Inorganic Chemistry

Highly Active Manganese-Based CO₂ Reduction Catalysts with Bulky NHC Ligands: A Mechanistic Study

Yong Yang, Zhenyu Zhang, Xiaoyong Chang, Ya-Qiong Zhang, Rong-Zhen Liao, and Lele Duan*



of the N-heterocyclic carbene (NHC), Mn-NHC complexes were found to be active for the reduction of CO₂ to CO with high activity. However, some NHC-based manganese complexes showed low catalytic activity and required very negative potentials. We report herein that complex *fac*-[Mn^I(bis-^{Mes}NHC)(CO)₃Br] [1; bis-^{Mes}NHC = 3,3-bis(2,4,6-trimethylphenyl)-(1,1'-diimidazolin-2,2'-diylidene)methane] could catalyze the electrochemical reduction of CO₂ to CO with high activity (TOF_{max} = 3180 ± 6 s⁻¹) at a less negative potential. Due to the introduction of the bulky Mes groups, a one-electron-reduced intermediate {[Mn⁰(bis-^{Mes}NHC)(CO)₃]⁰ (2[•])} was isolated as a packed



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"dimer" and crystallographically characterized. Stopped-flow Fourier-transform infrared spectroscopy was used to prove the direct reaction between doubly reduced intermediate fac-[Mn(bis-^{Mes}NHC)(CO)₃]⁻ and CO₂; the tetracarbonyl Mn complex [Mn⁺(bis-^{Mes}NHC)(CO)₄]⁺ ([2-CO]⁺) was captured, and its further reduction proposed as the rate-limiting step.

■ INTRODUCTION

Selective reduction of carbon dioxide to yield high-value-added products like CO, HCHO, MeOH, and CH_4 or higher- C_x products has attracted considerable attention. These reduction reactions require multiple electron/proton transfer and involve several bond cleavage/formation steps, so they are difficult to catalyze, leading to applied potentials that are higher than the thermodynamic values.¹ Thereby, the development of effective carbon dioxide reduction catalysts is challenging and essential for utilizing CO_2 as a C_1 feedstock to produce green fuels.

Molecular transition metal-based complexes have been often utilized for electrochemical CO₂ reduction and for systematically investigating the reaction mechanisms because of their rich structural and electronic tunability.^{2–5} Metal complexes, including cobalt,^{6–10} nickel,^{11–14} iron,^{15–18} ruthenium,^{19–23} rhenium,^{24–27} palladium,^{28,29} manganese,^{30–42} etc., have been shown to be capable of catalyzing electrochemical CO₂ reduction. Among these catalysts, the development of Mn-based electrocatalysts is a step forward toward affordable catalysts due to the abundance of manganese in the Earth. The first example, *fac*-[Mn^I(bpy)(CO)₃Br] (bpy = 2,2'-bipyridine), was reported by Bourrez et al.,³¹ and later several research groups studied the reaction mechanisms of the related catalysts.^{32,34} By changing the pyridyl ligand to NHC (N-heterocyclic carbene), the Agarwal group,^{35,36,39} the Royo group, and the Lloret-Fillol group⁴² developed Mn-NHC electrocatalysts for selective reduction of CO₂ to CO. In particular, complex *fac*-[Mn^I(bis-^{Me}NHC)(CO)₃Br] [A (Fig-

ure 1, right)] exhibited unprecedented activity [maximum turnover frequency (TOF_{max}) of 2100 s⁻¹] without addition of



Figure 1. Chemical structures of complexes 1 and A.

any Lewis acid. On the basis of FTIR-SEC studies and density functional theoretical (DFT) calculations, Royo, Lloret-Fillol, and their co-workers proposed the electrochemical CO_2 reduction mechanism by **A**. However, the first and second reduction potentials of this Mn-NHC complex are too close to separate from each other so that a two-electron reduction product is formed upon reduction. As a result, the FTIR-SEC spectra are very complex and could not be well resolved

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experimentally. In addition, no reduced Mn-NHC intermediate has been characterized by X-ray crystallography. On the other hand, Kubiak and co-workers reported that the dimerization of singly reduced Mn-bpy species could contribute to an overpotential and limit the activity of Mn catalysts. Thereby, bulky groups like ^{Mes}bpy (^{Mes}bpy = dimesityl-2,2'-bipyridine) were developed to eliminate dimerization and enhance the catalytic activity of Mn-based CO₂ reduction catalysts. We adopted this strategy and report herein an earth-abundant Mn-NHC catalyst, fac-[Mn^I(bis-^{Mes}NHC)(CO)₃Br] (1), bearing two bulky mesityl groups (Figure 1, left). As expected, complex 1 displayed higher activity (TOF_{max} = 3180 \pm 6 s⁻¹) and performed at a potential less negative than that of complex A toward electrochemical reduction of CO₂ to CO. Moreover, we carefully studied the infrared (IR) spectral evolution of 1 via stoichiometric reduction by a chemical reducing agent KC8. For the first time, one-electron-reduced intermediate $[Mn^{0}(bis-MesNHC)(CO)_{3}]^{0}$ (2) related to Mn-NHC-based CO₂ reduction catalysts was isolated and crystallographically characterized. Doubly reduced Mn-NHC complexes have long been proposed as the active species for CO₂ reduction, and herein, we demonstrated the direct reaction between fac- $[Mn^{-}(bis^{-Mes}NHC)(CO)_{3}]^{-}$ and CO_{2} via stopped-flow Fourier-transform infrared spectroscopy (FTIR) and a catalytic intermediate, tetracarbonyl Mn complex [Mn+(bis-MesNHC)- $(CO)_{4}^{+}$ ([2-CO]⁺), was observed.

EXPERIMENTAL SECTION

General Considerations. Anhydrous acetonitrile (CH₃CN), tetrahydrofuran (THF), and *n*-hexane were distilled and dried over molecular sieves, and THF and *n*-hexane were stored over a Na–K alloy. Tetrabutylammonium hexafluorophosphate (TBAP, Sigma-Aldrich, 98%) and tetrabutylammonium bromide (TBAB, Sigma-Aldrich, 98%) were dried under a vacuum at 100 °C overnight and stored in the glovebox. Potassium graphite (KC₈) was synthesized according to the literature and stored at -20 °C in a glovebox. Other reagents were used as received: 2,4,6-trimethylphenylamine (Heowns, 98%), a glyoxal solution (Macklin, 40% in H₂O), dibromomethane (Energy Chemical, 98%), and manganese pentacarbonyl bromide [Mn(CO)₅Br, Aldrich, 98%].

The ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz spectrometer at room temperature. Solvent residual peaks are treated as internal references, and ¹H chemical shifts are published relative to Me₄Si ($\delta = 0$). Elemental analysis was performed with a Thermoquest-Flash EA 1112 elemental analyzer for C, H, and N. Mass spectrometry (ESI-MS) was performed on a Q-Exactive instrument. Fourier-transform infrared (FTIR) spectra were recorded on the Bruker Alfa or V80 spectrometer. Crystal structure determinations were carried out using Bruker D8 VENTURE with Mo K α radiation under a N₂ stream at 100 K. The collected data were integrated by the software of Bruker SAINT, and the software of Olex was used to induce the structure of the complexes.

Synthesis of 3,3-Bis(2,4,6-trimethylphenyl)-[(1,1'diimidazolium)methane] Dibromide. The compound was synthesized according the literature procedures^{43,44} (Figure S1). The mixture of acetic acid (5.0 mL), a formaldehyde solution (37%, 1.5 mL), and an oxalaldehyde solution (37%, 2.3 mL) was heated to 70 °C while being stirred. An aqueous solution (2 mL) containing 2,4,6-trimethylaniline (2.695 g, 20 mmol) and ammonium acetate (1.54 g, 20 mmol) was added dropwise into the solution mentioned above, followed by addition of acetic acid (5.0 mL). The reaction mixture was stirred at 70 °C for 18 h. After being cooled to room temperature, the resulting brown solution was added slowly to a sodium bicarbonate solution (1.2 M, 150 mL) under stirring, after which the generated brownish solid was filtered. The crude product was dried under vacuum and purified by column chromatography to yield the product of 1-(2,4,6-trimethylphenyl)-1H-imidazole (2.6 g, 70%): ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 1H), 7.24 (s, 1H), 6.97 (s, 2H), 6.90 (s, 1H), 2.34 (s, 3H), 1.99 (s, 6H).

Under an atmosphere of nitrogen, the acetonitrile solution (5 mL) containing 1-(2,4,6-trimethylphenyl)-1H-imidazole (0.931 g, 5.0 mmol) and dibromomethane (0.3 mL, 4.0 mmol) was added in a pressure tube. The solution was heated to 160 °C for 1 h under microwave radiation. After the mixture had cooled to room temperature, a gray solid precipitated from the solution. The precipitate was filtered and washed with cold THF until it became a colorless solid and dried under vacuum to obtain the desired compound (0.89 g, 65%): ¹H NMR (400 MHz, CDCl₃) δ 11.33 (s, 2H), 9.82 (s, 2H), 7.95 (s, 2H), 7.28 (s, 2H), 7.05 (s, 4H), 2.38 (s, 6H), 2.08 (s, 12H).

Synthesis of the fac-[Mn^I(bis-MesNHC)(CO)₃Br] Complex (1). In the dark under a nitrogen atmosphere, $Mn(CO)_5Br$ (70 mg, 0.26 mmol) was dissolved in dry THF (15 mL), to which potassium tertbutoxide (52 mg, 0.46 mmol) was added. The reaction mixture was heated to 60 °C, and 3,3-bis(2,4,6-trimethylphenyl)-[(1,1'diimidazolium)methane] dibromide (108 mg, 0.2 mmol) was slowly added to the suspended solution. The suspension was stirred at 60 °C for 24 h. After the mixture had been cooled to room temperature, the solvent of THF was removed under vacuum and the resulting residue was suspended in CH_2Cl_2 (15 mL). The solution was filtered, and the orange-yellow filtrate was collected and removed under vacuum to yield the crude product. The product was purified by column chromatography to yield yellow powder (0.114 g, 73%): 'H NMR (400 MHz, DMSO-d₆) δ 7.84 (s, 2H), 7.37 (s, 2H), 7.02 (s, 2H), 6.97 (s, 2H), 6.84-6.75 (d, 2H), 6.47-6.37 (d, 2H), 2.29 (s, 6H), 2.08 (s, 6H), 1.82 (s, 6H); FTIR $\nu_{\rm CO}$ 2009 (s), 1929 (s), 1888 (s) cm⁻¹; ESI-MS (positive mode) $[1 - Br]^+$ 523.16. Elemental analysis calcd (%) for C₂₈H₂₈N₄O₃BrMn: C, 56.08; H, 6.75; N, 8.72. Found: C, 56.13; H, 6.52; N, 8.49.

Chemical Reduction. Complex 1 (0.008 mmol, 5.0 mg) was dissolved in THF (1 mL), followed by the addition of KC₈ (0.009 mmol, 1.2 mg). The color of the solution turned yellow to yellow-green gradually over 5 min. The FTIR spectrum of the solution shows that $\nu_{\rm CO}$ stretching bands of complex 1 disappeared and new $\nu_{\rm CO}$ stretching bands of neutral Mn⁰ complex 2• arose. The solution was centrifuged to remove the black solid (product of KC₈), and the solution of complex 2• was obtained.

To obtain the two-electron-reduced species 2^- , KC₈ (0.018 mmol, 2.4 mg) was added to the THF solution containing complex 1 (0.008 mmol, 5.0 mg). Due to the weak solubility in THF, the reduced species 2^- precipitated from the solution. The precipitate mixed together with a black solid (product of KC₈), and we cannot acquire pure complex 2^- . Therefore, we replaced KC₈ with a portion of sodium as the reductant. A portion of metal sodium (0.4 mmol, 10 mg) was added to the THF solution of complex 1 (0.008 mmol, 5 mg), and the solution was stirred until the FTIR spectrum proved that the $\nu_{\rm CO}$ stretching bands of complex 1 and its neutral complex 2° disappeared. The suspension was centrifuged, and the pure yellow solid of reduced species 2^- was obtained.

Crystal Preparation. Crystals of 1 were grown by diffusion of diethyl ether into the CH₂Cl₂ solution of complex 1. The CCDC number of complex 1 is 1960153. Crystals of 2° were grown by slow diffusion of hexane into a THF solution under -20 °C in an argon-filled glovebox. The crystals were selected using a microscope in a glovebox, and the selected crystal sample was immersed in perfluoropolyether for manipulation. The crystal structure of complex 2° cannot be refined well for three reasons. (1) During the test, the crystal easily cracked into several pieces, resulting in the bad quality of the crystal. (2) The size of the crystal is small and thin, leading to a high 2θ angle, and diffraction data were not available. (3) H₂O and O₂ reacted with complex 2° and destroyed the structure of complex during the test, although crystals were capped with perfluoropolyether. The CCDC number of complex 2° is 1960154.

Electrochemistry. All of the electrochemical experiments were performed with an electrochemical workstation (CHI 760) under rigorous air free conditions. Cyclic voltammetry (CV) measurements were carried out in a CH_3CN solution (0.1 M TBAP as the

supporting electrolyte). The glass carbon (3 mm) electrode, Pt wire, and Ag/AgNO₃ electrode were used as the working electrode, counter electrode, and reference electrode, respectively. Ferrocene (Fc) acted as an internal standard. All potentials reported in this paper are referenced versus the Fc^{+/0} redox couple and calculated to the Fc^{+/0} reference using $E(Fc^{+/0}) = E(Ag/AgNO_3) - 0.08$ V.

A homemade H-type electrochemical cell that was separated by a glass frit into cathodic and anodic compartments was used for controlled-potential electrolysis (CPE) experiment. The typical working conditions of the cathodic compartment are as follows. A glass carbon plate (3.14 cm²) was used as the working electrode, Ag/ AgNO₃ as the reference electrode, and 0.1 M TBAP/CH₃CN as the electrolyte solution. For the anodic compartment, Pt mesh was employed as the counter electrode and a CH₃CN solution containing 0.1 M TBAP and 0.5 M tetraethylammonium acetate tetrahydrate acting as a sacrificial agent (note that this reagent contains hydrated water, and the glass frit that separates the anode and cathode of Htype electrochemical cell will not completely prevent water from crossing over during electrolysis; oxidation of acetate produced CO₂ that does not contaminate the system) was used to avoid the oxidation of electrolyte TBAP. The electrolyte was purged with carbon dioxide for 15 min before electrolysis. The product of carbon monoxide was analyzed by a FuLi Instruments GC9790 Plus gas chromatograph with a thermal conductivity detector through an offline system (He as the carrier gas).

Fourier-Transform Infrared Reflectance Spectroelectrochemistry (FTIR-SEC). A homemade FTIR-SEC instrument was used for this study. The schematic diagram and pictures of the cell are shown in Figure S21. The cell consists of a glass carbon working electrode (10 mm), a Pt counter (15 mm \times 30 mm) electrode, and a Ag/AgNO₃ reference electrode and a CaF₂ plate as the optical window. The IR beam is directed to focus on the working electrode through the optical window, where it is reflected and ultimately directed to the Bruker Vertex 80 detector. The dry CH₃CN solution (0.2 M TBAP) prepared under an atmosphere of Ar or CO₂ is used as the electrolyte.

Stopped-Flow FTIR Spectroscopy. The stopped-flow FTIR measurements were performed using a Bruker Vertex 80 infrared spectrometer fitted with a stopped-flow apparatus (TgK Scientific SF-73) and a transmission mixing cell. A Bruker Vertex 80 instrument equipped with a liquid nitrogen-cooled RT-DLaTGS detector and a 4000 cm⁻¹ low-pass filter was controlled via the Bruker OPUS software. The stopped-flow apparatus is shown in Figure S18. The cell is made from two CaF₂ plates, with a cell volume of a few microliters and a 100 μ m path length. The cell is connected via PEEK tubing to a stepper motor syringe pump; the pump is controlled via the apparatus of a TgK Scientific SF-73 instrument that is placed in a glovebox. Prior to a measurement, the stopped-flow apparatus and transmission mixing cell were purged with Ar for 30 min, ensuring that no air was in the system. Then dry THF was injected into the mixing cell. In a typical measurement, one syringe was filled with a CO2-saturated THF solution and another filled with the solution of complex 2^- . The flow volume and rate of the syringe pump were set to 300 μ L and 1 mL s⁻¹, respectively. The scanner velocity was fixed at 320 kHz, and the wavenumber resolution set to 4 cm⁻¹. Spectra were recorded using a double-sided interferogram acquisition method. Overall, the setting mode provided a maximum acquisition rate of 54 spectra per second.

Computational Details. The DFT calculations were performed using the hybrid B3LYP-D3^{45,46} functional as implemented in the Gaussian 16 program package.⁴⁷ Geometries were optimized in the gas phase using the SDD⁴⁸ pseudopotential for Mn and Br, while $6\cdot$ 31G(d,p) basis sets were used for all other atoms. Analytic frequency calculations were then carried out to obtain the vibrational frequencies, and a scaling factor of 0.961 was used to simulate the IR spectra.

RESULTS AND DISCUSSION

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Synthesis and Characterization. Complex 1 was prepared by a reaction of the bis-^{Mes}NHC ligand (in situ generated from the ligand precursor by addition of KO^tBu) and $[Mn(CO)_5Br]$ with a moderate yield (see the reaction scheme in Figures S1 and S2).⁴² Complex 1 was explicitly characterized by ¹H NMR spectroscopy (Figures S3 and S4), elemental analysis, FTIR spectroscopy (Figure S5), and X-ray crystallography. The single-crystal X-ray diffraction structure of 1 is shown in Figure 2 (left), and its crystallographic data are



Figure 2. Single-crystal X-ray crystal structure of complexes 1 and 2[•]. Hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths and bond angles for complex 1: C1–N1, 1.361; N1–C2, 1.443; C2–N2, 1.458; N2–C3, 1.359; C1–Mn1, 2.058; C3–Mn1, 2.055; C4–Mn1, 1.836; C5–Mn1, 1.771; C6–Mn1, 1.824; C4–O1, 1.145; C5–O2, 1.142; C6–O3, 1.152; C1–Mn1–C3, 83.87; N1–C2–N2, 109.29. Selected bond lengths and bond angles for complex 2[•]: C1–N1, 1.392; N1–C2, 1.468; C2–N2, 1.436; N2–C3, 1.353; C1–Mn2, 2.043; C3–Mn2, 2.104; C4–Mn1, 1.823; C5–Mn1, 1.762; C6–Mn1, 1.640; C4–O1, 1.215; C5–O2, 1.215; C6–O3, 1.219; C1–Mn2–C3, 81.51; N1–C2–N2, 111.37.

listed in Tables S1 and S2. The coordination sphere of Mn is in the octahedral configuration, with $Mn-C_{NHC}$ bond lengths of 2.055-2.058 Å, slightly longer than those of the previously reported complex A by 2.041-2.043 Å.⁴² These results reveal that the electron-donating ability of bis-^{Mes}NHC is weaker than that of bis-MeNHC. One-electron-reduced product $[Mn^{0}(bis^{Mes}NHC)(CO)_{3}]^{0}$ (2) was synthesized via reduction of 1 with KC_8 (see details in the Experimental Section). The X-ray crystals of one-electron-reduced products were grown by vapor diffusion of pentane into a THF solution of the complex under -20 °C in the glovebox. As shown in Figure 2 (right), the reduction of complex 1 results in the loss of its bromo ligand, and the Mn coordination sphere of 2° is in the square pyramid configuration. The bulky MesNHC ligand inhibited Mn-Mn bond formation in the solid state, forming a five-coordinate, 17-electron complex 2°; however, two complexes 2° form a closely packed "dimer" in a solid, noted as $[2^{\bullet}-2^{\bullet}]$, with a shortest Mn-Mn distance of 3.490 Å (Figure S6), which is close to the Mn–Mn distance (3.572 Å) of the optimized structure of the "dimeric" Mn⁰ complex (Figure S7). In comparison, the Mn-Mn distance of $[Mn(bpy)CO_3]_2$ is 2.998 Å, much shorter than the Mn–Mn distance of $[2^{\bullet}-2^{\bullet}]^{.30}$ On the other hand, the IR spectrum of 2[•] in THF is very different from that of $\begin{bmatrix} 2^{\bullet}-2^{\bullet} \end{bmatrix}$ in the solid state (Figure 5), indicating the relatively strong interaction of two Mn^0 complexes in $[2^{\bullet}-2^{\bullet}]$. The selected bond lengths and angles as well as crystallographic data are listed in Tables S3 and S4. This is the first time that a crystal structure of a singly reduced Mn intermediate related to Mn-NHC-based carbon dioxide reduction catalysts is documented. Comparison of the crystal structures of complexes 1 and $\begin{bmatrix} 2^{\bullet}-2^{\bullet} \end{bmatrix}$ reveals significant shortening of the $Mn-C_{(CO)}$ bonds in $[2^{\bullet}-2^{\bullet}]$ as

compared to 1 (1.640, 1.762, and 1.823 Å vs 1.771, 1.824, and 1.836 Å, respectively). The C–O bond length increased from 1.142, 1.145, and 1.152 Å in the crystal structure of 1 to 1.215, 1.215, and 1.219 Å in $[2^{\bullet}-2^{\bullet}]$, respectively. These observations are similar to those in the literature.^{32,34} The metal center of complex $[2^{\bullet}-2^{\bullet}]$ has an electron cloud density that is higher than that of complex 1, and the π back-donation from the filled *d* orbital to the empty π^{\bullet} orbital of CO strengthens the Mn–C_(CO) bonds and weakens the C–O bonds. As a result, the Mn–C_(CO) bonds are elongated while the C–O bonds shortened.

Electrochemistry. The electrochemistry of 1 was studied under Ar- and CO₂-saturated conditions in acetonitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as an electrolyte. Under an Ar atmosphere, CV of complex 1 (0.5 mM) displays a broad reduction wave at -2.37 V (all potentials reported in this paper are vs Fc^{+/0}) (Figure 3a). Bromo ligand dissociation is



Figure 3. Cyclic voltammograms of 1 (0.5 mM) under (a) an Ar atmosphere and (b) a CO_2 -saturated atmosphere in anhydrous CH_3CN with 0.1 M TBAP as the electrolyte at a scan rate of 100 mV s⁻¹.

very common for diimine Mn-Br complexes [Mn(N^N)- $(CO)_{3}Br$ (N^N = diimine ligand), leading to the formation of an equilibrium mixture of $[Mn(N^N)(CO)_3(sol)]^+$ (sol = solvent molecule) and $[Mn(N^N)(CO)_3Br]^5$ Such a ligand dissociation reaction will broaden the reduction wave of the first electron transfer and shift the reduction wave toward the anodic direction. In our case, the NHC ligand is a stronger electron donor and will favor the ligand dissociation, as a result of which the bromo ligand dissociation cannot be avoid. Figure S8 shows that the cathodic peak current changes linearly with the square root of the scan rate in the range of $0.05-6.4 \text{ V s}^{-1}$, which implies reductive diffusion-limited processes for 1. The single reduction wave of A was previously assigned as a twoelectron process,⁴² and the same may apply to 1. To prove the two-electron reduction process, we have recorded the cyclic voltammograms of 1 and ferrocene (the oxidation of ferrocene is a standard one-electron process) under an Ar atmosphere (Figure S9). The consumed charge of the reduction wave at -2.37 V (2.098 × 10⁻⁵ C) for 1 is \sim 2 times as large as the oxidation wave of ferrocene (1.066 \times 10⁻⁵ C), indicating a two-electron process for 1. On the basis of previous studies of Mn-NHC catalysts, the two-electron process corresponds to the consecutive ECE processes.^{35,36,39,42} Upon the first electron reduction of 1 (the first "E" process), the Br- ligand dissociates from fac-[Mn⁰(bis-^{Mes}NHC)(CO)₃Br]⁻ (1⁻; the "C" process), leading to the formation of [Mn⁰(bis-^{Mes}NHC)- $(CO)_3]^0$ (2[•]). Then, the Mn⁰ species 2[•] is reduced to give $[Mn^{-}(bis^{-Mes}NHC)(CO)_{3}]^{-}(2^{-})$ upon the second electron reduction (the second "E" process). During the reverse scan, 2° displays an oxidation wave at -2.02 V. The oxidation wave

at -1.38 V was observed with a low current density. The cyclic voltammogram of A also displayed such an oxidation wave that is assigned to the oxidation process of the Mn⁰ dimer. In our case, due to the introduction of the bulky Mes groups, complex 2° could not dimerize in solution. Thereby, without further evidence we could not assign this oxidation wave. In comparison with the literature-documented complex A,⁴² the reduction potential of complex 1 is lower by 48 mV (Figure S10a). This is due to the weaker electron-donating ability of bis-^{Mes}NHC in comparison with that of bis-^{Me}NHC, as evidenced by the longer Mn–C_{NHC} bond in complex 1.

Under CO₂-saturated conditions, the cyclic voltammogram of complex 1 reveals a strong enhancement of the catalytic current at the first reduction wave with an onset potential at approximately -2.13 V and the current density at -2.37 V is 11 times higher than those under an Ar atmosphere (Figure 3b). For comparison, the cyclic voltammograms of complexes 1 and A under CO₂-saturated conditions are plotted in Figure S10b. Overpotential (η) is defined by the difference between equilibrium potential (E_{CO_2}) and catalytic potential of the CO₂ reduction reaction. Under our conditions, the equilibrium potential is difficult to estimate due to the unknown water concentration but both 1 and A share the same equilibrium potential as the reaction conditions are identical. The catalytic potential, as recommended by Appel and Helm,⁴⁹ is determined from the potential at half of the catalytic current, defined as $E_{\text{cat/2}}$ (Figure S10b). The overpotential difference between A and 1 could be estimated as $\eta_{\rm A}$ – η_1 = $|E_{\rm CO_2}$ – $|E_{\text{cat/2}(\mathbf{A})}| - |E_{\text{CO}_2} - E_{\text{cat/2}(\mathbf{1})}| = |E_{\text{cat/2}(\mathbf{A})} - E_{\text{cat/2}(\mathbf{1})}| = 70 \text{ mV}.$ Therefore, the overpotential of complex 1 is smaller than that of A by 70 mV due to the slightly weaker electron-donating ability of the bis-MesNHC.

The addition of water to the electrolyte could increase the catalytic current density, while the maximum current density was observed at 0.55 M H₂O. Further addition of water led to a dramatic decrease in catalytic activity (Figure S11a). However, the catalytic system becomes unstable in the presence of water. For instance, at 0.55 M H₂O, the cyclic voltammogram response gradually decreased upon multiple scans. The current density could be recovered after the glassy carbon electrode had been polished (Figure S11b). In addition, controlled-potential electrolysis experiments were performed under CO2-saturated CH3CN with 0.1 M TBAP in the presence of 0.55 M H_2O at an applied potential of -2.3 V. The current density decreased quickly in the first 10 min, and deposits obviously appeared on the surface of the electrode after 20 min (Figure S12). Those results revealed that complex 1 is unstable during the process of the electrocatalytic reaction under CO₂-saturated CH₃CN in the presence of H₂O. Thereby, dry conditions were used in the following study.

To study the kinetics of the electrocatalytic CO_2 reduction by complex 1, the cyclic voltammograms under catalytic conditions were studied by varying the catalyst concentration and the scan rate. A linear increase in the catalytic current on [1] was observed, indicating a first-order reaction in catalyst (Figure S13). The catalytic current plateaus of 1 are relatively independent of scan rate in the range of $0.6-1.0 \text{ V s}^{-1}$ (Figure 4a). The plot of i_c/i_p versus the inverse square root of the scan rate highlights that steady-state conditions and the pure kinetic regime are accomplished at high scan rates of >0.6 V s⁻¹ (Figure 4b). In this case, TOF of complex 1 was calculated from the i_c/i_p ratio using eq $1^{41,50}$ **Inorganic Chemistry**

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Figure 4. (a) Cyclic voltammograms of complex 1 (0.5 mM) in CO₂saturated CH₃CN with 0.1 M TBAP as the electrolyte at different scan rates (0.1–1.0 V s⁻¹). (b) Plot of TOF vs scan rate, with an inset of i_c/i_p vs the inverse square root of the scan rate, highlighting that steady-state conditions are accomplished at high scan rates (0.6–1.0 V s⁻¹).

$$\text{TOF}_{\text{max}} = 0.1992 \left(\frac{F\nu}{RT}\right) \left(\frac{n_{\text{p}}^{3}}{n_{\text{cat}}^{2}}\right) \left(\frac{i_{\text{c}}}{i_{\text{p}}}\right)^{2}$$
(1)

where F is the Faraday constant, R the gas constant, T the temperature, v the scan rate, n_p the number of electrons involved in the noncatalytic Faradaic process (two electrons for 1), n_{cat} the number of electrons required for a single catalytic cycle (two electrons for CO_2 to CO), i_c the catalytic current plateau, and i_p the peak current of the noncatalytic wave. As shown in Figure 4b, TOF_{max} (3180 ± 6 s⁻¹) was observed at a scan rate in the range of 0.6-1.0 V s⁻¹. Controlled-potential electrolysis (CPE) experiments were performed in a homemade H-type electrochemical cell to evaluate the stability of complex 1. As shown in Figure S14a, the current density gradually decreased from -1.9 to -1.5 mA cm⁻² over 110 min in a CO₂-saturated CH₃CN solution containing 0.1 M TBAP at an E_{appl} of -2.3 V. Gas chromatographic analysis confirmed that the product of electrochemical reduction of CO2 is CO with an average Faradaic efficiency of 95% (Figure S14b). A charge of 32 C passed over 110 min, corresponding to a TON_{CO} value of ~25. Under the same conditions but in the absence of complex 1, no CO and H₂ were detected in the CPE experiment. Isotope labeling experiments were conducted in a ¹³CO₂-saturated CH₃CN solution containing 1.0 mM complex 1 at an applied potential of -2.3 V. After electrolysis for 1 h, the gas phase product was analyzed by GC-MS and the results showed that ¹³CO was the main product with a small amount of ¹²CO (Figure S15; 11.4:1 ¹³CO:¹²CO). Thereby, we can conclude that complex 1 catalyzes electrochemical reduction of CO₂ to CO in a CO₂-saturated CH₂CN solution.

Chemical Reduction and Infrared Spectroscopy. The FTIR spectra of 1 and its singly and doubly reduced species in THF together with the spectrum of 2° in solid (denoted as $[2^{\bullet}-2^{\bullet}]$) are depicted in Figure 5, and their DFT-calculated CO stretching bands listed in Table S5. Similar to complex A_{1}^{42} complex 1 displays three characteristic ν_{CO} bands at 2009, 1929, and 1888 cm⁻¹. Upon addition of 1.1 equiv of KC₈ to a THF solution of 1, the resulting solution displayed two sets of $\nu_{\rm CO}$ stretching bands with the lower-intensity bands at 1975, 1886, and 1872 cm⁻¹ (labeled as purple triangles) and higherintensity bands at 1941, 1848, and 1828 cm⁻¹ (labeled as red stars). As time elapsed, the set of lower wavenumbers was gradually converted to the set of higher wavenumbers (Figure S16). For the five-coordinate, singly reduced species 2°, there are two possible configurations: fac- and mer-2° (Figure S17). According to our DFT calculations (Table S5), the calculated



Figure 5. FTIR spectra of *fac*-[Mn^I(bis-^{Mes}NHC)(CO)₃Br] (black, 1), the singly reduced species (red, 2[•] and unknown species X), solid $[2^{\bullet}-2^{\bullet}]$ dissolved in THF (purple), and the doubly reduced species [Mn⁻(bis-^{Mes}NHC)(CO)₃]⁻ (orange, 2⁻) in THF together with the ATR-IR spectrum of solid $[2^{\bullet}-2^{\bullet}]$ (blue).

IR stretching bands of these two isomers are very close to each other. Thereby, the bands labeled with stars and triangles are not likely due to the isomerization between fac- and mer-2°. In addition, the ATR-IR spectrum of the crystal solid of $\begin{bmatrix} 2^{\bullet}-2^{\bullet} \end{bmatrix}$ displays three $\nu_{\rm CO}$ bands at 1878, 1853, and 1811 cm⁻¹; redissolving solid $[2^{\bullet}-2^{\bullet}]$ in THF produced a yellow solution, showing three $\nu_{\rm CO}$ bands at 1975, 1886, and 1864 cm⁻¹, and these bands are almost identical to the bands denoted with triangles for the singly reduced species. We thereby conclude that the bands denoted with triangles are assigned to the solvated, singly reduced species 2°. It should be mentioned that the calculated IR spectra of monomeric 2° and dimeric $\begin{bmatrix} 2^{\bullet}-2^{\bullet} \end{bmatrix}$ are largely different from each other, further supporting our assignment. Unfortunately, the bands denoted with stars remain unresolved, and this unknown species is denoted as X.

The reduction of a Mn^0 solution by KC_8 leads to the formation of complex 2^- , which precipitated from the THF solution as a yellow solid together with graphite (the reaction product of KC_8). As a result, we could not obtain pure complex 2^- . Thereby, we used metallic sodium as a reductant and likely obtained the pure yellow precipitates of complex 2^- that showed low-energy ν_{CO} bands at 1863, 1710, and 1669 cm⁻¹ (Figure 5), in good agreement with the formation of Mn⁻ species.⁴² The doubly reduced species of Mn-NHC CO₂ reduction catalysts have not been previously isolated and experimentally characterized, while such reduced species of Mn-bpy-type CO₂ reduction catalysts, for instance, *fac*-[Mn¹(^{Mes} bpy)(CO)₃Br] (^{Mes}bpy = 6,6'-dimesityl-2,2'-bipyr-idine), were reported by the Kubiak group.³⁴

Reaction of CO₂ with Mn⁻. With the doubly reduced species in hand, we tested the direct chemical reaction between 2^- and CO₂, monitored by the stopped-flow FTIR spectroscopy. As shown in Figure S18, one syringe was filled with a CO₂-saturated THF solution and another syringe was filled with a suspension solution of doubly reduced species 2^- . Due to the poor solubility of 2^- , its suspension solution was used and thereby kinetic values of the reaction were not calculated due to the complex situation. Upon mixing, the FTIR spectral changes versus time were monitored (Figure S19) and selected spectra are plotted in Figure 6. No CO bands of 2^- were detected, indicating the poor solubility of 2^- in THF and the rapid reaction between 2^- and CO₂ via very likely the so-called metallocarboxylate intermediate [2-CO₂]^{-.51} As the reaction proceeded, the CO bands at 1976, 1886, and 1868 cm⁻¹



Figure 6. Plot of FTIR spectral change vs time of 2^- upon addition of CO₂ (0.28 M) in the stopped-flow experiment. Note that a band at 1670 cm⁻¹, assigned to free CO₃²⁻, is observed but not shown in Figure 6 for the sake of clarity.^{54,55}

(denoted with triangles) assigned to 2° appeared as the most intense bands and the intensities of the CO bands at 1941, 1848, and 1828 cm⁻¹ assigned to X (denoted with circles) gradually increased. Without knowing the structure of X, we were not able to propose any chemical convention related to X. A fourth intermediate was observed with CO bands at 2085, 1993, and 1969 cm^{-1} (denoted with stars) during the course of the reaction between 2^- and CO₂. Royo, Lloret-Fillol, and coworkers also observed similar CO stretching bands at 2090, 2002, and 1969 cm^{-1} for the A-catalyzed electrochemical CO₂ reduction reaction, and this intermediate was assigned to the tetracarbonyl intermediate $[Mn(bis-MeNHC)(CO)_4]^+$ on the basis of DFT calculations.⁴² Rochford and co-workers reported a tetracarbonyl Mn complex $[Mn^+([(MeO)_2Ph]_2bpy)(CO)_4]^+$ $\{[(MeO)_2Ph]_2bpy = 6,6'-bis(dimethoxyphenyl)-2,2'-bipyri$ dine} with CO stretching bands at 2106, 2026, 2018, and 1982 cm^{-1} , and this complex is stable but expels a CO molecule after one-electron reduction to produce the tricarbonyl Mn⁰ species.⁴¹ In addition, Cowan and co-workers also observed a tetracarbonyl Mn complex $[Mn(bpy)(CO)_4]^+$ during CO₂ reduction in situ at the electrode surface by vibrational sum-frequency generation spectroscopy.⁵² Recently, Andrew and co-workers directly synthesized a tetracarbonyl Mn complex $[Mn(bpy)(CO)_4]$ [SbF₆] with CO bands at 2130, 2046, 2024, and 1984 cm⁻¹, and this complex is an efficient electrocatalyst for the reduction of CO₂ in the presence of water.⁵³ In our case, when a THF solution of complex 1 was stirred for 36 h under 10 atm of CO, we observed new CO stretching bands at 2086, 1995, and 1969 cm⁻¹ (denoted with stars in Figure S20) and this species is assigned to the tetracarbonyl manganese complex $[Mn(bis-MesNHC)(CO)_4]^+$ $([2-CO]^+)$. The CO bands at 2085, 1993, and 1969 cm⁻¹ in the stopped-flow experiment are consistent with the CO stretching bands of this tetracarbonyl complex. Therefore, the fourth intermediate is assigned as the tetracarbonyl intermediate manganese complex.

Spectroelectrochemistry. A homemade IR spectroelectrochemistry cell as shown in Figure S21 that consists of a glass carbon working electrode, a Pt counter electrode, and a Ag/AgNO₃ reference electrode was used for this study. As depicted in Figure S22, the Fourier-transform infrared spectroelectrochemistry (FTIR-SEC) spectral changes of 1 under a CO₂ atmosphere at an applied potential of -2.2 V in a CH₃CN solution showed that the intensity of the CO stretching bands of 1 slightly decreased (denoted with triangles) and the differential spectra revealed the growth of new bands at 2089, 1997, 1971, 1686, and 1644 cm⁻¹. The

intensity of the bands at 1686 and 1644 cm⁻¹ (denoted with circles) rapidly increased, and these bands are assigned to $HCO_3^{-}/CO_3^{2^-}$ stretching.⁵⁵ The bands at 2089, 1997, and 1971 cm⁻¹ (denoted with stars) matched well with the FTIR spectrum of the tetracarbonyl Mn complex [2-CO]⁺. Unfortunately, we did not observe the CO bands of the metallocarboxylate intermediate, implying that its concentration is extremely low. These spectral changes match well with those observed in the stopped-flow FTIR experiments. Apparently, the tetracarbonyl Mn complex [2-CO]⁺ is stable at the Mn⁺ state. The buildup of [2-CO]⁺ and the undetectable amount of other intermediates suggest that [2-CO]⁺ might be the resting state.

Catalytic Cycle. The CO₂ reduction mechanisms of tricarbonyl Mn-bpy and Mn-NHC complexes have been discussed by several research groups.^{35,39,42} On the basis of our observations and previous mechanistic studies of other Mn CO₂ reduction catalysts, we could propose the following reaction mechanism (Figure 7). The starting complex **1** is first



Figure 7. Proposed electrochemical CO_2 reduction mechanism of complex 1.

reduced to generate the Mn^0 species, which is prone to bromide ligand dissociation, leading to the formation of 2°, and it can take one more electron to generate the doubly reduced 2⁻, which reacts fast with carbon dioxide and yields a metallocarboxylate intermediate [2-CO₂]⁻. Usually, Mn-bpy catalysts require Brønsted or Lewis acids to facilitate the formation of the metallocarboxylic acid or metallocarboxylate.⁵ For instance, $[Mn(^{Mes}bpy)(CO)_3]^-$ reacts with CO₂ in the presence of MeOH to afford the Mn-COOH species where the C–OH bond is cleaved upon reduction and protonation, leading to the formation of CO.³⁴ When MeOH is replaced by a Lewis acid Mg²⁺, a metallocarboxylate species [Mn(I)– CO₂Mg]⁺ is then proposed instead of the Mn-COOH species;

Inorganic Chemistry

the solvated CO₂ molecule as an electrophile attacks the oxygen atom of the metallocarboxylate, leading to the formation of CO and carbonate.³⁸ In comparison with the Mn-bpy catalysts, Mn-NHC catalysts are more electron rich in general, and thereby, their metallocarboxylate species are more electrophilic and can react with solvated CO₂ in the absence of additional acids. In our case, we proposed that the solvated CO₂ molecule acts as an oxygen atom acceptor, reacts with this metallocarboxylate, and thereafter cleaves one C-O bond of the carboxylate, leading to the formation of the tetracarbonyl complex $[2-CO]^+$. This complex is stable against CO liberation and requires further reduction to enable CO dissociation. Then, the tricarbonyl 2[•] is regenerated and the catalytic cycle closed. The buildup of the tetracarbonyl Mn⁺ intermediate suggests that the reduction of this intermediate to the Mn⁰ state might be the rate-limiting step when the doubly reduced catalyst is involved. Notably, Cowan and co-workers also observed the accumulation of the tetracarbonyl Mn-bpy species on the Au-Hg electrode using vibrational sumfrequency generation spectroscopy.⁵¹ This common phenomenon shared by both tricarbonyl Mn-bpy and Mn-NHC complexes suggested that more attention should be paid to the tetracarbonyl Mn species in order to understand further the limiting step of CO₂ reduction reaction by Mn catalysts.

CONCLUSIONS

We have described an earth-abundant metal complex fac- $[Mn^{I}(bis-MesNHC)(CO)_{3}Br]$ (1) that is capable of catalyzing the electrochemical reduction of CO₂ to CO with high activity with a TOF_{max} of 3180 \pm 6 s⁻¹. The introduction of two bulky Mes groups on the NHC ligand significantly prevents the dimerization of the singly reduced Mn species, weakens the electron-donating ability of NHC due to steric hindrance, and thereby decreases its onset potential. Furthermore, low-valence intermediates were characterized by FTIR spectroscopy, and the single-crystal X-ray diffraction structure of the singly reduced species 2° was successfully determined. The ratelimiting step for 1-catalyzed electrochemical CO₂ reduction is proposed to be the reduction of the tetracarbonyl Mn⁺ species to its Mn⁰ state on the basis of time-course FTIR spectroscopy studies. These findings enriched the CO₂ reduction chemistry of Mn-NHC catalysts and paved the way for the design of more efficient earth-abundant Mn-based CO₂ reduction catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01364.

Additional experimental results, including ¹H NMR spectra, FTIR spectra, FTIR-SCE spectra, electrochemical curves, i-t curves, and tables of results on related complexes obtained herein (PDF)

Accession Codes

CCDC 1960153–1960154 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 Author

Lele Duan – Department of Chemistry and Shenzhen Grubbs Institute and Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology (SUSTech), Shenzhen 518055, P. R. China; orcid.org/0000-0003-1662-5817; Email: duanll@ sustech.edu.cn

Authors

- **Yong Yang** Department of Chemistry, Southern University of Science and Technology (SUSTech), Shenzhen 518055, P. R. China
- **Zhenyu Zhang** Department of Chemistry, Southern University of Science and Technology (SUSTech), Shenzhen 518055, P. R. China
- Xiaoyong Chang Department of Chemistry, Southern University of Science and Technology (SUSTech), Shenzhen 518055, P. R. China
- Ya-Qiong Zhang Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China
- Rong-Zhen Liao Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China;
 orcid.org/0000-0002-8989-6928

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c01364

Notes

The authors declare no competing financial interest.

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