Acknowledgments are made to the National Science Foundation under Grant No. CHE-8304230 for support of this research.

Registry No. CH_3OH, 67-56-1; H_3CCH_2OH, 64-17-5; $H_3C(CH_2)_2OH$, 71-23-8; $H_3CCH(OH)CH_3$, 67-63-0; $H_2C{=}CHCH_2OH$, 107-18-6; $H_2C{=}CHCH(OH)CH_3$, 627-27-0; $C_6H_5CH_2OH$, 100-51-6; 4-$H_3COC_6H_4CH_2OH$, 105-13-5; 4-$O_2NC_6H_4CH_2OH$, 619-73-8; 4-$FC_6H_4CH_2OH$, 459-56-3; $H_3CC_6H_4CH_2OH$, 589-18-4; $C_6H_5CH(CH_3)OH$, 98-85-1; $(C_6H_5)_2CHOH$, 91-01-0; $[(bpy)_2(py)RuO]^{2+}$, 76582-01-9; D_2, 7782-39-0; cyclohexanol, 108-93-0.

Supplementary Material Available: Table A, values of k_{obsd} for the oxidation of the alcohols in 0.1 M $TEAP/CH_3CN$ by $[(bpy)_2(py)Ru(O)]^{2+}$; Table B, values of k_{obsd} for the oxidation of alcohols in aqueous solution by $[(bpy)_2(py)Ru(O)]^{2+}$ (7 pages). Ordering information is given on any current masthead page.

Carbon Dioxide Chemistry and Electrochemistry of a Binuclear "Cradle" Complex of Ni(0), $Ni_2(\mu\text{-}CNMe)(CNMe)_2(PPh_2CH_2PPh_2)_2$

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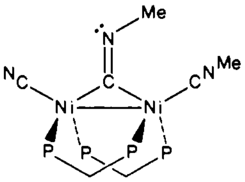
Abstract: The binuclear Ni(0) complex, $Ni_2(\mu\text{-}CNMe)_2(CNMe)(dppm)_2$, **1**, undergoes two one-electron oxidations ($E_{1/2}$ = −0.51 and −0.83 V vs. Ag/AgCl) to form the complex, $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2^{2+}$, **2**. The crystal structure of **2** as the PF_6^- salt has been determined. Complex **2** crystallized in the space group $P2_1$ with a = 13.659 (3) Å, b = 14.852 (4) Å, c = 17.970 (3) Å, β = 101.44 (1)°, V = 3573.0 (2) Å^3, and Z = 2. The structure was refined to convergence (R = 0.056, R_w = 0.073) for 4036 unique data over the range $4° \leq 2\theta \leq 45°$ by using Mo Kα radiation. Complex **2** exhibits an unusual *trans,cis*-diphosphine configuration at the Ni centers and contains a semibridging isocyanide. The electrochemical behavior of **2** in the presence of CO_2 has been examined. Complex **2** reacts with CO_2 by an EC electrochemical mechanism to afford the CO_2 complex $Ni_2(\mu\text{-}CNMeCO_2)(CNMe)_2(dppm)_2$, **3**. Complex **3** also has been prepared by reaction of **1** with CO_2(l). Prolonged reaction of **1** with CO_2(l) leads to complete carbonylation and $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$, **4**. The results of labeling experiments using $^{13}CO_2$ and 99% ^{13}C-enriched $Ni_2(\mu\text{-}^{13}CNMe)(^{13}CNMe)_2(dppm)_2$ are interpreted in terms of a reaction pathway involving O-atom transfer from CO_2 to the carbon atom of the bridging isocyanide of **1**.

The activation and reduction of carbon dioxide are areas of intense interest.[1-3] The preparation, structure, and N-alkylation chemistry of the "cradle"-type complex $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$, **1** (dppm = bis(diphenylphosphino)methane) were recently described.[4] We now report the role the nucleophilicity of the μ-methyl isocyanide ligand of complex **1** plays in activating the CO_2 molecule. We also report the 2e$^-$redox chemistry of **1**. Together, the chemical and electrochemical characteristics of **1** provide an interesting opportunity for electrochemically induced CO_2 activation.



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Experimental Section

Materials and Physical Measurements. All manipulations were performed in an N_2 atmosphere by using Schlenk techniques or a glovebox. Solvents were reagent grade and were distilled over the appropriate drying agents. $K^{13}CN$ and $^{13}CO_2$ (99 atom %) were purchased from Aldrich Chemical Co. Methyl isocyanide was prepared by literature procedures.[15,16] ^1H NMR and ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4 and ^1H chemical shifts to Me_4Si. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR. Microanalyses were performed by Galbraith Laboratories by using a LECO high-temperature analyzer.

Preparation of $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ (1). Complex **1** was prepared as recently reported[4] or by reduction of a benzene slurry of $[Ni(CNMe)_4][PF_6]_2$ with Na/Hg in the presence of bis(diphenylphosphino)methane.

Preparation of $[Ni_2(CNMe)_3(dppm)_2]^{2+}$ (2). $[Ni_2(CNMe)_3(dppm)_2][BF_4]_2$ (**2**) was isolated by electrolytic oxidation of **1** at 0.00 V vs. Ag/AgCl. A solution of 0.037 g of **1** in 0.1 M TBAF/THF was placed in the center compartment of a three-compartment cell which was contacted by a glassy carbon working electrode. A Pt gauze counter electrode contacting $[FeCp_2][PF_6]$/electrolyte solution and Ag/AgCl reference electrode were placed in the counter and reference electrode compartments, respectively. The average current density over 6 h was

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[†] Author to whom correspondence pertaining to crystallographic studies should be addressed.

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Table I. Summary of Crystal Data and Data Collection Parameters

formula	$Ni_2P_6F_{12}O_3N_3C_{68}H_{77}$
fw	1515.64
space group	$P2_1$
a, Å	13.659 (3)
b, Å	14.852 (4)
c, Å	17.970 (3)
β, deg	101.44 (1)
V, Å^3	3573.0 (2)
Z	2
d_{calcd} g cm^{-3}	1.409
crystal dimensions, mm	0.48 × 0.42 × 0.36
temp, °C	22.0
radiation (wavelength, Å)	Mo Kα (0.71073Å)
monochromater	graphite
linear abs coeff, cm^{-1}	7.37
absorption correction applied	empirical[a]
diffractometer	Enraf-Nonius CAD4
scan method	θ–2θ
h,k,l limits	−14–14,0–15,0–19
2θ range, deg	4.00–45.00
scan width, deg	0.90 + 0.35 tan θ
take-off angle, deg	4.90
programs used	Enraf-Nonius SDP
F_{000}	1568.0
p-factor used in weighting	0.070
unique data	4868
data with $I > 3.0\sigma(I)$	4036
no. of variables	772
largest shift/esd in final cycle	0.33
R	0.056
R_w	0.073
goodness of fit	1.646

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Table II. Selected Bond Distances (Å) and Angles (deg) for **2**

atom 1	atom 2	distance
Ni(1)	Ni(2)	2.439 (1)
Ni(1)	P(11)	2.198 (3)
Ni(1)	P(12)	2.237 (3)
Ni(1)	C(10)	1.84 (1)
Ni(1)	C(30)	2.19 (1)
Ni(2)	P(21)	2.242 (3)
Ni(2)	P(22)	2.269 (3)
Ni(2)	C(20)	1.84 (1)
Ni(2)	C(30)	1.824 (9)
P(11)	C(1)	1.848 (9)
P(11)	C(1111)	1.84 (1)
P(11)	C(1121)	1.81 (1)
P(12)	C(2)	1.84 (1)
P(12)	C(1211)	1.83 (1)
P(12)	C(1221)	1.841 (9)
P(21)	C(1)	1.84 (1)
P(21)	C(2111)	1.82 (1)
P(21)	C(2121)	1.836 (9)
P(22)	C(2)	1.882 (9)
P(22)	C(2211)	1.82 (1)
P(22)	C(2221)	1.86 (1)
N(11)	C(10)	1.14 (1)
N(11)	C(12)	1.41 (2)
N(21)	C(20)	1.14 (1)
N(21)	C(22)	1.40 (2)
N(31)	C(30)	1.15 (1)
N(31)	C(32)	1.48 (1)

atom 1	atom 2	atom 3	angle
Ni(2)	Ni(1)	P(11)	87.19 (8)
Ni(2)	Ni(1)	P(12)	83.33 (7)
Ni(2)	Ni(1)	C(10)	175.9 (3)
Ni(2)	Ni(1)	C(30)	46.0 (2)
P(11)	Ni(1)	P(12)	163.6 (1)
P(11)	Ni(1)	C(10)	94.4 (3)
P(11)	Ni(1)	C(30)	94.1 (2)
P(12)	Ni(1)	C(10)	95.9 (3)
P(12)	Ni(1)	C(30)	88.9 (3)
C(10)	Ni(1)	C(30)	130.0 (4)
Ni(1)	Ni(2)	P(21)	107.08 (9)
Ni(1)	Ni(2)	P(22)	110.96 (7)
Ni(1)	Ni(2)	C(20)	93.2 (3)
Ni(1)	Ni(2)	C(30)	59.7 (3)
P(21)	Ni(2)	P(22)	137.9 (1)
P(21)	Ni(2)	C(20)	96.4 (3)
P(21)	Ni(2)	C(30)	92.2 (3)
P(22)	Ni(2)	C(20)	98.8 (3)
P(22)	Ni(2)	C(30)	91.7 (3)
C(20)	Ni(2)	C(30)	152.9 (4)
C(10)	N(11)	C(12)	170 (1)
C(20)	N(21)	C(22)	175 (1)
C(30)	N(31)	C(32)	171.8 (9)
P(11)	C(1)	P(21)	111.7 (5)
P(12)	C(2)	P(22)	110.3 (5)

55 μA/cm^2. Spectroscopically pure **2** was obtained with a current efficiency of 91%, determined by coulometry. Complex **2** can also be isolated as the PF_6^- salt by chemical oxidation of **1** with 2 equiv of $[FeCp_2][PF_6]$. To a 15-mL benzene solution of **1** (0.166 g, 0.16 mmol) was added 3 mL of a 5/1 THF/acetonitrile solution of $[FeCp_2][PF_6]$ (0.109 g, 0.33 mmol). The red solution turned to deep blue. To this was added approximately 40 mL of toluene, affording a dark-blue microcrystalline solid: yield, 0.146 g, 68%; IR (KBr) ν(CN) 2204, 2188, 2093 cm^{-1}; $^{31}P\{^1H\}$ NMR (H_3PO_4 external, CD_3CN) δ 23.4 (s); ^{1}H NMR (CD_2Cl_2) δ 7.40 (br, 40 H), 3.55 (partly obscurred by THF of solvation), 2.70 (m, 9 H). Anal. Calcd for $C_{64}H_{69}N_3Ni_2P_6F_{12}$: C, 53.25; H, 4.82; N, 2.91. Found: 53.27; H, 4.84; N, 3.31. X-ray quality crystals were prepared by slow evaporation of a THF solution.

Crystal Data Collection and Reduction. A dark-blue crystal of **2** was mounted on a glass fiber with epoxy and transferred to the diffratometer. Complex **2** crystallized in space group $P2_1$ with a = 13.659 (3) Å, b = 14.852 (4) Å, c = 17.970 (3) Å, β = 101.44 (1)°, V = 3573.0 (2) Å^3, Z = 2, and ρ_{calcd} = 1.409 g/cm^3 for formula unit $Ni_2P_6F_{12}O_3N_3C_{68}H_{77}$ with three THF molecules of crystallization. Intensity data were collected at 22 °C using Mo Kα radiation (λ = 0.71073 Å) by the θ–2θ scan technique in the range $4° \leq 2\theta \leq 45°$ on a locally modified CAD4 diffractometer. A total of 4868 unique data were collected over hkl limits $-14 \leq h \leq 14$, $0 \leq k \leq 15$, $0 \leq l \leq 19$. Three standard reflections were monitored every 60 min and showed no evidence of crystal instability. The structure was refined by MULTAN–least-squares–Fourier methods and was refined to R and R_w values of 0.056 and 0.073 for 772 parameters and 4036 observations with $F^2 > 3\sigma(F^2)$. The linear absorption coefficient μ = 7.37 cm^{-1}, and an empirical absorption correction based on a series of ψ scans was applied to the data. The quantities minimized in refinement, the programs used to solve the structure, and the computer used in refinement have been described previously.[12] The esd of an observation of unit weight is 1.646. A summary of crystal data and collection parameters appears in Table I. Selected bond distances and angles are given in Table II. Complete tables including positional parameters with esds, general temperature factor expressions, bond distances and angles, and observed and calculated structure factors are found in the supplementary material.

Reactions of Complex 1 with CO_2(l). Isolation of $Ni_2(\mu\text{-CNMeCO}_2)(CNMe)_2(dppm)_2$ (3) and $Ni_2(\mu\text{-CO})(CO)_2(dppm)_2$(4). Liquid CO_2 reactions were performed in a LECO-MRA-114R pressure reactor. Typically 3 L of CO_2 gas was condensed into a 5-mL reactor containing 0.1 g of complex **1** at 25 °C, resulting in an average pressure of 1500 psi. The mixture was allowed to react for at least 24 h. The reactor was vented into a dry ice/2-propanol trap to collect volatiles and then opened in an inert atmosphere box to collect solid products.

$Ni_2(\mu\text{-CNMeCO}_2)(CNMe)_2(dppm)_2$ (**3**) was isolated from the high-pressure reactor by extraction of the remaining solids into acetonitrile followed by precipitation with hexane. Complex **3** was independently prepared by addition of a catalytic amount (1%) of $NaPF_6$ to a CO_2-saturated solution of **1** in THF: IR (KBr) ν(CN) 2134 (s), 1528 (m), ν(CO) 1646 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (THF) δ 22.4 (AA′BB′).

$Ni_2(\mu\text{-CO})(CO)_2(dppm)_2$ (**4**) was isolated quantitatively as a yellow crystalline solid from reactions of **1** in CO_2(l) after reaction times greater than 48 h: IR (KBr) ν(CO) 1967 (sh), 1947 (s), 1784 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (THF) δ 23.4 (s). The spectral data are in excellent agreement with those reported by Stanley[11] and with authentic **4** prepared independently from $Ni(COD)_2$ (COD = cyclooctadiene), dppm, and CO.[18]

Labeling Studies with $^{13}CO_2$ and ^{13}CNMe. Reaction of 1 with $^{13}CO_2$(l). Complex **1** (~0.1 g) was loaded in the high-pressure reactor described above. The reactor was cooled to −190 °C and pressurized with ~1 L of 99% ^{13}C-enriched $^{13}CO_2$. Sufficient $^{12}CO_2$ (~2 L) was added to bring the total pressure to ~1400 psi at 25 °C. The reactor was allowed to

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(18) Gong, J.; Kubiak, C. P., unpublished results.

(19) del Rosario, R.; Kubiak, C. P., unpublished results.

stand for 24 h and then opened inside a glovebox. The gas-phase mixture was determined to be 35% $^{13}CO_2$/65% $^{12}CO_2$ by mass spectrometry. The yellow–green solid was examined by IR (KBr): IR [3 (^{13}C)] ν(CN) 2134 (s), 1528 (m), ν(CO) 1641 (m), 1618 (m); [4] ν(CO) 1966 (sh), 1948 (s), 1785 (m) cm^{-1}, corresponding to a mixture of 3, 35% ^{13}C-enriched at the carbonyl, and 4, with carbon in natural abundance in each of the three CO ligands.

[Ni(^{13}CNMe)$_4$][PF$_6$]$_2$. The complex was prepared by reaction of ^{13}CNMe,[16] generated in situ, with NiSO$_4$ and NH$_4$PF$_6$.[12] Silver ^{13}C-cyanide (99% enriched, prepared from K^{13}CN and AgNO$_3$, 1.937 g, 0.0144 mol) was placed in a 50-mL Pyrex high-pressure reactor. After addition of 0.90 mL of MeI (99%, 0.0145 mol) by syringe, the reactor was heated with shaking at 70–75 °C for 2 h. The mixture became a dark-brown liquid. Upon cooling to room temperature, a solution of 2.4 g of KCN (0.037 mol) in ≈6 mL of water was added by syringe, and the contents were vigorously shaken until all solids dissolved. The reactor was attached to a 100-mL Schlenk flask which served as a trap for ^{13}CNMe. The volatiles from the reaction mixture were distilled into the trap (cooled in liquid N$_2$) under vacuum until only a thick paste remained in the reactor. To facilitate distillation, the reactor was warmed by using a water bath at 40–45 °C. The trap subsequently was placed under N$_2$, and a solution of 0.65 g of NiSO$_4$·6H$_2$O (0.0025 mol) and 0.78 g of NH$_4$PF$_6$ (0.0048 mol) in water was added by cannula to the frozen ^{13}CNMe–water mixture. The trap was allowed to warm gradually to room temperature. A bright golden-yellow precipitate formed and was filtered. After washing with ethanol, the precipitate was taken up in a minimum amount of acetone and filtered. Treatment of the red–orange filtrate with excess ethanol resulted in the precipitation of crystalline [Ni(^{13}CNMe)$_4$][PF$_6$]$_2$ which was filtered, washed with EtOH, and dried in vacuo overnight: yield, 0.59 g (31% based on Ag^{13}CN): IR (KBr) ν(CN) 2254 (sh), 2242 (s), 2232 (s), 2191 (m) cm^{-1}. For comparison, for [Ni(^{12}CNMe)$_4$][PF$_6$]$_2$: IR (KBr) ν(CN) 2299 (sh), 2286 (s), 2275 (s), 2231 (m) cm^{-1}.

Ni$_2$(^{13}CNMe)$_3$(dppm)$_2$, 1(^{13}C). [Ni(^{13}CNMe)$_4$][PF$_6$]$_2$ (0.25 g, 0.49 mmol) was added to a solution of 0.19 g (0.49 mmol) of dppm in 60 mL of benzene. The slurry was stirred over Na/Hg for 28 h. After insoluble materials were allowed to settle, the mixture was filtered through Celite to give an orange filtrate which was concentrated to ≈5 mL. Addition of ≈8 mL of hexane precipitated red–orange Ni$_2$(^{13}CNMe)$_3$(dppm)$_2$, 1(^{13}C), which was filtered, washed with ether and hexane, and dried in vacuo: yield, 0.16 g (~0.16 g (~64%); IR (KBr) ν(CN) 2046 (s), 2022 (s), 1683 (m) cm^{-1}.

Reaction of Ni$_2$(^{13}CNMe)$_3$(dppm)$_2$, 1(^{13}C), with ^{12}CO$_2$(l). Complex 1(^{13}C) (~20 mg) was reacted with ^{12}CO$_2$(l) (~2400 psi) for 3 days at 25 °C in a high-pressure reactor as described above. The reactor was opened inside a glovebox. Inspection of all solid portions by IR gave identical spectra corresponding to Ni$_2$(μ-^{13}CO)(^{13}CO)$_2$(dppm)$_2$, 4(^{13}C): IR (KBr) ν(CO) 1921 (sh), 1902 (s), 1744 (m) cm^{-1}.

Results and Discussion

Electrochemistry of 1/2 in the Absence and Presence of CO$_2$. The cyclic voltammogram of 1 in 0.1 M TBAF/THF (TBAF = tetrabutylammonium fluoroborate) exhibits two quasireversible oxidations at $E_{1/2}$ = –0.51 and –0.83 vs. Ag/AgCl reference. These electrochemical results combined with coulometric studies indicate that complex 1 undergoes an overall two-electron oxidation. Bulk electrooxidation of 1 therefore was performed, and the new binuclear complex, [Ni$_2$(CNMe)$_3$(dppm)$_2$][BF$_4$]$_2$, 2, was obtained in excellent yield. Complex 2 was obtained analytically pure and characterized by IR, NMR, and an X-ray crystal structure described below. The cyclic voltammogram of 2 in 0.1 M TBAF/THF exhibits the same two couples evident in the cyclic voltammogram of 1 and is shown in Figure 1.

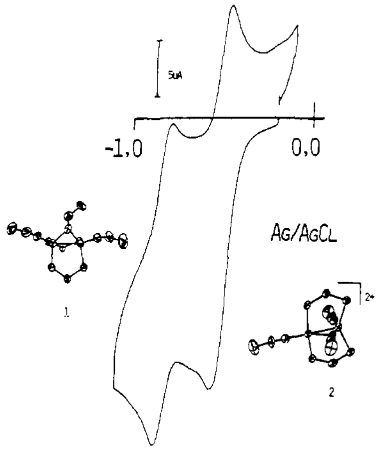


Figure 1. Cyclic voltammogram of [Ni$_2$(CNMe)$_3$(dppm)$_2$][PF$_6$]$_2$ in 0.1 M TBAF/THF.

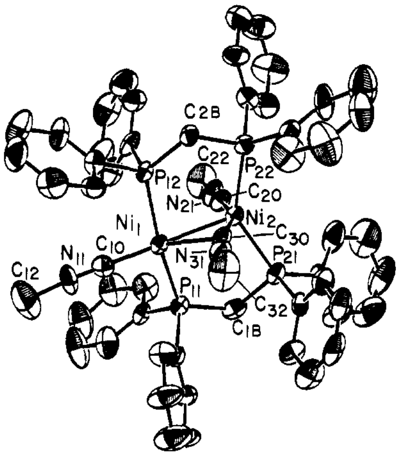
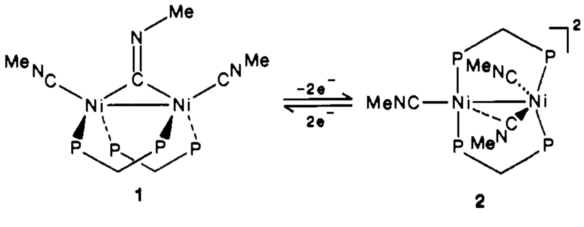


Figure 2. ORTEP drawing of the [Ni$_2$(CNMe)$_3$(dppm)$_2$]$^{2+}$ cation with all non-hydrogen atoms.

An ORTEP drawing of the [Ni$_2$(CNMe)$_3$(dppm)$_2$]$^{2+}$ cation is presented in Figure 2. Selected bond distances and bond angles appear in Table II. The structure is highly reminiscent of the Rh(0) "non-A-frame", Rh$_2$(CO)$_3$(dppm)$_2$,[10] with which it is isoelectronic. The coordination geometry about Ni(1) is approximately square planar, with Ni(2) occupying one of the four coordination sites. The Ni(1)–Ni(2) separation, 2.439 (1) Å, is consistent with a Ni–Ni single bond.[12] The major difference in the structure of 2 compared to Rh$_2$(CO)$_3$(dppm)$_2$ is evident at Ni(2). While the coordination geometry about the second metal in both structures is best described as trigonal bipyramidal (TBP), the axial and equatorial ligands are different. In the structure of 2 the equatorial coordination sites about Ni(2) consist of the two dppm phosphorus atoms, P(22) and P(21), and Ni(1); ∠Ni(1)–Ni(2)–P(21) = 107.08 (9)°; ∠Ni(1)–Ni(2)–P(22) = 110.96 (7)°; ∠P(21)–Ni(2)–P(22) = 137.9 (1)°. The corresponding apical sites are occupied by the semibridging and terminal isocyanide carbons, C(30) and C(20), ∠C(20)–Ni(2)–C(30) = 152.9 (4)°. The structure of 2 at Ni(2) is related to the corresponding structure of Rh$_2$(CO)$_3$(dppm)$_2$ by an effective Berry pseudorotation. Thus, the M–M interaction (equatorial) and semibridging ligand (axial) of the TBP of 2 are interchanged to assume axial and equatorial positions, respectively, in Rh$_2$(CO)$_3$(dppm)$_2$. The structure of 2 may be viewed as resulting from the interaction of a locally tetrahedral 18e$^-$, Ni^{0}L$_4$ fragment with a T-shaped, 14e$^-$, Ni^{II}L$_3$ fragment. This formulation presumes a dative coordinate Ni → Ni interaction, similar to that described for [Ni$_2$(μ-CNMe)(CNMe)$_3$(dppm)$_2$]$^{2+}$.[12] Together the structures of 1[4] and 2 represent a rare example of the structural characterization of both sides of a 2e$^-$ redox couple, eq 1. In view of the structure of 2 it is interesting to speculate whether the electrochemical oxidation of 1 involves one or both metal centers.



(1)

The electrochemistry relating complexes 1 and 2 appears markedly different under an atmosphere of CO$_2$. In the presence of CO$_2$, the second cathodic wave at –0.83 V vs. Ag/AgCl in the cyclic voltammogram of 1/2 shows current enhancement. Both return anodic waves also vanish. The cyclic voltammograms of

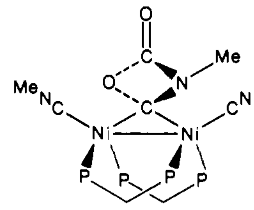
Table III. Summary of Infrared Data for Isotopically Substituted **1**, **3**, and **4**[a]

	ν(CO), cm^{-1}	ν(CN), cm^{-1}
$Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$, **1**		2082 (s), 2055 (s), 1715 (m)
$Ni_2(\mu\text{-}^{13}CNMe)(^{13}CNMe)_2(dppm)_2$, **1**(^{13}C)		2046 (s), 2022 (s), 1683 (m)
$Ni_2(\mu\text{-}CNMe(CO_2))(CNMe)_2(dppm)_2$, **3**	1646 (m), 1727 (m, br)[b]	2134 (s), 1528 (m)
$Ni_2(\mu\text{-}CNMe(^{13}CO_2))(CNMe)_2(dppm)_2$, **3**(^{13}C)	1618 (m), 1641 (m, br)[b]	2134 (s), 1528 (m)
$Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$, **4**	1967 (sh), 1947 (s), 1784 (m)	
$Ni_2(\mu\text{-}^{13}CO)(^{13}CO)_2(dppm)_2$, **4**(^{13}C)	1921 (sh), 1902 (s), 1744 (m)	

[a] All spectra were taken in KBr pellets. [b] Assigned as $\overline{CNC(O)O}$ skeletal admixture.

solutions of **2** in 0.1 M $NaPF_6$/MeCN in the presence and absence of CO_2 are shown in Figure 3. The characteristic features of the cyclic voltammogram of **1**/**2** are restored after removal of CO_2 with a N_2 purge. The appearance of the cyclic voltammogram in the presence of CO_2 (Figure 3B) and its scan rate dependence are consistent with an EC electrochemical mechanism.[13] These results suggest that subsequent to the reduction of **2** to **1**, complex **1** reacts irreversibly with CO_2. We therefore focused our studies on the stoichiometric chemistry of **1** with CO_2.

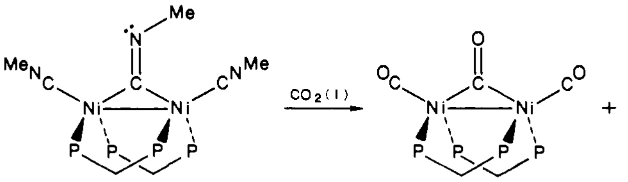
Reaction Chemistry of 1 in the Presence of CO_2. Pure solutions of **1** do not react with CO_2 at 1 atm. Upon addition of a catalytic amount of $NaPF_6$ (~1/100 equiv), however, **1** reacts to form the green complex **3**. Complex **3** exhibits IR and $^{31}P\{^1H\}$ NMR data very similar to the aminocarbyne complexes of Ni which we reported earlier,[4] ν(CN) 2131, 1528 cm^{-1}; $^{31}P\{^1H\}$: δ 22.4 (AA′BB′). There is, in addition, a ν(CO) band at 1646 cm^{-1}. This band shifts to 1618 cm^{-1} when $^{13}CO_2$ is substituted for $^{12}CO_2$ (Table III). In the presence of trace quantities of H_2O, solutions of **3** instantaneously undergo N-protonation and decarboxylation to yield the aminocarbyne complex, $[Ni_2(\mu\text{-}CNMe(H))(CNMe)_2(dppm)_2]^+$.[4] On the basis of the above spectroscopic data and the known reactivity of **1**, the structure below is proposed for complex **3**.



3

The cyclic voltammetric behavior of **2** in the presence of CO_2 and $NaPF_6$ supporting electrolyte is thus attributed to the formation of **3**. In particular, the reduction of **2** by two electrons ($E < -0.83$ V vs. Ag/AgCl) has been demonstrated to produce **1**. In the presence of CO_2 *and* Na^+ ions, **1** rapidly forms the CO_2 cycloadduct, **3**. We note that **1** does not react with CO_2 at 1 atm in the absence of Na^+ nor does it react with Na^+ alone. The nature of the CO_2 cycloadduct **3** is further clarified by results of reactions with liquid CO_2, described below.

Reactions of 1 with CO_2(l). Pressurization of **1** with liquid CO_2 leads to two nickel-containing products. When the reaction was run for >48 h at 1500–2200 psi and 25 °C, **1** reacted completely to form a yellow crystalline solid, identified as $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$, **4**. This product is the CO cradle complex of Ni(0)



1 **4**

$$\mathbf{3} + (MeN{=}C{=}NMe)_n \qquad (2)$$

recently reported by Stanley et al.[11] The identity of complex **4** was confirmed by comparison with the reported spectroscopic data, which were in excellent agreement, as well as with authentic $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$, independently prepared in this laboratory.[18] The reaction of **1** with liquid CO_2 represents a net 6e$^-$ reduction of three molecules of CO_2 to CO. The methyl isocyanide ligand is apparently the initial oxygen atom acceptor (vide infra). However, the organic product in this reaction is polymeric *N*,*N*′-dimethyl carbodiimide.[14] Sacrificial deoxygenations of CO_2 to CO have been reported previously.[5-8] The formal CO_2 O-atom transfer to isocyanides to give isocyanates and CO has also been claimed,[9] but not mechanistically established. The novel feature of eq 2 is that all three isocyanides react and that the product is a carbodiimide, not an isocyanate. At shorter reaction times of **1** with CO_2(l), a mixture of **3** and **4** was isolated. This result suggests that the CO_2 cycloadduct **3** is on the reaction pathway which finally gives the tricarbonyl complex **4**. An interesting question pertaining to the mechanism of eq 2 therefore is whether the CO carbon atoms are derived from CO_2 or CNMe. When the liquid CO_2 reaction was run with 35% $^{13}CO_2$, no label was found incorporated into the CO ligands of **4**. However, 35% ^{13}C incorporation was found in the $CNMeCO_2$ moiety of **3**. We have also examined the isotopic course of reactions in which the methyl isocyanide ligands of **1** were labeled. Figure 4a shows the IR spectrum of **1** which has been >99% ^{13}C-enriched at the methyl isocyanide ligands. Figure 4b shows the spectrum of the sole nickel-containing product isolated when the reaction of **1**(^{13}C) with $^{12}CO_2$(l) was run to completion. The product is **4**, >99% ^{13}C-enriched in each of its three CO ligands. Table III summarizes the values of ν(CN) and ν(CO) observed in the IR spectra of **1**, **3**, and **4** and their isotopically substituted variants derived from $^{13}CO_2$ or ^{13}CNMe. These observations are interpreted in terms of complexation of CO_2 to the μ-CNMe ligand of **1** to give **3**, followed by O-atom/NMe interchange between CO_2 and the

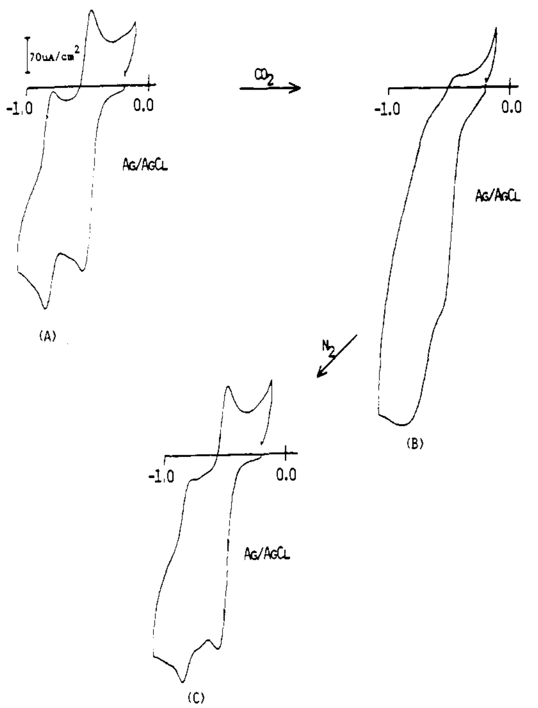


Figure 3. Cyclic voltammograms of $[Ni_2(CNMe)_3(dppm)_2][PF_6]_2$, **2**, in 0.1 M $NaPF_6$/MeCN. (A) Initial voltammogram of solution under N_2. (B) Same solution after exposure to CO_2 (2 min). (C) Same solution after purging with N_2 (5 min).

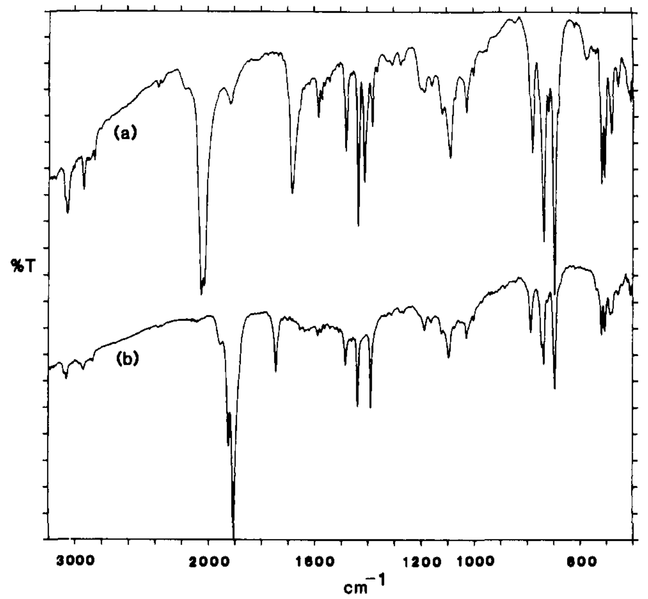
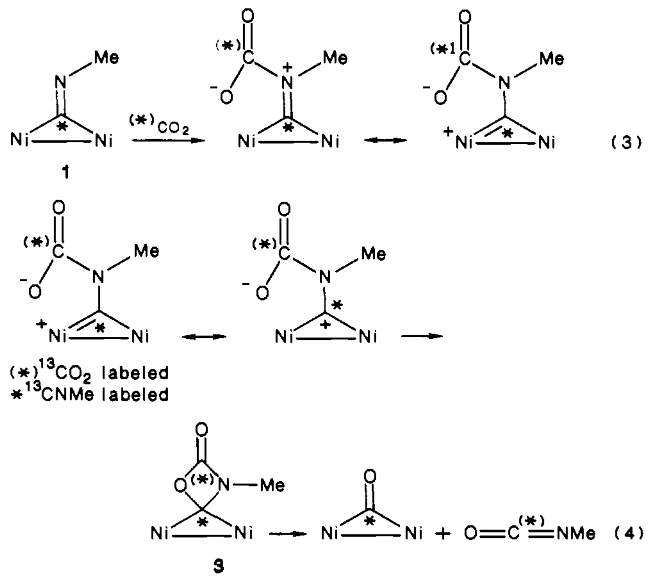


Figure 4. (a) FTIR spectrum of >99% ^{13}C-enriched $Ni_2(^{13}CNMe)_3(dppm)_2$, **1**(^{13}C). (b) FTIR spectrum of the product obtained by reaction of **1**(^{13}C) with $^{12}CO_2$(l), corresponding to >99% ^{13}C-enriched $Ni_2(^{13}CO)_3(dppm)_2$, **4**(^{13}C).

μ-CNMe ligand. In particular, the results obtained from the reaction of **1**(^{13}C) with $^{12}CO_2$(l) unambiguously establish that the coordinated CO carbon atoms of **4** are derived from the methyl isocyanide ligands of **1**. The initial fate of the carbon dioxide carbon atom very likely is methyl isocyanate formation. The results are consistent with the mechanism depicted in eq 3 and 4. Presumably, the *N,N'*-dimethyl carbodiimide results from the increased reactivity of methyl isocyanate relative to CO_2 in the O/NMe interchange reaction. Indeed, **1** does react with isocyanates to give **4** and the corresponding carbodiimides. We suspect the role of the Na^+ ion in catalyzing the formation of **3** in fluid solution at 1 atm of CO_2 is to stabilize charge-separated zwitterionic carbyne intermediates, prior to cyclization leading to **3**, eq 4. A similar mode of CO_2 activation by Li^+ has recently been reported for $W(CO)_5^{2-}$.[20] Nucleophilic cyclization to **3** has precedence in the observation that the related complex, $[Ni_2(\mu\text{-}(CNMe)(Me))(CNMe)_2(dppm)_2]^+$, does undergo nucleophilic attack at the carbyne carbon by H^-.[4,19] The CO_2 cycloadduct **3** either can revert to **1** with CO_2 loss or form methyl isocyanate and CO. However, we have not isolated methyl isocyanate or the mono- and dicarbonyl intermediates leading to **4**. This suggests that the intermediates may be significantly more reactive than **1** and CO_2 in the O/NMe interchange reaction. The apparent substitution of three isocyanide ligands by carbon monoxide, eq 2, with complete retention of the metal–carbon bonding framework is unprecendented.



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Supplementary Material Available: Tables of crystal data and conditions for data collection, positional parameters, general temperature factors, and bond distances and angles (15 pages); tables of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Organic Residues Introduced during Metal Oxide Functionalization

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Abstract: Silica and alumina supports have been functionalized with reagents of the general formula $(C_2H_5O)_3Si(CH_2)_nX$ where X is a donor group capable of coordinating to metal complexes. The attachment of iridium clusters to the phosphinated support has been shown to lead to $(AL)\text{-}PPh_2Ir_4(CO)_{11}$, $(AL)(\text{-}PPh_2)_2Ir_4(CO)_{10}$, and $(AL)(\text{-}PPh_2)_3Ir_4(CO)_9$ ((AL) is the abbreviated form of $Al_2O_3\text{-}O\text{-}Si(CH_2)_2$). The attached iridium cluster reacts with a gaseous mixture of $H_2/CO/HCl$ to form products which result from organic residues introduced during functionalization of the oxide. Failure to recognize this problem leads to adventitious carbon sources in catalytic processes that can lead to incorrect conclusions, and reaction of these materials with HCl enables one to detect these organic residues and to clean the surface. A reaction scheme for the decomposition of ethoxy groups of the phosphinosilane to methyl chloride is included.

The recent literature contains many examples of silica and alumina supports that have been functionalized with the reagents of the general formula $(C_2H_5O)_3Si(CH_2)_nX$ where X is a donor group capable of coordinating to metal complexes.[1,2] A thorough study of the hydrolysis of ethoxy groups by surface silanol groups has been reported along with the effects of curing these reagents.[3]

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