Electrochemical Reduction of Carbon Dioxide

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Received July 14, 2004

Dinuclear Ni(0) complexes [Ni₂(μ-dppa)₂(μ-CNR)(CNR)₂] (R = Me (1), n-Bu (2), and 2,6-
Me₂C₆H₃ (3); dppa = bis(diphenylphosphine)amine) were synthesized in good yields by
reacting Ni(COD)₂ with dppa and the corresponding isocyanide. The X-ray structure of
complex 1 is reported. The electrochemistry and spectroelectrochemistry of each complex
are also reported. Complex 2 exhibits an irreversible 1 e⁻ reduction at −0.99 V vs ferrocene
in its cyclic voltammogram. When the cyclic voltammetry was performed in the presence of
CO₂, a substantial current enhancement was observed for the reduction wave. Spectroelec-
trochemical as well as isotope labeling studies show that 2 is singly reduced to a radical
anion species that is reactive toward CO₂, yielding the disproportionation products CO and
CO₂²⁻. In the presence of H⁺ donors (residual water), reduction of CO₂ to formate is a
competing process.

Introduction

Carbon dioxide is the end product of many industrial
and biological processes; however, only plants can
effectively regenerate useful products from it. The
electrocatalytic reduction of carbon dioxide to organic
elements has drawn the attention of many research
groups.1–5 Bis(diphenylphosphine)methane (dppm) is
frequently used as a supporting ligand in transition
metal complexes that show activity toward the reduction
of CO₂.1 Polynuclear complexes containing dppm have
been shown to react with CO₂ photochemically,2 elec-
trochemically,3 and chemically.4 Similar disphosphines
such as bis(diphenylphosphino)amine (dppa) have
received less attention in the development of polynuclear
complexes.2 Recently, dinuclear5 and trinuclear6 nickel
complexes with dppa as a supporting ligand have been
reported. In our continuing studies of carbon dioxide
activation using polynuclear transition metal complexes,
we describe the synthesis, characterization, and elec-
trocatalytic properties of dinuclear nickel complexes
[Ni₂(μ-dppa)₂(μ-CNR)(CNR)₂] (R = Me, n-Bu, xylyl) with
bridging dppa ligands. In addition, the X-ray structure of
complex [Ni₂(μ-dppa)₂(μ-CNCH₃)(CNCH₃)₂], 1, is reported.

Experimental Section

Materials and Physical Measurements. All manipula-
tions were performed under a nitrogen atmosphere using a
glovebox or Schlenk techniques. Ni(COD)₂, MeNC, and the
ligand NH(PPh₂)₂ (dppa) were synthesized according to lit-
erature procedures.7,8 CN(n-Bu) and CN(2,6-Me₂C₆H₃), CN(2,6-
Me₂C₆H₃) = CNxylyl, were purchased from Aldrich and used
without further purification. Isotopically labeled chemicals
(H₂¹⁶O, ¹³CO₂) were purchased from Cambridge Isotope Labo-
ratories, Inc. The carbon dioxide concentration in acetonitrile
solutions was measured using an IR method reported previ-
ously.9 Solvents were purchased from Fisher Scientific and
purified by passing through aluminum oxide columns
under nitrogen pressure.¹H and ³¹P NMR spectra were
obtained using a Varian Mercury 400 spectrometer, and ³¹P
NMR spectra were referenced with respect to external 85%
H₃PO₄. Elemental analyses were performed by Midwest
Microlab. KBr FTIR spectra were recorded using Mattson
Research Series 1) and Bruker (Equinox 55) spectrophotom-
eters. Cyclic voltammetric (CV) measurements were carried
out using a BAS-CV-50w electrochemical workstation.
The working electrodes were a platinum disk (CV) or a platinum
mesh (coulometry). The supporting electrolyte was tetrabutyl-
ammonium hexafluorophosphate (TBAPF₆⁻). All potentials
are reported with respect to a ferrocene/ferrocenium (Fc/Fc⁺)
reference electrode. The spectroelectrochemical (SEC) mea-
surements were performed in a cell constructed by our group
and reported previously.¹⁰ Bulk electrolysis at a potential of
−1.3 V and temperature of −70 °C was used to generate the
reduced species. The electrochemical cell was held in a
specially constructed brass circulation unit inside the drybox
and connected to an outside refrigerated circulating bath. The
EPR experiments were performed using a Bruker continuous

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wave E500 spectrometer of the Elexsys Series at 5 K in frozen THF. Density functional calculations (DFT) were done using a hybrid functional developed by Becke along with Perdew and Wang correlation, using the LANL2DZ basis set (b3pw91/LanL2DZ) as implemented in Gaussian98.

| Table 1. Crystal Data and Collection Parameters for 1 |
|-----------------|------------------|
| formula         | C$_{2}$H$_{12}$N$_{3}$P$_{3}$Ni$_{2}$ |
| fw              | 1010.28          |
| space group     | P1               |
| crys syst       | triclinic        |
| a, Å            | 12.8286(10)      |
| b, Å            | 13.5102(11)      |
| c, Å            | 14.9130(12)      |
| α, deg          | 81.9030(10)      |
| β, deg          | 85.7970(10)      |
| γ, deg          | 74.0030(10)      |
| V, Å$^3$        | 2458.2(3)        |
| Z               | 2                |
| d$_{calc}$, g cm$^{-3}$ | 1.366 |
| crys dimens, mm | 0.2 × 0.2 × 0.1 |
| temperature, K  | 100(2)           |
| F$_{000}$       | 1052             |
| GOF             | 0.964            |
| final R indices | [I > 2σ(I)] R1 = 0.0531 |


Figure 1. ORTEP diagram (thermal ellipsoid 50%) for complex [Ni$_{2}$(μ$_{2}$-dppa)$_{2}$(CNMe)$_{3}$(CNMe)$_{2}$](n-Bu$_{2}$, 2; xylyl, 3). The phenyl rings are omitted for clarity. Selected bond length (Å) and angles (deg): Ni(1)−Ni(2), 2.5174(9); Ni(1)−P(1), 2.1694(14); Ni(2)−P(2), 2.1876(15); Ni(1)−C(49), 1.9055(15); Ni(2)−C(49), 1.914(5); Ni(1)−C(53), 1.256(5); Ni(2)−C(51), 1.803(5); P(3)−N(5), 1.706(4); P(4)−N(5), 1.710(4); C(49)−N(1), 1.220(7); C(1)−C(50), 1.446(8); C(53)−N(3), 1.146(7); C(53)−C(54), 1.425(8); C(51)−N(2), 1.163(8); N(2)−C(52), 1.423(10); P(1)−Ni(1)−P(4), 113.02(5); P(2)−Ni(2)−P(3), 110.04(6); C(53)−Ni(1)−C(49), 95.0(2); C(51)−Ni(2)−C(49), 101.83(3); C(53)−Ni(1)−Ni(2), 141.87(17); C(51)−Ni(2)−Ni(1), 148.3(2); P(3)−N(5)−P(4), 115.8(2); P(2)−N(4)−P(1), 117.3(2).

CIF file for complex 1 has been deposited with the Cambridge Crystallographic Database (Deposition Number 212125). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis. Dppa reacts with Ni(COD)$_{2}$ in the presence of aryl and alkyl isocyanides (CNR) to give the dinuclear nickel complexes Ni$_{2}$(μ$_{2}$-dppa)$_{2}$(μ$_{2}$-CNMe)-(CNMe)$_{2}$ in good yield. These complexes are iso-electronic and similar overall to dppm-bridged dimers reported earlier. All of the complexes are air sensitive. They were fully characterized by $^{31}$P and $^{1}$H NMR, elemental analysis, and IR. Like the dppm analogues, the different isocyanide ligands do not affect the $^{31}$P NMR chemical shift (69 ± 1 ppm) significantly, indicating that the orbitals involving the phosphorus nickel bonds do not interact appreciably with those involved in nickel−isocyanide bonding.

Molecular Structure of Complex 1. The structure of 1, Figure 1, appears similar to its dppm analogue Ni$_{2}$(μ$_{2}$-dppm)$_{2}$(μ$_{2}$-CNR)$_{2}$ in Table 1. Complex 1 has a “W-frame” or “cradle” type structure with two μ-bridging dppa ligands between the nickel atoms and three isocyanide ligands, of which two are terminal and one is bridging to the two metal centers. Crystal data and data collection parameters for complex 1 are summarized in Table 1.

of the electrochemical oxidations (reduction peaks d and e after oxidations a and b). The scan toward negative potentials shows an irreversible reduction at −0.99 V (peak f). Peak g corresponds to reoxidation of the organonickel radical anion, expected by reduction f. It is also evident that at room temperature these species are not sufficiently structurally stable for their reoxidation to be seen in the reverse scan, even at a high scan rate (500 mV s\(^{-1}\)).

Peak f shifts cathodically by 23 mV when the scan rate is increased from 200 to 500 mV s\(^{-1}\). The CVs recorded for complexes 1 and 3 in THF (complexes 1 and 3 are less soluble in acetonitrile) have the same overall shape with little variation in their redox potentials. The reduction peak at ca. −1.0 V, in the case of complex 2 (peak f, Figure 2), is quite small for complexes 1 and 3. This suggests either sluggish kinetics in the reduction of these complexes or an increased instability of the electrochemically reduced species. This may be explained because of greater reactivity of the radical anions of these complexes in THF solvent.

**Spectroelectrochemical (SEC) Studies.** A IR-SEC cell\(^{(11)}\) was employed to investigate the electronic and structural changes when 2 is reduced or oxidized. Figure 3a–c shows the IR–SEC response in the ν(CN) region at −1.3, 0.0, and +0.2 V vs Ag wire at −35 °C, respectively. Upon reduction at −1.3 V, the bands at 2086 and 1710 cm\(^{-1}\), which correspond to the terminal and bridging isocyanides, respectively, decreased and new bands grew in at 2050 and 1676 cm\(^{-1}\) with clear isosbestic points at 2069 and 1693 cm\(^{-1}\). The simultaneous shift of both bands by 36 to 34 cm\(^{-1}\) to lower energy is consistent with electron density being added to the π*\(c\text{-}N\) orbitals while maintaining the overall “W-frame” structure of the dimer.

Ligand-based reduction is consistent with theoretical calculations involving complex 2, which are discussed later. Reoxidation at −0.35 V gave the starting neutral species 2\(^{0}\). The reversible structural changes that accompany ET (peak f, Figure 2) and the cathodic shift of f with an increase in scan rate strongly suggest an \(E_{\text{rev}}\) mechanism for the reduction process f\(^{20}\).

When the sample was oxidized at 0 V (peak a in CV), the bands at 2086 and 1710 cm\(^{-1}\), which correspond to the neutral species, disappeared, and a new band at 2134 cm\(^{-1}\) grew in, suggesting that a significant amount of charge has been removed from the CN bridge after the 1 e\(^{-}\) oxidation occurs (Figure 3b, 2\(^{-}\) species). Oxidation of the neutral species 2\(^{0}\) at more positive potentials (+0.20 V) is accompanied by a rapid appearance and disappearance of species 2\(^{+}\) (2134 cm\(^{-1}\)), followed by new bands at 2169 and 2024 cm\(^{-1}\) (Figure 3c). A clean isosbestic point at 2152 cm\(^{-1}\) links this transformation. These results are consistent with an internal redox disproportionation reaction of the two Ni(I)–Ni(I) centers to a Ni(II)–Ni(0) formulation with one of the isocyanides bonded to a Ni(II) (2169 cm\(^{-1}\)) and the other to a Ni(0) center (2024 cm\(^{-1}\)). Similar redox disproportions are observed in other nickel dimers upon 2 e\(^{-}\) oxidations.\(^{(19)}\) These changes are chemically reversible, and the neutral 2\(^{0}\) species can be

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regenerated by electrolysis at −0.7 V. The SEC results are summarized in Scheme 1.

To obtain more information about the nature of the species formed during the electrochemical reduction (peak f in Figure 2), an EPR experiment was performed. Because the reduced species is unstable at −35 °C, bulk electrolysis was performed at −70 °C using a special electrochemical setup (see Materials and Physical Measurements section). After electrolysis, the sample was transferred to an EPR tube and kept in liquid nitrogen for EPR evaluation. The EPR signal in frozen THF solution at 4 K (see Supporting Information for spectrum) is broad and has an average $g$-value of 2.05. Although the EPR spectrum is not sufficiently resolved to make definitive conclusions about the structure of the reduced species, the fact that upon reduction the generated species is not EPR silent tells us about the radical nature of this electrochemically generated species. Ligand-based reduction is in agreement with IR spectroelectrochemical results and the ligand-centered character of the LUMO in the isoelectronic Ni$_2$(dppa)$_2$(CO)$_3$ complex, as well as the calculated LUMO for complex 1 (see below). Also, the broad appearance of the EPR spectrum could be related to an unpaired electron occupying a degenerate LUMO (see theoretical calculations below), where fast spin relaxation is expected.

**Cyclic Voltammetry in the Presence of CO$_2$.** The cyclic voltammograms of complex 2 in the presence of concentrations of CO$_2$ (0.0025, 0.050, and 0.100 M), Figure 4, showed a large [CO$_2$]-dependent increase in current of the cathodic wave at −1.0 V while the oxidation waves remained unchanged.

The current increases with increasing CO$_2$ concentrations indicate an electrochemical process that is bimolecular and directly involves CO$_2$. The simplest mechanism is represented by eqs 1 and 2.

\[
[Ni_2]^0 + e^- \rightarrow [Ni_2]^{--} \tag{1}
\]

\[
[Ni_2]^{--} + CO_2 \xrightarrow{k'} [Ni_2]^0 + CO_2^{--} \tag{2}
\]

After purging with argon, the cyclic voltammogram returns to its original shape. According to eqs 3 and 4, derived by Saveant and Vianello, the limiting current for a catalytic reaction with reversible charge
transfer is proportional to the rate constant and independent of the scan rate.

\[ i = nFACo \sqrt{Dk_f} \] (3)

\[ k_f = k'[CO_2] \] (4)

where \( i \) is the observed cathodic current at -1.3 V, \( n \) is the number of transferred electrons during the electrochemical reaction, \( A \) is the area of the working electrode, \( F \) is the Faraday constant, \( Co \) is the concentration of the \([Ni_2]^0\) species in the bulk, \( D \) is the diffusion coefficient, calculated from the CV data,\(^{23}\) and \( k' \) is the rate constant for the homogeneous electron transfer reaction between the electrochemically reduced organonickel radical and CO_2.

For a large value of \( k_f \) (eq 3) and very cathodic potentials, no wave should be observed. In our system, the cyclic voltammogram in the cathodic region shows no differences at scan rates between 20 and 500 mV s\(^{-1}\), adding support to the mechanism proposed above (eqs 1 and 2). The rate constant \( k' \) for the bimolecular reaction eq 2, evaluated according to eqs 3 and 4 from the CV data, equals 29.0 M\(^{-1}\) s\(^{-1}\). This is a significantly higher value, compared to the previously studied nickel cluster radicals \([Ni_3(\mu_2-dppm)_3(\mu_2-L)(\mu_3-I)] \) \( (L = CNR, R = CH_3, i-C_4H_9, C_6H_{11}, C_6H_2C_6H_5, t-C_4H_9, 2,6-Me_2C_6H_3; L = CO) \), where the rate constants for the rate-limiting step in the reduction of CO_2 by the clusters, \( k_{CO_2} \) (M\(^{-1}\) s\(^{-1}\)), were estimated to range between 1.6 and 0.01, having the lower values for the more sterically hindered clusters.\(^{24}\)

It is interesting to note that the isostructural complex \([Ni_2(\mu_2-dppm)_2(\mu_2-CNMe)(CNMe)_2] \) has two quasi-reversible oxidation peaks. In the presence of CO_2, the second cathodic wave shows current enhancement in the cyclic voltammogram, which was interpreted in terms of an EC mechanism, resulting from an irreversible chemical reaction with CO_2 to give a \([Ni_2(\mu_2-dppm)_2(\mu_2-CNMe)(CNMe)_2]CO_2 \) complex, where the C and O atoms of CO_2 and C and N atoms of the bridging isocyanide form a four-membered ring.\(^{17}\) The rupture of the four-membered ring of this intermediate leads to the formation of carbonyl complex \([Ni_2(\mu_2-dppm)_2(\mu_2-CO)(CO)_2] \), confirmed by isotopic labeling studies.

**IR SEC Results in the Presence of CO_2.** A 0.1 mM solution of complex 2 in acetonitrile (TBAP 0.1 M) with CO_2 was injected into the IR SEC cell. Large currents \((~5 \text{ mA})\) were observed when the solution was electrolyzed at -1.3 V vs a silver pseudoreference electrode. Figure 5 shows that the spectral changes in the \( \nu (\text{NC}) \) region were very different from those observed upon reduction of complex 2 in argon-saturated CH_3CN solution at this potential (Figure 3a).

![Figure 5](image-url)

The \( \nu (\text{NC}) \) band at 2086 cm\(^{-1}\), corresponding to terminally coordinated isocyanides, decreased slightly in intensity, and new bands at 2004, 1980, 1950, 1926, 1685, and 1650 cm\(^{-1}\) were observed. Toward the end of the electrolysis, the bands around 2000 cm\(^{-1}\) are slightly shifted, with the most intense absorptions at 2004, 1953, 1916, and 1868 cm\(^{-1}\).

The two bands at 1685 and 1650 cm\(^{-1}\) are similar to the bands reported for carbonate anion in acetonitrile solution.\(^{25}\) The bands at 2004, 1980, 1950, and 1926 cm\(^{-1}\) are similar to those reported for terminal and

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bridging carbonyls in dpmp$^{26}$ and dppa$^{5}$ nickel dimers. These results suggest that the CO$_2$ reductively disproportionates into CO and CO$_3^{2-}$ and that the CO is “trapped” by the nickel catalyst, explaining why no bands in the region of free CO (2138 cm$^{-1}$) grow in during the electrolysis. The ready and reversible uptake of CO by [Ni$_2$(μ-2-dppm)(μ-CO)](CO)$_2$ and [Ni$_2$(μ-2-dppa)(μ-2-CO)](CO)$_2$ was reported.$^{5,26}$ An equilibrium like the one shown in Scheme 2 may explain the shift in the Ni–CO region toward the end of the electrolysis, where the concentration of CO is expected to be higher. Also, such an equilibrium leads to a complex mixture of nickel species in solution considering that CO and isocyanides compete for the {Ni$_2$(dpaa)$_2$} fragment, explaining the rather large number of bands in the Ni–CO region. To determine the identity of the bands that appeared around 2000 cm$^{-1}$, an acetonitrile/TBAP solution of complex 2 was saturated with CO and injected into a liquid IR cell. Together with those bands, corresponding to complex 2, new ones appeared at 2004, 1980, 1950, 1926, 1953, and 1868 cm$^{-1}$. No bands in the vicinity of 2138 cm$^{-1}$, typically for free CO, were observed.

The obvious question that follows is, do these carbonyl species show electrocatalytic activity toward CO$_2$? Under similar conditions, the CO dimer [Ni$_2$(μ-2-dppa)$_2$(μ-2-CO)](CO)$_2$, synthesized according to a literature method,$^{5}$ did not show any electrocatalytic activity with respect to CO$_2$ reduction. This experiment offers a plausible explanation of how catalytic activity is lost during the electrochemical reduction. Formate results from the reaction of the anion radical CO$_2^-$ with a proton. The role of residual water on the electrocatalytic reaction was investigated with spectroelectrochemical reductions of CO$_2$-saturated anion radical solutions that also contained H$_2$O or D$_2$O (for spectra see Supporting Information). The spectral changes in the 2000–1600 cm$^{-1}$ infrared region were only slightly different from those in the absence of water. When traces of H$_2$O are present, new bands at 1609 and 1333 cm$^{-1}$, assigned as formate,$^{25}$ grow in. Addition of H$_2$O or D$_2$O has no effect on those bands in the Ni–CO region, but the carbonate bands collapse, probably due to hydrogen bonding of the carbonate anion. When the solvent was dried with superacid alumina,$^{27,28}$ the formate peaks at 1609 and 1333 cm$^{-1}$ do not appear. In our systems, we are able to reach electrochemical windows of +2 and −3.0 V with acetonitrile/ TBAP solutions after purification through a column filled with previously calcinated superacid aluminum oxide. Even in this super dry solvent the catalytic activity of our system toward CO$_2$ remains the same, ruling out the water as the possible cause of the current enhancement observed during electrochemical reductions.

In an attempt to trap the “generated” CO$_2^-$ radical, large quantities of cyclohexene as a quencher ($>1.5$ M) in acetonitrile solution were introduced. The IR SEC shows no new bands at 1728 cm$^{-1}$, expected for a carboxylic acid. We conclude that these results are consistent with the single electron reduction of CO$_2$ to CO$_2^-$, but the radical anion does not appear to react as a free radical, but rather a trapped (coordinated) one.

**Theoretical Calculations.** Figure 6 shows the HOMO–LUMO frontier orbitals for complex 2. The HOMO frontier molecular orbital reveals a strong contribution of metal orbitals (p$_x$ and d$_{xy}$) bonding to the μ-bridging isocyanide ligands and the phosphorus atoms. The d electrons are in σ orbitals delocalized between both metals, across the conjugated bridging ligand. This orbital is bonding with respect to the Ni–C (μ-CNMe) bond, but it is a Ni–Ni antibonding orbital, with a nodal plane passing through the μ-CNMe bridge.

The plane is perpendicular to the Ni–Ni axis and bisects the molecule in two symmetrical fragments. The LUMO is further delocalized to the isocyanide phenyl rings with a small contribution from carbon and nitrogen at the terminal isocyanide ligands and having strong π* character. This picture is supported by the

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IR of the reduced [2]− species obtained in the SCE experiment, where νCN stretching frequencies of terminal and bridging ligands are shifted by 36 and 34 cm⁻¹, respectively, toward lower energy upon reduction. The next two orbitals below the HOMO (HOMO⁻¹ and HOMO⁻²) are close in energy and have similar symmetry (ΔE(HOMO−HOMO⁻¹) = 0.3208 eV). A similar picture is observed for the higher energy LUMO⁺¹ and LUMO⁺² orbitals (ΔE(LUMO⁺¹−LUMO) = 0.1041 eV).

Conclusions

Complexes 1–3 are 1 e⁻ electrocatalysts for the reduction of carbon dioxide. Reduction of the dinuclear nickel(0) complexes is largely ligand-localized, on the basis of theoretical calculations and SEC results, where the π* orbital of the phenyl ring on the xylyl isocyanide can shuttle electrons in and out of the closed-shell d10–d10 [Ni2] system. The products of carbon dioxide electroreduction in the presence of complexes 1–3 are mainly CO and CO₂, with small amounts of formate formed when residual water is present. Complexes 1–3 also react with carbon monoxide, leading to formation of carbonyl-containing species that are not active toward CO₂ reduction.

Acknowledgment. The authors wish to thank the DOE (DE-FG03-99ER14992) for support of this research. E.S.-M. thanks Dr. Brian Breedlove for his contributions to the manuscript preparation.

Supporting Information Available: Spectroscopic and electrochemical data of the complexes 1, EPR spectra of 2−, and control IR SEC experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0494723