of the Electrochemical and Photochemical Reduction of CO₂ with Earth-Abundant Metal Complexes. Selective Production of CO vs HCOOH by Switching of the Metal Center. *J. Am. Chem. Soc.* **2015**, *137*, 10918–10921.
- (7) Kang, P.; Chen, Z.; Brookhart, M.; Meyer, T. J. Electrocatalytic Reduction of Carbon Dioxide: Let the Molecules Do the Work. *Top. Catal.* **2015**, *58*, 30–45.
- (8) Papish, E. T.; Das, S.; Silprakob, W.; Boudreaux, C. M.; Manafe, S. Proton Responsive and Hydrogen Bonding Ligands in Organometallic Chemistry. In *Comprehensive Organometallic Chemistry*, 2021; Vol. IV, DOI: [10.1016/B978-0-12-820206-7.00080-9](https://doi.org/10.1016/B978-0-12-820206-7.00080-9).
- (9) Wang, W.-H.; Himeda, Y.; Muckerman, J. T.; Manbeck, G. F.; Fujita, E. CO₂ Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO₂ Reduction. *Chem. Rev.* **2015**, *115*, 12936–12973.
- (10) Huan, T. N.; Dalla Corte, D. A.; Lamaison, S.; Karapinar, D.; Lutz, L.; Menguy, N.; Foldyna, M.; Turren-Cruz, S.-H.; Hagfeldt, A.; Bella, F.; Fontecave, M.; Mougél, V. Low-cost high-efficiency system for solar-driven conversion of CO₂ to hydrocarbons. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 9735–9740.
- (11) Costentin, C.; Robert, M.; Savéant, J.-M. Current Issues in Molecular Catalysis Illustrated by Iron Porphyrins as Catalysts of the CO₂-to-CO Electrochemical Conversion. *Acc. Chem. Res.* **2015**, *48*, 2996–3006.
- (12) Guo, Z.; Cheng, S.; Cometto, C.; Anxolabéhère-Mallart, E.; Ng, S.-M.; Ko, C.-C.; Liu, G.; Chen, L.; Robert, M.; Lau, T.-C. Highly Efficient and Selective Photocatalytic CO₂ Reduction by Iron and Cobalt Quaterpyridine Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 9413–9416.
- (13) Bonin, J.; Maurin, A.; Robert, M. Molecular catalysis of the electrochemical and photochemical reduction of CO₂ with Fe and Co metal based complexes. Recent advances. *Coord. Chem. Rev.* **2017**, *334*, 184–198.
- (14) Cometto, C.; Chen, L.; Lo, P.-K.; Guo, Z.; Lau, K.-C.; Anxolabéhère-Mallart, E.; Fave, C.; Lau, T.-C.; Robert, M. Highly Selective Molecular Catalysts for the CO₂-to-CO Electrochemical Conversion at Very Low Overpotential. Contrasting Fe vs Co Quaterpyridine Complexes upon Mechanistic Studies. *ACS Catal.* **2018**, *8*, 3411–3417.
- (15) Matsuoka, S.; Yamamoto, K.; Ogata, T.; Kusaba, M.; Nakashima, N.; Fujita, E.; Yanagida, S. Efficient and selective electron mediation of cobalt complexes with cyclam and related macrocycles in the *p*-terphenyl-catalyzed photoreduction of carbon dioxide. *J. Am. Chem. Soc.* **1993**, *115*, 601–609.
- (16) Rosas-Hernández, A.; Steinlechner, C.; Junge, H.; Beller, M. Earth-abundant photocatalytic systems for the visible-light-driven reduction of CO₂ to CO. *Green Chem.* **2017**, *19*, 2356–2360.
- (17) Boudreaux, C. M.; Liyanage, N. P.; Shirley, H.; Siek, S.; Gerlach, D. L.; Qu, F.; Delcamp, J. H.; Papish, E. T. Ruthenium(II) complexes of pyridinol and N-heterocyclic carbene derived pincers as robust catalysts for selective carbon dioxide reduction. *Chem. Commun.* **2017**, *53*, 11217–11220.
- (18) Das, S.; Rodrigues, R. R.; Lamb, R. W.; Qu, F.; Reinheimer, E.; Boudreaux, C. M.; Webster, C. E.; Delcamp, J. H.; Papish, E. T. Highly Active Ruthenium CNC Pincer Photocatalysts for Visible-Light-Driven Carbon Dioxide Reduction. *Inorg. Chem.* **2019**, *58*, 8012–8020.

- (19) Ouyang, T.; Hou, C.; Wang, J.-W.; Liu, W.-J.; Zhong, D.-C.; Ke, Z.-F.; Lu, T.-B. A Highly Selective and Robust Co(II)-Based Homogeneous Catalyst for Reduction of CO₂ to CO in CH₃CN/H₂O Solution Driven by Visible Light. *Inorg. Chem.* **2017**, *56*, 7307–7311.
- (20) Yoo, C.; Kim, Y.-E.; Lee, Y. Selective Transformation of CO₂ to CO at a Single Nickel Center. *Acc. Chem. Res.* **2018**, *51*, 1144–1152.
- (21) Burks, D. B.; Davis, S.; Lamb, R. W.; Liu, X.; Rodrigues, R. R.; Liyanage, N. P.; Sun, Y.; Webster, C. E.; Delcamp, J. H.; Papish, E. T. Nickel(II) pincer complexes demonstrate that the remote substituent controls catalytic carbon dioxide reduction. *Chem. Commun.* **2018**, *54*, 3819–3822.
- (22) Li, X.; Yu, J.; Jaroniec, M.; Chen, X. Cocatalysts for Selective Photoreduction of CO₂ into Solar Fuels. *Chem. Rev.* **2019**, *119*, 3962–4179.
- (23) Chai, X.; Huang, H.-H.; Liu, H.; Ke, Z.; Yong, W.-W.; Zhang, M.-T.; Cheng, Y.-S.; Wei, X.-W.; Zhang, L.; Yuan, G. Highly efficient and selective photocatalytic CO₂ to CO conversion in aqueous solution. *Chem. Commun.* **2020**, *56*, 3851–3854.
- (24) Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, Photons, Protons and Earth-Abundant Metal Complexes for Molecular Catalysis of CO₂ Reduction. *ACS Catal.* **2017**, *7*, 70–88.
- (25) Liyanage, N. P.; Dulaney, H. A.; Huckaba, A. J.; Jurss, J. W.; Delcamp, J. H. Electrocatalytic Reduction of CO₂ to CO With Re-Pyridyl-NHCs: Proton Source Influence on Rates and Product Selectivities. *Inorg. Chem.* **2016**, *55*, 6085–6094.
- (26) Das, S.; Nuggeoda, D.; Qu, F.; Boudreaux, C. M.; Burrow, P. E.; Figgins, M. T.; Lamb, R. W.; Webster, C. E.; Delcamp, J. H.; Papish, E. T. Structure Function Relationships in Ruthenium Carbon Dioxide Reduction Catalysts with CNC Pincers Containing Donor Groups. *Eur. J. Inorg. Chem.* **2020**, *2020*, 2709–2717.
- (27) Rodrigues, R. R.; Boudreaux, C. M.; Papish, E. T.; Delcamp, J. H. Photocatalytic Reduction of CO₂ to CO and Formate: Do Reaction Conditions or Ruthenium Catalysts Control Product Selectivity? *ACS Appl. Energy Mater.* **2019**, *2*, 37–46.
- (28) Rosenthal, J. Progress Toward the Electrocatalytic Production of Liquid Fuels from Carbon Dioxide. In *Prog. Inorg. Chem.*, Karlin, K. D., Ed.; Wiley: Hoboken, NJ, 2014; Vol. 59, p 40.
- (29) Ogata, T.; Yanagida, S.; Brunschwig, B. S.; Fujita, E. Mechanistic and Kinetic Studies of Cobalt Macrocycles in a Photochemical CO₂ Reduction System: Evidence of Co-CO₂ Adducts as Intermediates. *J. Am. Chem. Soc.* **1995**, *117*, 6708–6716.
- (30) Liu, D.-C.; Wang, H.-J.; Ouyang, T.; Wang, J.-W.; Jiang, L.; Zhong, D.-C.; Lu, T.-B. Conjugation Effect Contributes to the CO₂-to-CO Conversion Driven by Visible-Light. *ACS Appl. Energy Mater.* **2018**, *1*, 2452–2459.
- (31) Liu, D.-C.; Wang, H.-J.; Wang, J.-W.; Zhong, D.-C.; Jiang, L.; Lu, T.-B. Highly efficient and selective visible-light driven CO₂-to-CO conversion by a Co-based cryptate in H₂O/CH₃CN solution. *Chem. Commun.* **2018**, *54*, 11308–11311.
- (32) Chan, S. L.-F.; Lam, T. L.; Yang, C.; Yan, S.-C.; Cheng, N. M. A robust and efficient cobalt molecular catalyst for CO₂ reduction. *Chem. Commun.* **2015**, *51*, 7799–7801.
- (33) Chan, S. L.-F.; Lam, T. L.; Yang, C.; Lai, J.; Cao, B.; Zhou, Z.; Zhu, Q. Cobalt(II) tris(2-pyridylmethyl)amine complexes [Co(TPA)X]⁺ bearing coordinating anion (X = Cl[−], Br[−], I[−] and NCS[−]): synthesis and application for carbon dioxide reduction. *Polyhedron* **2017**, *125*, 156–163.
- (34) Ouyang, T.; Huang, H.-H.; Wang, J.-W.; Zhong, D.-C.; Lu, T.-B. A Dinuclear Cobalt Cryptate as a Homogeneous Photocatalyst for Highly Selective and Efficient Visible-Light Driven CO₂ Reduction to CO in CH₃CN/H₂O Solution. *Angew. Chem., Int. Ed.* **2017**, *56*, 738–743.
- (35) Liu, D.-C.; Huang, H.-H.; Wang, J.-W.; Jiang, L.; Zhong, D.-C.; Lu, T.-B. Highly Efficient and Selective Visible-Light Driven CO₂-to-CO Conversion by a Co(II) Homogeneous Catalyst in H₂O/CH₃CN Solution. *ChemCatChem* **2018**, *10*, 3435–3440.
- (36) Yao, Y.; Gao, Y.; Ye, L.; Chen, H.; Sun, L. Highly efficient photocatalytic reduction of CO₂ and H₂O to CO and H₂ with a cobalt bipyridyl complex. *J. Energy Chem.* **2018**, *27*, 502–506.
- (37) Shimoda, T.; Morishima, T.; Kodama, K.; Hirose, T.; Polyansky, D. E.; Manbeck, G. F.; Muckerman, J. T.; Fujita, E. Photocatalytic CO₂ Reduction by Trigonal-Bipyramidal Cobalt(II) Polypyridyl Complexes: The Nature of Cobalt(I) and Cobalt(0) Complexes upon Their Reactions with CO₂, CO, or Proton. *Inorg. Chem.* **2018**, *57*, 5486–5498.
- (38) Crudden, C. M.; Allen, D. P. Stability and reactivity of N-heterocyclic carbene complexes. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273.
- (39) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485–496.
- (40) Junge, K.; Papa, V.; Beller, M. Cobalt–Pincer Complexes in Catalysis. *Chem. Eur. J.* **2019**, *25*, 122–143.
- (41) Mukherjee, A.; Milstein, D. Homogeneous Catalysis by Cobalt and Manganese Pincer Complexes. *ACS Catal.* **2018**, *8*, 11435–11469.
- (42) Siek, S. *Catalytic Small Molecule Reduction Using Late Transition Metal Complexes of Carbon and Nitrogen Donor Chelates*; The University of Alabama: Tuscaloosa, AL, 2017.
- (43) Ibrahim, A. D.; Tokmic, K.; Brennan, M. R.; Kim, D.; Matson, E. M.; Nilges, M. J.; Bertke, J. A.; Fout, A. R. Monoanionic bis(carbene) pincer complexes featuring cobalt(I–III) oxidation states. *Dalton Trans.* **2016**, *45*, 9805–9811.
- (44) Tokmic, K.; Markus, C. R.; Zhu, L.; Fout, A. R. Well-Defined Cobalt(I) Dihydrogen Catalyst: Experimental Evidence for a Co(I)/Co(III) Redox Process in Olefin Hydrogenation. *J. Am. Chem. Soc.* **2016**, *138*, 11907–11913.
- (45) Yu, R. P.; Darmon, J. M.; Milsmann, C.; Margulieux, G. W.; Stieber, S. C. E.; DeBeer, S.; Chirik, P. J. Catalytic Hydrogenation Activity and Electronic Structure Determination of Bis(arylimidazol-2-ylidene)pyridine Cobalt Alkyl and Hydride Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 13168–13184.
- (46) Spentzos, A. Z.; Barnes, C. L.; Bernskoetter, W. H. Effective Pincer Cobalt Precatalysts for Lewis Acid Assisted CO₂ Hydrogenation. *Inorg. Chem.* **2016**, *55*, 8225–8233.
- (47) Merz, L. S.; Blasius, C. K.; Wade, H.; Gade, L. H. Square Planar Cobalt(II) Hydride versus T-Shaped Cobalt(I): Structural Characterization and Dihydrogen Activation with PNP–Cobalt Pincer Complexes. *Inorg. Chem.* **2019**, *58*, 6102–6113.
- (48) Alawisi, H.; Al-Afyouni, K. F.; Arman, H. D.; Tonzetich, Z. J. Aldehyde Decarbonylation by a Cobalt(I) Pincer Complex. *Organometallics* **2018**, *37*, 4128–4135.
- (49) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B.; Ellwood, S. N-Heterocyclic “Pincer” Dicarbene Complexes of Cobalt(I), Cobalt(II), and Cobalt(III). *Organometallics* **2004**, *23*, 4807–4810.
- (50) Fernández, S.; Franco, F.; Casadevall, C.; Martín-Diaconescu, V.; Luis, J. M.; Lloret-Fillol, J. A Unified Electro- and Photocatalytic CO₂ to CO Reduction Mechanism with Aminopyridine Cobalt Complexes. *J. Am. Chem. Soc.* **2020**, *142*, 120–133.
- (51) Gonglach, S.; Paul, S.; Haas, M.; Pillwein, F.; Sreejith, S. S.; Barman, S.; De, R.; Müllegger, S.; Gerschel, P.; Apfel, U.-P.; Coskun, H.; Aljabour, A.; Stadler, P.; Schöfberger, W.; Roy, S. Molecular cobalt corrole complex for the heterogeneous electrocatalytic reduction of carbon dioxide. *Nat. Commun.* **2019**, *10*, 3864.
- (52) Zhu, C.-Y.; Zhang, Y.-Q.; Liao, R.-Z.; Xia, W.; Hu, J.-C.; Wu, J.; Liu, H.; Wang, F. Photocatalytic reduction of CO₂ to CO and formate by a novel Co(II) catalyst containing a cis-oxygen atom: photocatalysis and DFT calculations. *Dalton Trans.* **2018**, *47*, 13142–13150.
- (53) Roy, L.; Al-Afyouni, M. H.; DeRosh, D. E.; Mondal, B.; DiMucci, I. M.; Lancaster, K. M.; Shearer, J.; Bill, E.; Brennessel, W. W.; Neese, F.; Ye, S.; Holland, P. L. Reduction of CO₂ by a masked two-coordinate cobalt(I) complex and characterization of a proposed oxodicobalt(II) intermediate. *Chem. Sci.* **2019**, *10*, 918–929.
- (54) Hollingsworth, R. L.; Beattie, J. W.; Grass, A.; Martin, P. D.; Groysman, S.; Lord, R. L. Reactions of dicobalt octacarbonyl with dinucleating and mononucleating bis(imino)pyridine ligands. *Dalton Trans.* **2018**, *47*, 15353–15363.

- (55) Mika, L. T.; Tuba, R.; Tóth, I.; Pitter, S.; Horváth, I. T. Molecular Mapping of the Catalytic Cycle of the Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene in the Presence of Pyridine in Methanol. *Organometallics* **2011**, *30*, 4751–4764.
- (56) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J. V.; Verschoor, G. C. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
- (57) Papish, E. T.; Donahue, T. M.; Wells, K. R.; Yap, G. P. A. How are tris(triazolyl)borate ligands electronically different from tris(pyrazolyl)borate ligands? A study of $(\text{Ttz}^{\text{tBu,Me}})\text{CuCO}$ [$\text{Ttz}^{\text{tBu,Me}} = \text{tris}(3\text{-t-butyl-5-methyl-1,2,4-triazolyl})\text{borate}$]. *Dalton Trans.* **2008**, *22*, 2923–2925.
- (58) Edgell, W. F.; Yang, M. T.; Koizumi, N. The Nature of the Solution of Sodium Tetracarbonylcobaltate(–I) in Various Solvents. *J. Am. Chem. Soc.* **1965**, *87*, 2563–2567.
- (59) Darensbourg, D. J.; Darensbourg, M. Y. Infrared determination of stereochemistry in metal complexes: An application of group theory. *J. Chem. Educ.* **1970**, *47*, 33–35.
- (60) Rossini, E.; Bochevarov, A. D.; Knapp, E. W. Empirical Conversion of pK_a Values between Different Solvents and Interpretation of the Parameters: Application to Water, Acetonitrile, Dimethyl Sulfoxide, and Methanol. *ACS Omega* **2018**, *3*, 1653–1662.
- (61) Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill Book Co.: New York, NY, US, 1987; p 800.
- (62) Pegis, M. L.; Roberts, J. A. S.; Wasylenko, D. J.; Mader, E. A.; Appel, A. M.; Mayer, J. M. Standard Reduction Potentials for Oxygen and Carbon Dioxide Couples in Acetonitrile and N,N-Dimethylformamide. *Inorg. Chem.* **2015**, *54*, 11883–11888.
- (63) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. A local proton source enhances CO_2 electroreduction to CO by a molecular Fe catalyst. *Science* **2012**, *338*, 90–94.
- (64) Kuramochi, Y.; Ishitani, O.; Ishida, H. Reaction mechanisms of catalytic photochemical CO_2 reduction using Re(I) and Ru(II) complexes. *Coord. Chem. Rev.* **2018**, *373*, 333–356.
- (65) Das, S.; Nuggeoda, D.; Yao, W.; Qu, F.; Figgins, M. T.; Lamb, R. W.; Webster, C. E.; Delcamp, J. H.; Papish, E. T. Sensitized and Self-Sensitized Photocatalytic Carbon Dioxide Reduction Under Visible Light with Ruthenium Catalysts Shows Enhancements with More Conjugated Pincer Ligands. *Eur. J. Inorg. Chem.* **2022**, *2022*, No. e202101016.
- (66) Cornils, B.; Herrmann, W. A.; Wong, C.-H.; Zanthoff, H.-W. *Catalysis from A to Z: A Concise Encyclopedia*, 4th ed.; Wiley, 2013; pp 1–2516.
- (67) Edgell, W. F.; Barbetta, A. Studies of solution character by molecular spectroscopy. VI. Experimental methods in ion site characterization. Solvents with simple site character. *J. Am. Chem. Soc.* **1974**, *96*, 415–423.
- (68) Edgell, W. F.; Lyford, J.; Barbetta, A.; Jose, C. I. Studies of some aspects of solution character by molecular spectroscopy. IV. Multiplicity and nature of the $\text{Co}(\text{CO})_4^-$ environments in certain solvents. *J. Am. Chem. Soc.* **1971**, *93*, 6403–6406.
- (69) Widegren, J. A.; Finke, R. G. A review of the problem of distinguishing true homogeneous catalysis from soluble or other metal-particle heterogeneous catalysis under reducing conditions. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317–341.
- (70) Cai, Z.; Wang, H.; Xiao, C.; Zhong, M.; Ma, D.; Kou, Y. Hydroformylation of 1-hexene over ultrafine cobalt nanoparticle catalysts. *J. Mol. Catal. A: Chem.* **2010**, *330*, 94–98.
- (71) Guminski, C. The Co-Hg (cobalt-mercury) system. *J. Phase Equilib.* **1993**, *14*, 643–647.
- (72) Luborsky, F. E. The Kinetics of Growth of Colloidal Cobalt Particles in Mercury. *J. Phys. Chem.* **1958**, *62*, 1131–1132.
- (73) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. Development of an Efficient Photocatalytic System for CO_2 Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies. *J. Am. Chem. Soc.* **2008**, *130*, 2023–2031.
- (74) Guo, Z.; Yu, F.; Yang, Y.; Leung, C.-F.; Ng, S.-M.; Ko, C.-C.; Cometto, C.; Lau, T.-C.; Robert, M. Photocatalytic Conversion of CO_2 to CO by a Copper(II) Quaterpyridine Complex. *ChemSusChem* **2017**, *10*, 4009–4013.
- (75) Liyanage, N. P.; Yang, W.; Guertin, S.; Sinha Roy, S.; Carpenter, C. A.; Adams, R. E.; Schmehl, R. H.; Delcamp, J. H.; Jurs, J. W. Photochemical CO_2 reduction with mononuclear and dinuclear rhenium catalysts bearing a pendant anthracene chromophore. *Chem. Commun.* **2019**, *55*, 993–996.
- (76) Thoi, V. S.; Kornienko, N.; Margarit, C. G.; Yang, P.; Chang, C. J. Visible-Light Photoredox Catalysis: Selective Reduction of Carbon Dioxide to Carbon Monoxide by a Nickel N-Heterocyclic Carbene–Isoquinoline Complex. *J. Am. Chem. Soc.* **2013**, *135*, 14413–14424.
- (77) Buß, F.; Mehlmann, P.; Mück-Lichtenfeld, C.; Bergander, K.; Dielmann, F. Reversible Carbon Dioxide Binding by Simple Lewis Base Adducts with Electron-Rich Phosphines. *J. Am. Chem. Soc.* **2016**, *138*, 1840–1843.
- (78) Gayton, J. N.; Li, Q.; Sanders, L.; Rodrigues, R. R.; Hill, G.; Delcamp, J. H. Pyridyl CO_2 Fixation Enabled by a Secondary Hydrogen Bonding Coordination Sphere. *ACS Omega* **2020**, *5*, 11687–11694.
- (79) Villiers, C.; Dognon, J. P.; Pollet, R. P. T.; Pierre, T.; Ephritikhine, M. An Isolated CO_2 Adduct of a Nitrogen Base: Crystal and Electronic Structures. *Angew. Chem., Int. Ed. Engl.* **2010**, *49*, 3465.
- (80) Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. 1,3-Dimethylimidazolium-2-carboxylate: the unexpected synthesis of an ionic liquid precursor and carbene- CO_2 adduct. *Chem. Commun.* **2003**, 28–29.
- (81) Alkorta, I.; Trujillo, C.; Sánchez-Sanz, G.; Elguero, J. Solvent and Substituent Effects on the Phosphine + CO_2 Reaction. *Inorganics* **2018**, *6*, 110.

Recommended by ACS

Cooperativity in Highly Active Ethylene Dimerization by Dinuclear Nickel Complexes Bearing a Bifunctional PN Ligand

Chunyu Feng, Pierre Braunstein, et al.

DECEMBER 18, 2020
ORGANOMETALLICS

READ 

Catalytic Conversion of Atmospheric CO_2 into Organic Carbonates by Nickel(II) Complexes of Diazepane-Based N4 Ligands

Sethuraman Muthuramalingam, Ramasamy Mayilmurugan, et al.

SEPTEMBER 19, 2019
INORGANIC CHEMISTRY

READ 

Pincer-Nickel Catalyzed Selective Guerbet-Type Reactions

Vinay Arora, Akshai Kumar, et al.

AUGUST 05, 2021
ORGANOMETALLICS

READ 

Cationic Cobalt–Thiolate Complexes for the Dehydrogenative Coupling of $n\text{Bu}_3\text{SnH}$

Saravanakumar Elangovan, Martin Oestreich, et al.

MARCH 09, 2022
ORGANOMETALLICS

READ 

Get More Suggestions >