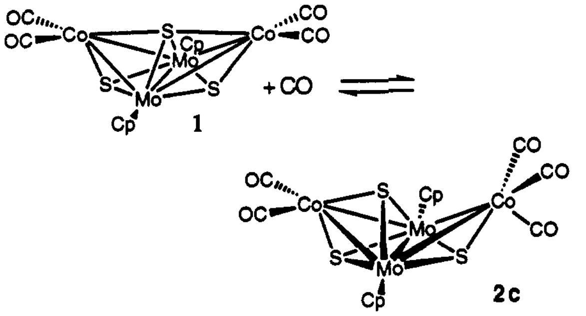

(3)

(δ 1.76) for the methyl protons. The infrared spectrum, obtained with an internal reflectance cell, shows two ν_{CO} bands at 2040 (m) and 1958 (s, br) cm^{-1}, which may be assigned to the $Co(CO)_3$ fragment. The two peaks at 1987 (s) and 1940 (sh) cm^{-1} are assigned to the $Co(CO)_2$ group. The formation of **2c** may account for the lack of desulfurization catalysis when **1** is heated with thiols at 150 °C under 1000 psi of CO.[22]

While Co–S bond breaking clearly occurs in the course of these carbonyl substitution reactions, kinetic studies are necessary to determine if this occurs prior to nucleophilic attack in a preequilibrium step or if Co–S bond breakage is initiated by the nucleophile. These studies are currently underway; preliminary results indicate that the conversion of **2** to **3** is also reversible.

The electronic unsaturation of cluster **1**, and consequently the weaker Co–(μ_4-S) bond,[23] accounts for its unusual reactivity toward nucleophiles. Cluster **1** has 60 valence shell electrons (VSE) but only 5 M–M bonds (rather than the 6 M–M bonds usually present in 60-VSE clusters). Addition of a nucleophile to **1** converts it into an electronically saturated, 62-VSE, 5-M–M-bonded cluster. Although this type of reaction should be general, the sparse number of unsaturated clusters limits the known examples.[3e,i,12,13,24]

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Supplementary Material Available: Tables listing X-ray data, atomic positional parameters, thermal parameters, bond distances, bond angles, and H atom coordinates (18 pages). Ordering information is given on any current masthead page.

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Carbon Dioxide Chemistry of the Trinuclear Complex $[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3][PF_6]$. Electrocatalytic Reduction of Carbon Dioxide

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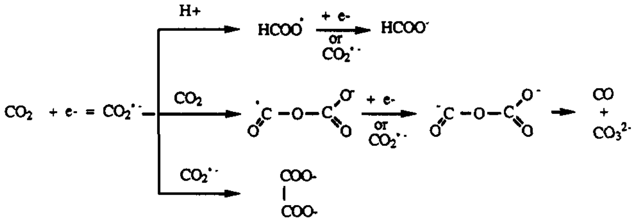
Received April 3, 1992

Summary: The triangular nickel complex $[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3][PF_6]$ (**1**) is an electrocatalyst for the reduction of CO_2. Complex **1** exhibits a reversible single-electron reduction at $E_{1/2} = -1.09$ V vs Ag/AgCl. In the presence of CO_2, **1** reduces CO_2 by an apparent EC′ electrochemical mechanism. The reduction products correspond to the reductive disproportionation of CO_2 to CO and CO_3^{2-}. Isotope labeling studies with $^{13}CO_2$ indicate that $^{13}CO_2^{\bullet-}$ disproportionation produces only ^{13}CO and $^{13}CO_3^{2-}$. In the presence of an H^+ donor, only HCO_2^- is observed.

Scheme I



The reduction of carbon dioxide has been investigated by chemical,[1-18] electrochemical,[19-25] and photochemical[26-30] means. The direct reduction of carbon dioxide at most electrode surfaces is impeded by large overpotentials for

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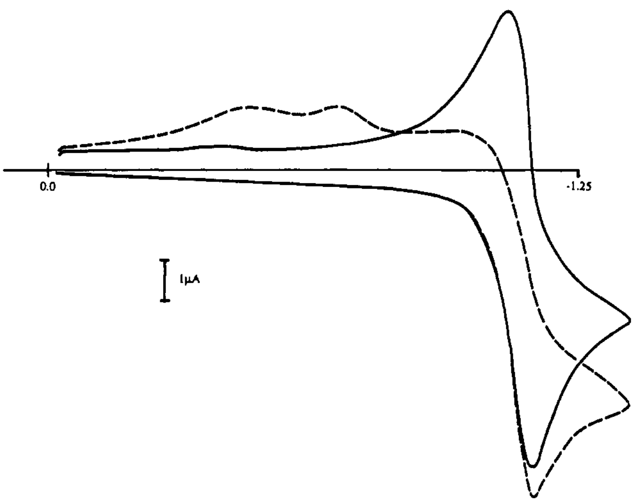


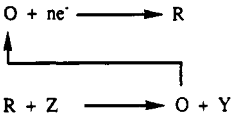
Figure 1. Cyclic voltammograms of $[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3][PF_6]$ (1) in 0.1 M $NaPF_6$/MeCN: (—) initial voltammogram of a solution under N_2; (- - -) the same solution after exposure to CO_2 (3 min).

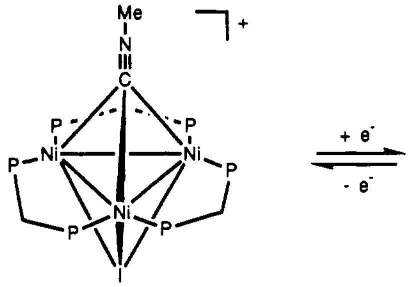
the electron-transfer process. The kinetic overpotentials necessary for the reduction of carbon dioxide can be reduced by transition-metal electrocatalysts to mediate electron transfer to CO_2. In general, the products of CO_2 reduction are formate, oxalate, or carbonate and carbon monoxide.[31] Scheme I summarizes generally accepted mechanisms for the formation of these products.

We previously described facile, reversible oxygen atom transfers between carbonate and carbon monoxide mediated by the iridium carbonate complex $Ir_2(CO_3)(CO)_2(Me_2PCH_2PMe_2)_2$.[32] We have also reported the electrochemical two-electron reduction of the dinickel complex $[Ni_2(CNMe)_3(dppm)_2]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$) and the ensuing multiple-bond metathesis reactions of the reduced species with carbon dioxide to form $Ni_2(CO)_3(dppm)_2$ and dimethylcarbodiimide.[8] As a continuation of our studies of the activation of carbon dioxide we report the electrochemistry of the trinickel complex $[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3]^+$ and its electrocatalytic reduction of carbon dioxide.

The trinickel complex $[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3][PF_6]$ (1) was recently reported.[33] Complex 1 possesses a strongly bonding Ni_3^{2+} core with each pair of Ni atoms bridged by one dppm to form a nearly planar $[Ni_3(dppm)_3]^{2+}$ core. The triangulo cluster is capped by an iodide on one face and by an unusual linear, symmetrically triply bridging methyl isocyanide on the other face. A surprising aspect of the $\mu_3\text{-}\eta^1$-isocyanide is its high ν(CN) stretching frequency of 1925 cm^{-1}. This has been interpreted in terms of an unusually weak interaction between the filled d orbitals of the Ni_3^{2+} core and the π^* orbitals of the isocyanide. Complex 1 undergoes a reversible one-electron reduction at $E_{1/2} = -1.09$ V vs Ag/AgCl reference, to form the cluster radical $[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3]$ (2). The one-electron nature of the reduction wave of 1 is indicated by a peak-to-peak separation, ΔE_{pp}, of 60 mV as well as by a one-to-one correspondence of i_c values with the decamethylferrocene couple, $FeCp^*{}_2{}^{+/0}$. A Na/Hg amalgam reduction of 1 in THF affords a brown/green solution of the neutral paramagnetic complex 2. Complex 2 is extremely air sensitive and is unstable in most solvents other than THF and benzene. The EPR spectrum of 2 shows a seven-line response due to hyperfine coupling to the six equivalent dppm phosphorus atoms; a_P = 52 G. The IR spectrum of 2 shows ν(CN) = 1653 cm^{-1}, a 270-cm^{-1} decrease compared to the signal for 1.

Scheme II





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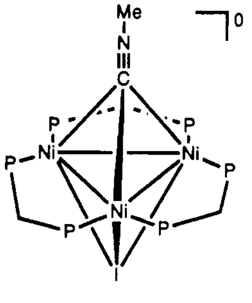

2

The cyclic voltammogram of complex 1 appears markedly different under an atmosphere of carbon dioxide. In the presence of carbon dioxide, the cathodic wave at −1.09 V vs Ag/AgCl shows current enhancement, while the return anodic wave essentially vanishes. Figure 1 shows the effect of carbon dioxide on the cyclic voltammogram of 1. The characteristic features of the cyclic voltammogram of 1 are restored after removal of carbon dioxide with a nitrogen purge. These results, together with the reaction chemistry discussed below, are interpreted in terms of a catalytic EC′ electrochemical mechanism for CO_2 reduction, as outlined in Scheme II.[34]

We have examined both the heterogeneous and the homogeneous electron transfers involved in the electrocatalytic reduction of CO_2 by 1. Using a Pt rotating-disk

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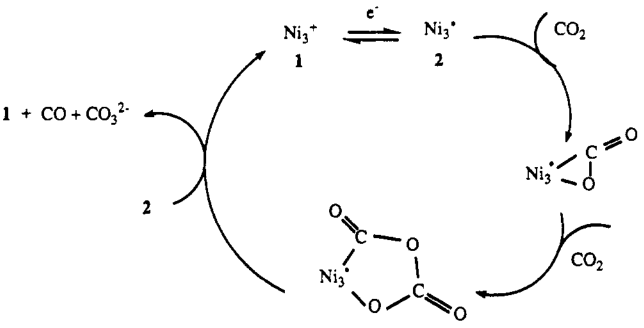
Scheme III



electrode, the heterogeneous electron transfer rate constant, k_e, for the reduction of 1 was found to be 0.023 cm s^{-1}. The homogeneous rate constant, k_{CO_2}, for the reaction between 2 and CO_2 was studied by cyclic voltammetry. When the scan rate was varied, the value of the steady-state limiting current was found (i.e. the region where catalysis, not diffusion, determines the current). The value for k_{CO_2} so determined was 0.011 M^{-1} s^{-1}.[34]

Further experiments were performed to obtain the turnover number of the catalyst. Using a dilute sample of 1 (2 μM in CH_3CN with TBAP as supporting electrolyte), seven turnovers were seen within 3 h using a Pt-gauze electrode. In addition, a steady-state current was reached in the current vs time plot, indicative of a catalytic reaction.[34]

The reduction of CO_2 by the electrocatalyst 1 occurs at a potential of −1.09 V vs Ag/AgCl, which is over 1 V less than the value of $E°(CO_2/CO_2^{\bullet -})$ = −2.16 V vs Ag/AgCl reported by Saveant and Amatore.[23] This result is clearly inconsistent with direct "outer sphere" reduction of CO_2 to $CO_2^{\bullet -}$. It is, however, consistent with the formation of an adduct of CO_2 with the reduced form of the trinickel cluster 2. A second CO_2 molecule may then be inserted into the adduct in a "head-to-tail" fashion. Subsequent electron transfer from a second equivalent of 2, followed by asymmetric disproportionation of the head-to-tail dimer of CO_2, results in CO and CO_3^{2-}. The proposed mechanism is outlined in Scheme III.

THF solutions of 2 react with carbon dioxide in the presence of $NaPF_6$ to re-form complex 1. The reduction of CO_2 to CO was verified by gas chromatography. The solvent was removed under vacuum, and the resulting solid was washed with CH_2Cl_2 to obtain a purple solution of pure complex 1 and a white solid. Infrared data for the white solid showed a strong band at 1450 cm^{-1} and a weaker band at 1632 cm^{-1}, consistent with the presence of carbonate. Indeed, the carbonate was precipitated with barium triflate. Formate was not observed in scrupulously dried solvents. However, when CO_2 entrained in D_2O vapor is passed through a THF solution of 2, DCO_2^- becomes the primary CO_2 product by IR spectroscopy. Under these conditions, only traces of CO are observed by GC. The results suggest that cluster-bound $CO_2^{\bullet -}$ may be intercepted by protonation to ultimately produce formate. Isotope labeling studies with $^{13}CO_2$ followed by IR analysis confirmed that CO and CO_3^{2-} were derived only from CO_2. Our results are consistent with an "inner-sphere" reduction of CO_2 by 2 to produce cluster-bound $CO_2^{\bullet -}$. The $CO_2^{\bullet -}$ undergoes head-to-tail condensation with a second CO_2 molecule and reduction by 2 to afford the reductive disproportionation products CO and CO_3^{2-}. Oxalate was not observed under any conditions employed in these studies.

Our continued studies are focusing on electrocatalytic systems related to 1 to effect carbon–carbon bond-forming reactions between $CO_2^{\bullet -}$ groups.

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Reaction of $[Fe\{C(=O)N^iPr_2\}(CO)_4]^-$ with Trifluoroacetic Anhydride: Molecular Structure of $[Fe(CF_3)\{\eta^2\text{-}C(=O)N^iPr_2\}(CO)_2(PPh_3)]$

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Received December 20, 1991

Summary: The reactions of the (carbamoyl)tetracarbonylferrate $[Fe\{C(=O)N^iPr_2\}(CO)_4]^-$ with $(CF_3CO)_2O$ and PPh_3 provide the structurally characterized trifluoromethyl-carbamoyl complex $[Fe(CF_3)\{\eta^2\text{-}C(=O)N^iPr_2\}(CO)_2(PPh_3)]$. A similar reaction with Ph_3SnCl and PPh_3 provides the stannyl derivative $[Fe(SnPh_3)\{\eta^2\text{-}C(=O)N^iPr_2\}(CO)_2(PPh_3)]$.

We have recently reported that the metal carbonyls $[M(CO)_n]$ (n = 6, M = Cr, Mo, W; n = 5, M = Fe) react successively with lithium diisopropylamide, trifluoroacetic anhydride, and triphenylphosphine to provide the aminomethylidyne complexes $[M(\equiv CN^iPr_2)(O_2CCF_3)(CO)_{n-3}(PPh_3)]$.[1] The formulation of these compounds as alkylidyne complexes was based on spectroscopic and elemental microanalytical data, and we have confirmed this for the chromium complex by its reaction with potassium hydrotris(pyrazol-1-yl)borate to provide $[Cr(\equiv CN^iPr_2)(CO)_2\{\kappa^3\text{-}HB(pz)_3\}]$ (pz = pyrazol-1-yl), which we have structurally characterized.[2] While subsequent reactivity studies on the group 6 derivatives have provided results

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