$|t|$ for the exact value of $\epsilon_0 = -0.573\,73\ |t|$. In the text we used regular-polygon linear polyenes for eq 20. We obtained its ϵ_1 by fixing ϵ_0 of eq A1 to −2.1355 and by using a least-squares fit with $N = 8$–12. The estimated value is $\epsilon_1 = 1.17 \pm 0.01$. The PPP energies of the regular-polygon linear polyenes are −7.661 42, −11.887 06, −16.112 24, −20.347 85, and −24.592 42 for $N = 4$–12, respectively. Extrapolations for the HF theory and different V_0 are made by the same procedure.

Mediated Electrochemical Reduction of CO_2. Preparation and Comparison of an Isoelectronic Series of Complexes

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Abstract: The preparation and characterization of complexes of the type $[M(triphos)L](BF_4)_2$ are described (for M = Ni, L is $P(OMe)_3$ and PEt_3; for M = Pd, L is CH_3CN, $P(OMe)_3$, PEt_3, $P(CH_2OH)_3$, and PPh_3; for M = Pt, L is PEt_3; triphos is $PhP(CH_2CH_2PPh_2)_2$). On the basis of cyclic voltammetry and bulk electrolysis experiments, the Pd complexes are shown to catalyze the electrochemical reduction of CO_2 to CO in acidic acetonitrile solutions. The analogous Ni and Pt complexes are not catalysts for CO_2 reduction under the same conditions. Kinetic studies have been carried out on $[Pd(triphos)(PEt_3)](BF_4)_2$ and a mechanism for the reduction of CO_2 is proposed.

The chemistry of CO_2 is receiving increasing attention for a variety of reasons including its potential as a C_1 feedstock,[1] the increase in atmospheric CO_2 concentration,[2] and its possible use as a substrate for storing solar energy.[3] However, the electrochemical reduction of CO_2 at most metal electrodes is accompanied by an overvoltage of 1–1.5 V and results in a variety of products.[4] This high overvoltage has prompted the search for more suitable electrodes and catalysts capable of mediating the electrochemical reduction of CO_2. The use of indium electrodes,[5] electrodes modified with polymers containing Pd,[6] and carbon electrodes modified with cobalt phthalocyanine complexes[7] have all resulted in significant lowering of the overpotential for heterogeneous CO_2 reductions. Homogeneous catalysts including porphyrins and tetraaza macrocyclic complexes,[8,9] $Rd(dppe)_2Cl$,[10] iron sulfur clusters,[11] bipyridine complexes,[12,13] and formate dehydrogenase[14] also significantly lower the overpotential.

In this paper, we report the synthesis and characterization of a new series of isoelectronic complexes, some of which are capable of mediating the electrochemical reduction of CO_2 to CO. The ability of these complexes to mediate the electrochemical reduction of CO_2 is dependent on the metal and on ligand structure. These catalysts appear to have mechanistic features different from other homogeneous catalysts that mediate the electrochemical reduction of CO_2, and operate at potentials approximately 0.6 V positive of other homogeneous catalysts, excluding formate dehydrogenase.

Experimental Section

Physical Measurements. Infrared spectra were obtained on Nujol mulls using a Perkin-Elmer 599B spectrophotometer. All of the BF_4 salts show a broad strong infrared absorption between 900 and 1150 cm^{-1}. A Varian E109 spectrometer was used for obtaining EPR spectra. EPR spectra were recorded on 1×10^{-3} M dichloromethane solutions. A JEOL FX90Q FT NMR spectrometer equipped with a tunable, variable-temperature probe was used to collect ^1H, ^{31}P, and ^{13}C NMR spectra. Me_4Si was used as an internal reference for ^1H and ^{13}C spectra. A capillary filled with phosphoric acid was used as an external reference for ^{31}P NMR spectra. All ^{31}P NMR spectra were proton decoupled.

Electrochemical measurements were carried out with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. A Houston Instruments Model 2000 x-y recorder was used for plotting cyclic voltammograms. A silver wire was dipped in concentrated nitric acid, then dipped in concentrated hydrochloric acid, and rinsed with distilled water. After drying, this wire was used as a pseudo-reference electrode. This reference electrode was separated from the working and counter electrode compartments by a Vycor frit. Ferrocene was used as an internal standard. The potential of ferrocene vs. aqueous SCE in 0.2 N $LiClO_4$ solution of acetonitrile is reported to be +0.307 V.[15] All of our measurements were carried out in 0.2 N NEt_4BF_4 solutions of acetonitrile. In this solution, we found the potential of ferrocene to be +0.40 V vs. aqueous SCE. For cyclic voltammetry, a glassy carbon disk electrode

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(IBM) was used as the working electrode, and a platinum wire was used as a counter electrode. All compounds were studied by cyclic voltammetry over a range of scan rates from 50 to 500 mV/s. Plots of i_p vs. $v^{1/2}$ were used to determine if the electron-transfer processes were under diffusion control. All waves for the complexes described give linear plots.

Bulk electrolysis experiments were typically carried out as follows. An acetonitrile solution (20 mL, 0.80×10^{-3} M in catalyst **5b**, 1.3×10^{-2} M in HBF_4, and 0.2 M in NEt_4BF_4) was placed under 1 atm of CO_2 and electrolyzed at a pyrolytic graphite electrode having an area of approximately 6 cm^2. A total of 23 C was passed in this experiment. Both the gas and solution phases were analyzed by gas chromatography. The products of the reduction were CO and H_2. In this experiment, 5.5 mol of CO was produced per mole of catalyst before the catalyst became inactive (~0.5 h). The current efficiency for the production of CO under the experimental conditions described was 74% with the remaining charge being used to generate hydrogen. The working, counter, and reference electrodes were all separated by Vycor frits. High-pressure experiments were carried out in a stainless steel bomb (Parr Instrument Co.) fitted with electrical leads.

Gas chromatography of the gases above the solution was carried out using a 100/120 Carbosieve S-II, stainless steel coulumn with dimensions 10 ft × $^1/_8$ in. from Supelco: coulumn temperature, 105 °C; flow rate, 30 mL/m; He carrier gas; thermal conductivity detector; CO retention time, 5 min 10 s. Elemental analyses were performed by Spang Microanalytical Laboratories.

Syntheses. Acetonitrile and dichloromethane were dried by distillation from calcium hydride under nitrogen. Toluene, tetrahydrofuran (THF), and hexanes were distilled from sodium benzophenone ketyl under nitrogen. Except where mentioned, all reactions were carried out using standard Schlenk techniques. The product metal complexes are all air stable in the solid state and in solution with the exception of [Pd(triphos)P(OMe)$_3$]. [Ni(triphos)(CH$_3$CN)](BF$_4$)$_2$,[16] [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$,[17] and [Pt(C$_8$H$_{12}$OCH$_3$)(OCH$_3$)]$_2$[18,19] were prepared by literature methods.

P(CH$_2$OH)$_3$. The preparation of P(CH$_2$OH)$_3$[20,21] was modified by vacuum distillation of the crude product at 115 °C (50 μ). The distillate turned into a white solid on cooling. This solid was washed with diethyl ether and dried at 50 °C in vacuo for 5 h. ^{1}H NMR (dimethyl-d_6 sulfoxide): CH$_2$O, 3.84 ppm (overlapping dd (i.e., t), J_{PH} = 5.5, J_{CH-OH} = 5.5 Hz); OH, 4.63 ppm (overlapping dt (i.e., q), J_{P-OH} = 5.5 Hz). ^{31}P NMR: −26.5 ppm (s). ^{13}C NMR: CH$_2$O, 56.2 ppm (d, J_{PC} = 10 Hz).

[Ni(triphos)(PEt$_3$)](BF$_4$)$_2$. PEt$_3$ (0.10 mL, 0.7 mmol) was added via syringe to an orange solution of [Ni(triphos)(CH$_3$CN)](BF$_4$)$_2$[16] (0.40 g, 0.5 mmol) in dichloromethane (50 mL). The red solution was stirred at room temperature for 10 h. After the volume of the solvent was reduced in vacuo, the yellow microcrystalline product was collected by filtration and recrystallized from a mixture of dichloromethane and hexanes. The product was dried at 50 °C for 5 h to give a yield of 0.31 g (70%). ^{1}H NMR (acetone-d_6): Et, 0.6–1.5 ppm (m); CH$_2$CH$_2$, 2.5–3.2 ppm (m); Ph, 7.4–8.0 ppm (m). ^{31}P NMR (acetone-d_6): PEt$_3$, 4.0 ppm (dt, $J_{P_c-PEt_3}$ = 174, $J_{P_t-PEt_3}$ = 48 Hz); terminal phosphorus atoms of tridentate ligand (P$_t$), 53.3 ppm (dd, $J_{P_c-P_t}$ = 32 Hz); central phosphorus atom of tridentate ligand (P$_c$), 107.0 ppm (dt). Anal. Calcd for C$_{40}$H$_{48}$B$_2$F$_8$NiP$_4$: C, 54.28; H, 5.47; Ni, 6.63; P, 14.00. Found: C, 54.19; H, 5.43; Ni, 6.42; P, 13.90.

[Ni(triphos)P(OMe)$_3$](BF$_4$)$_2$. The procedure used for the preparation of this complex was very similar to that described for [Ni(triphos)(PEt$_3$)](BF$_4$)$_2$. The product was recrystallized from a mixture of acetone and hexanes with a yield of 72%. ^{1}H NMR (acetone-d_6): OMe, 3.34 ppm (t, J_{PH} = 6 Hz); CH$_2$CH$_2$, 2.5–3.7 ppm (m); Ph, 7.3–8.0 ppm (m). ^{31}P NMR (acetone-d_6): The second-order spectrum can be simulated at two fields using the following parameters: P$_t$, 59.07 ppm ($J_{P_tP_c}$ = 32, $J_{P_t-P(OMe)_3}$ = 73 Hz); P$_c$, 111.68 ppm ($J_{P_c-P(OMe)_3}$ = 310 Hz); P(OMe)$_3$, 110.32 ppm. Anal. Calcd for C$_{37}$H$_{42}$B$_2$F$_8$NiO$_3$P$_4$: C, 49.87; H, 4.76; Ni, 6.59; P, 13.90. Found: C, 49.92; H, 4.75; Ni, 6.22; P, 13.68.

[Pd(triphos)(CH$_3$CN)](BF$_4$)$_2$. A solution of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$[17] (0.88 g, 2.0 mmol) in acetonitrile (20 mL) was added to a solution of triphos (1.06 g, 2.0 mmol) in dichloromethane (30 mL). The reaction mixture was stirred for 2 h and the solvent removed in vacuo. The resulting yellow solid (1.63 g, 95%) was dried under vacuum at 50 °C for 5 h. ^{1}H NMR (dichloromethane-d_2): CH$_3$CN, 2.08 ppm (s); CH$_2$CH$_2$, 2.4–3.2 ppm (m); Ph, 7.5–7.8 ppm (m). ^{31}P NMR (dichloromethane-d_2): P$_t$, 54.6 ppm (d, $J_{P_tP_c}$ = 7 Hz); P$_c$, 116.4 ppm (t). IR: CN stretches 2285 (w), 2315 (w) cm^{-1}. Anal. Calcd for C$_{36}$H$_{36}$NB$_2$F$_8$P$_3$Pd: C, 50.54; H, 4.24; N, 1.64; P, 10.86; Pd, 12.44. Found: C, 50.29; H, 4.28; N, 1.35; P, 10.48; Pd, 12.02.

[Pd(triphos)(PEt$_3$)](BF$_4$)$_2$. PEt$_3$ (0.10 mL, 0.7 mmol) was added via syringe to a solution of [Pd(triphos)(CH$_3$CN)](BF$_4$)$_2$ (0.43 g, 0.50 mmol) in dichloromethane (50 mL). The resulting suspension was stirred overnight; then hexane (40 mL) was added. The volume of the reaction mixture was reduced to 30 mL in vacuo, and a white solid was collected by filtration. After the solid was dried in vacuo at 50 °C for 5 h, the yield was 0.37 g (86%). ^{1}H NMR (dichloromethane-d_2): Et, 0.5–1.3 ppm (m); CH$_2$CH$_2$, 2.6–3.5 ppm (m); Ph, 7.2–7.8 ppm (m). ^{31}P NMR (dichloromethane-d_2): PEt$_3$, 11.3 ppm (dt, $J_{P_c-PEt_3}$ = 300 Hz, $J_{P_t-PEt_3}$ = 29 Hz); P$_t$, 54.4 ppm (dd, $J_{P_cP_t}$ = 9 Hz); P$_c$, 109.0 ppm (dt). Anal. Calcd for C$_{40}$H$_{48}$B$_2$F$_8$P$_4$Pd: C, 51.50; H, 5.20; P, 13.28; Pd, 11.41. Found: C, 51.22; H, 5.21; P, 13.29; Pd, 11.18.

[Pd(triphos)P(OMe)$_3$](BF$_4$)$_2$. The procedure used to prepare this complex was similar to that of [Pd(triphos)(PEt$_3$)](BF$_4$)$_2$. The product was recrystallized from a mixture of dichloromethane and hexanes with a yield of 85%. ^{1}H NMR (acetonitrile-d_3): CH$_3$O, 3.22 ppm (four-line pattern); CH$_2$CH$_2$, 2.7–3.6 ppm (m); Ph, 7.2–7.6 ppm (m). ^{31}P NMR (acetonitrile-d_3): The second-order spectrum can be simulated at two fields using the following parameters: P$_t$, 56.82 ppm ($J_{P_tP_c}$ = 9, $J_{P_t-P(OMe)_3}$ = 37 Hz); P$_c$, 116.17 ppm ($J_{P_c-P(OMe)_3}$ = 490 Hz); P(OMe)$_3$, 108.81 ppm. Anal. Calcd for C$_{37}$H$_{42}$B$_2$F$_8$O$_3$P$_4$Pd: C, 47.34; H, 4.52; P, 13.20; Pd, 11.33. Found: C, 47.42; H, 4.45; P, 13.10; Pd, 11.13.

[Pd(triphos)PPh$_3$](BF$_4$)$_2$. See [Pd(triphos)(PEt$_3$)](BF$_4$)$_2$. The yield was 84%. ^{1}H NMR (dichloromethane-d_2): CH$_2$CH$_2$, 2.4–3.5 ppm (m); Ph, 6.8–7.5 ppm (m). ^{31}P NMR (dichloromethane-d_2): PPh$_3$, 18.2 ppm (dt, $J_{P_c-PPh_3}$ = 310, $J_{P_t-PPh_3}$ = 27 Hz); P$_t$, 53.6 ppm (dd, $J_{P_tP_c}$ = 10 Hz); P$_c$, 113.0 ppm (dt). Anal. Calcd for C$_{52}$H$_{48}$B$_2$F$_8$P$_4$Pd: C, 57.99; H, 4.50; P, 11.50; Pd, 9.88. Found: C, 57.37; H, 4.39; P, 11.22; Pd, 9.50.

[Pd(triphos)P(CH$_2$OH)$_3$](BF$_4$)$_2$. See [Pd(triphos)(PEt$_3$)](BF$_4$)$_2$. The crude product was recrystallized from a mixture of acetonitrile and ether, yield 79%. ^{1}H NMR (acetonitrile-d_3): CH$_2$O, 3.49 ppm (s, br); OH, 3.17 ppm (s, br); CH$_2$CH$_2$, 2.5–3.5 ppm (m); Ph, 7.5–7.9 ppm (m). ^{31}P NMR (acetonitrile-d_3): P(CH$_2$OH)$_3$, 6.4 ppm (dt, $J_{P_c-P(CH_2OH)_3}$ = 271, $J_{P_t-P(CH_2OH)_3}$ = 29 Hz); P$_t$, 52.1 ppm (dd, $J_{P_cP_t}$ = 10 Hz); P$_c$, 114.5 ppm (dt).

[Pd(triphos)P(OMe)$_3$]. Hydrazine (5 mL, 95%) was added to a suspension of [Pd(triphos)P(OMe)$_3$](BF$_4$)$_2$ (2.35 g, 2.50 mmol) in toluene (70 mL). The reaction mixture was stirred for 3 days to form a clear yellow solution. The solution was filtered and the solvent removed under vacuum. The resulting solid was washed with hexanes and dried to yield 1.45 g (76%). ^{1}H NMR (dichloromethane-d_2): CH$_2$CH$_2$, 1.8–3.0 ppm (m); CH$_3$O, 3.37 ppm (d, J_{PH} = 12 Hz); Ph, 7.0–7.8 ppm (m). ^{31}P NMR (toluene-d_8): P$_t$, 27.0 ppm (dd, $J_{P_t-P_c}$ = 51, $J_{P_t-P(OMe)_3}$ = 34 Hz); P$_c$, 37.2 ppm (overlapping dt, $J_{P_c-P(OMe)_3}$ = 49 Hz); P(OMe)$_3$, 172.5 ppm (dt). Anal. Calcd for C$_{37}$H$_{42}$O$_3$P$_4$Pd: C, 58.08; H, 5.54. Found: C, 58.28; H, 5.69.

[Pt(COD)(CH$_3$CN)$_2$](BF$_4$)$_2$. [Pt(C$_8$H$_{12}$OCH$_3$)(OCH$_3$)]$_2$[18,19] (0.50 g, 0.684 mmol) was dissolved in a mixture of dichloromethane (70 mL) and acetonitrile (2 mL). A solution of tetrafluoroboric acid in diethyl ether (0.3 mL, 50%) was added via syringe. The reaction mixture was stirred for 0.5 h to form a fine white precipitate. The product was collected on a glass frit by filtration in air and dried in vacuo at 50 °C for 5 h. The yield was 0.35 g (92%). ^{1}H NMR (acetonitrile-d_3): CH$_3$CN, 1.95 ppm (s); CH$_2$, 2.3–2.8 ppm (m); vinyl protons, 6.21 ppm with Pt satellites (J_{PtH} = 70 Hz). IR: CN stretches at 2340 and 2305 cm^{-1}. Anal. Calcd for C$_{12}$H$_{18}$N$_2$B$_2$F$_8$Pt: C, 25.78; H, 3.25; N, 5.01. Found: C, 25.32; H, 3.18; N, 4.92.

[Pt(triphos)(CH$_3$CN)](BF$_4$)$_2$. A solution of [Pt(COD)(CH$_3$CN)$_2$](BF$_4$)$_2$ (0.28 g, 0.50 mmol) in acetonitrile (20 mL) was added to a solution of triphos (0.27 g, 0.50 mmol) in dichloromethane (30 mL). The resulting yellow solution was stirred for 1 h, and the solvent was removed in vacuo to form a yellow solid. Dichloromethane (50 mL) was added to the solid, and the resulting solution was filtered. A white solid was isolated by removing the solvent in vacuo. The yield was 0.45 g (96%). This product was used without further purification to prepare [Pt(triphos)(PEt$_3$)](BF$_4$)$_2$. ^{1}H NMR (dichloromethane-d_2): CH$_3$CN, 2.02 ppm (s); CH$_2$CH$_2$, 3.2–1.8 ppm (m); Ph, 7.3–8.1 ppm (m). ^{31}P NMR (dichloromethane-d_2): P$_t$, 55.4 ppm (s, ^{195}Pt satellites, J = 1184 Hz); P$_c$, 90.7 ppm (s, ^{195}Pt satellites, J = 1653 Hz).

[Pt(triphos)(PEt$_3$)](BF$_4$)$_2$. PEt$_3$ (1.0 mL, 7 mmol) was added via syringe to a solution of [Pt(triphos)(CH$_3$CN)](BF$_4$)$_2$ (0.45 g, 0.48 mmol) in acetone (50 mL); the reaction mixture was stirred for 1 h. Solvent was removed in vacuo to reduce the volume of the reaction mixture to ~10 mL. The resulting white precipitate was collected by filtration in air, washed with diethyl ether (100 mL), and dried in vacuo at 50 °C for 5 h, yield 0.33 g (67%). ^{1}H NMR (dimethyl-d_6 sulfoxide): Et,

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Table I. Comparison of Cyclic Voltammetry Data for $[M(triphos)L](BF_4)_2$ Complexes

compound	$E_{1/2}$(II/I)	$E_{1/2}$(II/0)	$E_{1/2}$(I/0)
$[Ni(triphos)(CH_3CN)](BF_4)_2$	−0.48(70, 1.01, 1.0)[a]		−0.86 (irr)[b]
$[Ni(triphos)(PEt_3)](BF_4)_2$	−0.37(90, 0.97, 0.9)		−0.65 (60, 1.04, 1.0)
$[Ni(triphos)P(OMe)_3](BF_4)_2$		−0.45 (55, 0.97, 2.0)	
$[Pd(triphos)(CH_3CN)](BF_4)_2$		−0.90 (irr), −0.5 (irr)[c]	
$[Pd(triphos)(PEt_3)](BF_4)_2$		−0.72 (43, 1.02, 1.9)	
$[Pd(triphos)(PPh_3)](BF_4)_2$		−0.57 (43, 1.09, 1.9)	
$[Pd(triphos)P(OMe)_3](BF_4)_2$		−0.61 (60, 1.10, 1.9)	
$[Pd(triphos)P(CH_2OH)_3](BF_4)_2$		−0.75 (65, 1.10, 2.0)	
$[Pt(triphos)(PEt_3)](BF_4)_2$		−0.93 (45, 1.03, 2.0)	

[a] All potentials are given in volts vs. SCE. The first number in parentheses indicates the difference in potential for the peak current for the cathodic and anodic waves. The second number in parentheses indicates the ratio of the peak anodic current to the peak cathodic current, i_{P_a}/i_{P_c}. The third number in parentheses indicates the number of electrons passed per molecule in controlled-potential electrolysis experiments. [b] irr designates an irreversible reduction or oxidation with the potential corresponding to the peak current and not $E_{1/2}$. [c] This anodic wave is associated with the cathodic wave at −0.90 V.

0.5–1.3 ppm (m); CH_2CH_2, 2.3–3.4 ppm (m); Ph, 7.5–7.8 ppm (m). ^{31}P NMR (dimethyl-d_6 sulfoxide): PEt_3, 6.7 ppm (dt, $J_{P_c-PEt_3}$ = 276, $J_{P_t-PEt_3}$ = 22 Hz; ^{195}Pt satellites, J = 2317 Hz); P_t, 45.0 ppm (d, ^{195}Pt satellites, J = 2390 Hz); P_c, 99.7 ppm (d, ^{195}Pt satellites, J = 1969 Hz). Anal. Calcd for $C_{40}H_{48}B_2F_8P_4Pt$: C, 47.03; H, 4.74; F, 14.88. Found: C, 46.71; H, 4.39; F, 14.84.

Results and Discussion

Preparation and Characterization of Metal Complexes. Reaction of triphos with $[Ni(CH_3CN)_6](BF_4)_2$, $[Pd(CH_3CN)_4](BF_4)_2$, and $[Pt(COD)(CH_3CN)_2](BF_4)_2$ results in the formation of $[M(triphos)(CH_3CN)](BF_4)_2$ complexes. The ^{31}P NMR spectra of these complexes consist of a doublet and a triplet for the terminal and central phosphorus atoms, respectively, of the coordinated tridentate ligand. The presence of coordinated acetonitrile in these complexes is indicated by the observation of infrared bands between 2280 and 2315 cm^{-1}. In addition, the ^1H NMR spectrum of each complex exhibits a single resonance between 2.0 and 2.1 ppm that is assigned to the methyl resonance of coordinated acetonitrile. These spectral results are consistent with the formulation of these compounds as square-planar complexes **1–3**.

The acetonitrile ligand is easily displaced from **1–3** by addition of a phosphine ligand, eq 1. Complexes **4–6** have been characterized by ^{31}P and ^1H NMR spectroscopy, infrared spectroscopy, cyclic voltammetry, and elemental analysis. The ^{31}P NMR spectra of complexes **4–6** can generally be described as doublets of triplets assigned to the resonances for central phosphorus atom of the tridentate ligand and the monodentate phosphine, and a doublet of doublets assigned to the resonance for the terminal phosphorus atoms of the tridentate ligand. The doublets for the central phosphorus atom and the monodentate ligand arise from the strong trans-coupling of these ligands to each other. These doublets are further split into triplets by coupling to the terminal phosphorus atoms of the triphosphine ligand. The doublet of doublets for the terminal phosphorus atoms arise from coupling to the central phosphorus atom and the monodentate phosphine ligand. In some instances, the ^{31}P NMR spectra are second order. In these cases, the spectra can be readily simulated using reasonable values for chemical shifts and coupling constants which are given in the Experimental Section. Also described in the Experimental Section are the ^1H NMR spectra and infrared spectra, all of which are consistent with the formulation of these complexes.

$$[M(triphos)(CH_3CN)](BF_4)_2 + PR_3 \xrightarrow{CH_2Cl_2} \left[\begin{array}{c} P_t \\ | \\ P_c-M-PR_3 \\ | \\ P_t \end{array}\right](BF_4)_2 + CH_3CN \quad (1)$$

1. M=Ni
2. M=Pd
3. M=Pt

4. M=Ni, PR_3=(a) $P(OMe)_3$, (b) PEt_3
5. M=Pd, PR_3=(a) $P(OMe)_3$, (b) PEt_3, (c) PPh_3, (d) $P(CH_2OH)_3$
6. M=Pt, PR_3=PEt_3

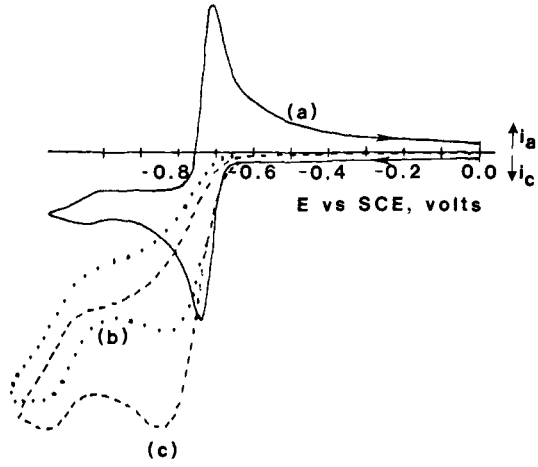


Figure 1. (a) The solid line is a cyclic voltammogram of a 1.0×10^{-3} M solution of $[Pd(triphos)(PEt_3)](BF_4)_2$. (b) The dotted line is of the same solution after addition of aqueous HBF_4 to produce a 1×10^{-2} M solution. (c) The dashed line illustrates the increase in current which is observed when CO_2 is bubbled through the acidic solution for 5 min. The solutions were all 0.2 N NEt_4BF_4 in acetonitrile. The working electrode was glassy carbon, the counter electrode was a Pt grid, and the reference electrode was SCE.

Reduction of $[Pd(triphos)P(OMe)_3](BF_4)_2$ with hydrazine results in the clean formation of $[Pd(triphos)P(OMe)_3]$. Similar reactions of $[Pd(triphos)(PEt_3)](BF_4)_2$ and $[Pd(triphos)(PPh_3)](BF_4)_2$ with hydrazine produce mixtures of products from which we have been unable to isolate [Pd(triphos)L] complexes. Cyclic voltammograms of $[Pd(triphos)P(OMe)_3]$ are identical with those of $[Pd(triphos)P(OMe)_3](BF_4)_2$ as expected. The ^{31}P NMR spectrum of $[Pd(triphos)P(OMe)_3]$ is consistent with the presence of the tridentate ligand and $P(OMe)_3$ in the coordination sphere of palladium. The central phosphorus atom of the tridentate ligand does not show the large downfield shift typically observed in square-planar,[16] square-pyramidal,[22] trigonal-bipyramidal,[16,22] or octahedral metal complexes.[23] We have observed this phenomenon in other tetrahedral metal complexes as well.[16]

Electrochemical Studies of $[M(triphos)L](BF_4)_2$ Complexes. Table I shows the results of cyclic voltammetry and controlled-potential electrolysis studies of the $[M(triphos)L](BF_4)_2$ complexes. Cyclic voltammograms of **4a**, **5a–d**, and **6** all show quasi-reversible, two-electron reductions at potentials between −0.45 and −0.93 V vs. SCE in acetonitrile. The cyclic voltammogram of **5b** is shown in trace a of Figure 1. The two-electron nature of the reductions for these complexes is supported by two observations. First, the differences in potentials for the cathodic and anodic peaks are generally less than 60 mV (see Table I). A 58-mV peak-to-peak separation is expected for a reversible one-electron reduction, and

(22) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076. DuBois, D. L.; Mason, R.; Meek, D. W. *J. Organomet. Chem.* **1976**, 114, C30. Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616.
(23) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

a value of 29 mV is expected for a two-electron reduction.[15] The observation of peak-to-peak separations of less than 60 mV is consistent with two-electron processes that are slightly broadened by kinetic or resistance effects. Second, bulk electrolyses of these complexes carried out at 100 to 200 mV negative of $E_{1/2}$ result in the passage of approximately 2.0 electrons per molecule (see Table I). The quasi-reversible, two-electron reductions of these complexes are expected to involve structural changes from square-planar to pseudo-tetrahedral geometries.[24] The nickel complex **4b** undergoes two sequential, quasi-reversible, one-electron reductions. Controlled-potential electrolysis of **4b** at −0.5 V vs. SCE in dichloromethane results in the passage of 0.9 electron per molecule and the formation of a stable Ni(I) complex which can be observed by EPR spectroscopy (single broad resonance with $g = 2.08$).

The cyclic voltammograms of complexes **4a,b** and **5a–d** are unaffected by the presence of CO_2. This is true for CO_2 pressures of up to 75 psi in dry acetonitrile. This indicates that the Ni(0) and Pd(0) complexes formed on reduction do not react rapidly with CO_2. This observation is also supported by the fact that [Pd(triphos)P(OMe)$_3$] does not react with CO_2. In contrast, the isoelectronic platinum complex, [Pt(triphos)(PEt$_3$)](BF$_4$)$_2$, interacts strongly with CO_2 on reduction, and the cyclic voltammogram exhibits an irreversible reduction under CO_2. The wave corresponding to the Pt(II/0) couple becomes reversible again upon purging CO_2 from the solution. The difference in the ability of the metal (0) complexes to bind CO_2 is tentatively attributed to the increased nucleophilicity expected for the Pt complex since its redox potential is approximately 0.2 V more negative than the analogous Pd complex.

In the presence of acid, the reduction waves corresponding to the (II/0) and (I/0) couples become irreversible indicating that the M(0) complexes formed react rapidly with acid. This is shown for complex **5b** in Figure 1, trace b. Addition of CO_2 to acidic acetonitrile solutions of complexes **5a–d** results in a further increase in current as shown in trace c of Figure 1 for **5b**. This increase in current is attributed to CO_2 reduction, and is not observed for any of the Ni or Pt complexes. That CO_2 is being catalytically reduced is supported by three observations. (1) Purging the solution with N_2 results in the return of the cyclic voltammogram to the appearance observed for just the complex plus acid (Figure 1, trace b). (2) The amount of current is directly proportional to the CO_2 pressure from 1 to 5 atm (Figure 2). (3) Between 3 and 10 equiv of CO per equivalent of catalyst are detected in bulk electrolysis experiments with current efficiencies for CO production of up to 74%. Hydrogen is also produced in these experiments and accounts for the remaining charge passed during electrolysis.

A number of control experiments were carried out to confirm that the palladium complexes were responsible for the observed CO_2 reduction. No CO was detected in control experiments in which no catalyst was present. To eliminate the possibility that CO_2 reduction is due to metallic palladium deposited on the electrode during electrolysis, the following experiment was performed. Carbon electrodes that had been immersed in a catalyst solution and used to reduce CO_2 were removed from solution and immersed in an identical solution without catalyst. No catalytic activity was observed. When these electrodes were returned to the solution containing the catalyst, CO_2 reduction was observed again. Finally, no CO is detected in bulk electrolysis experiments carried out in the absence of CO_2, and no CO is detectable by gas chromatography in the CO_2 used in the experiments. These results indicate that reduction of CO_2 is the source of CO and not the solvent, catalyst, or an impurity in the CO_2.

As can be seen from Table II, only palladium complexes of the type [Pd(triphos)L](BF$_4$)$_2$ (where L is CH$_3$CN, PEt$_3$, PPh$_3$, and P(OMe)$_3$) are active catalysts. The isoelectronic and isostructural nickel and platinum complexes containing the tridentate phosphine ligand lack catalytic activity. A second important observation is that none of the bis(diphosphine) metal complexes of nickel, palladium, or platinum are active. The observation that the bis(diphosphine) palladium complexes are not active is evidence that dissociation of one of the four phosphorus atoms is necessary for catalysis. This result is also consistent with the observation that an excess of the monodentate phosphine ligand retards the catalytic reaction. These results emphasize the importance of both the ligand and the metal in determining catalytic activity and establish a structure–reactivity relationship for this class of complexes. This represents the first time such an isoelectronic and isostructural series of complexes has been compared for their ability to catalyze the electrochemical reduction of CO_2.

We are also interested in understanding the mechanism of this catalytic process. The difference in peak currents observed at a glassy carbon electrode immersed in solution containing catalyst and acid in the presence of CO_2 ($i_{p_{CO_2}}$, curve c of Figure 1), and in the absence of CO_2 (i_p, curve b of Figure 1) is quite reproducible at clean electrode surfaces, and provides a convenient method for monitoring the initial rate of CO_2 reduction. Kinetic experiments using this technique show that the current has a linear dependence on CO_2 pressure and catalyst concentration (Figures 2 and 3). Since the current is a direct measurement of the initial rate of CO_2 reduction, the linear dependence of current on CO_2 pressure and catalyst concentration implies the reaction is first order in CO_2 and in the catalyst. It is also found that the rate of CO_2 reduction is retarded by the addition of the monodentate phosphine ligand. The dependence of the reaction rate on acid concentration is complex. For a 1.6×10^{-3} M solution of **5b**, the rate of CO_2 reduction increases as the acid concentration increases to 2.9 ×

Table II. Evaluation of Metal Complexes for Their Ability To Mediate the Electrochemical Reduction of CO_2

complex[a]	activity
[Ni(dppe)$_2$](BF$_4$)$_2$	−
[Ni(triphos)(CH$_3$CN)](BF$_4$)$_2$	−
[Ni(triphos)(PEt$_3$)](BF$_4$)$_2$	−
[Ni(triphos)P(OMe)$_3$](BF$_4$)$_2$	−
[Pd(dppe)$_2$](BF$_4$)$_2$	−
[Pd(triphos)(CH$_3$CN)](BF$_4$)$_2$	+
[Pd(triphos)P(OMe)$_3$](BF$_4$)$_2$	+
[Pd(triphos)(PEt$_3$)](BF$_4$)$_2$	+
[Pd(triphos)(PPh$_3$)](BF$_4$)$_2$	+
[Pd(triphos)P(CH$_2$OH)$_3$](BF$_4$)$_2$	+
[Pd(dppp)(PEt$_3$)$_2$](BF$_4$)$_2$	−
[Pt(dppe)$_2$](BF$_4$)$_2$	−
[Pt(triphos)(PEt$_3$)](BF$_4$)$_2$	−

[a] Where dppe is bis(1,2-diphenylphosphino)ethane and dppp is bis(1,3-diphenylphosphino)propane.

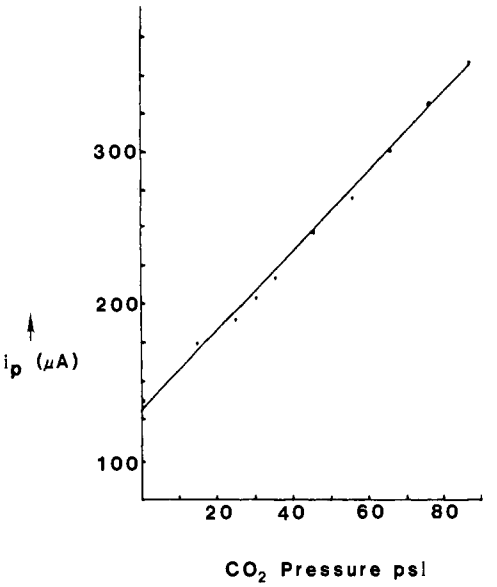


Figure 2. This plot shows the peak current, i_p, for the cathodic wave observed in trace c of Figure 1 as a function of CO_2 pressure.

(24) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

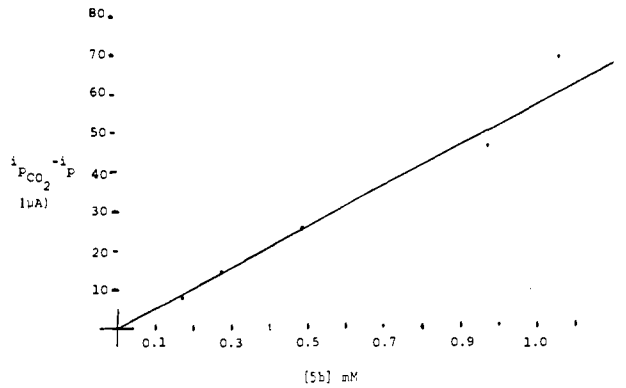


Figure 3. Graph showing the dependence of the rate of CO_2 reduction on catalyst concentration. Vertical axis shows the difference in peak currents observed for a glassy carbon electrode (approximately 0.4 cm^2 in area) immersed in a solution containing catalyst and acid in the presence of CO_2 ($i_{P_{CO_2}}$) and in the absence of CO_2 (i_p). The horizontal axis displays the millimolar concentration of **5b**.

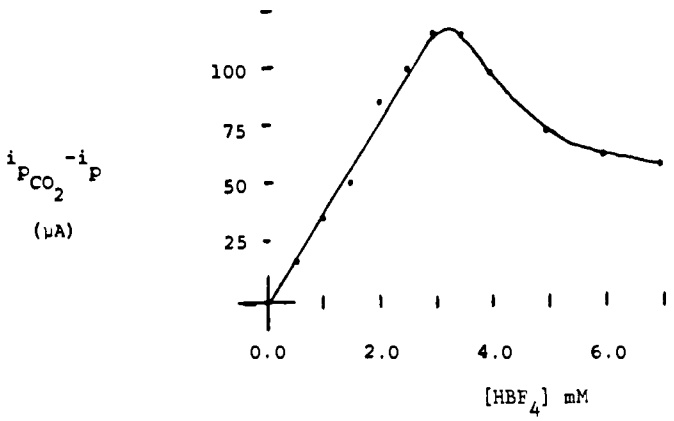
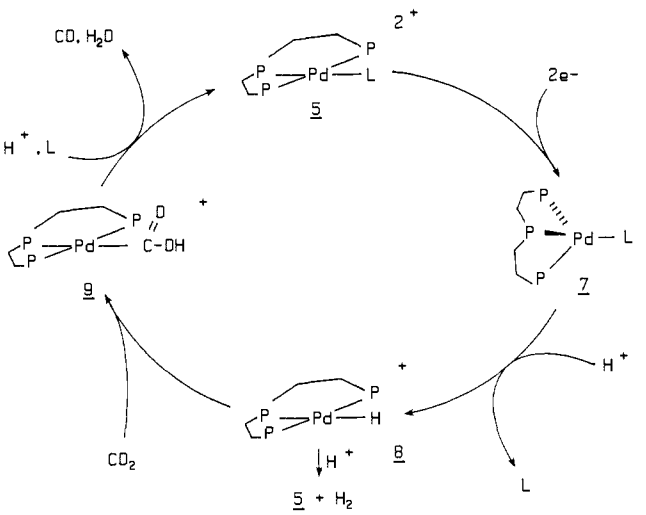


Figure 4. Graph showing rate dependence on acid concentration for a 1.6×10^{-3} M solution of **5b**. Vertical axis shows the difference in peak currents observed for a glassy carbon electrode immersed in a solution of catalyst and acid in the presence of CO_2 ($i_{P_{CO_2}}$) and in its absence (i_p). The horizontal axis displays the millimolar acid concentration.

10^{-2} M, and then decreases at higher concentrations as shown in Figure 4. The first-order dependence of the rate on catalyst, CO_2, and acid at low concentrations is consistent with a mechanism in which insertion of CO_2 into a Pd–H bond is the rate-limiting step as shown in Scheme I. The inhibition observed on addition of excess phosphine ligand indicates that dissociation of a phosphine ligand is necessary for CO_2 insertion. The decrease in the rate of CO_2 reduction at higher acid concentrations is consistent with a competing reaction of the metal hydride complex, **8**, with acid to form the observed by-products H_2 and **5b**. In support of such a side reaction, the complex [Pd(triphos)P(OMe)$_3$] reacts with HBF_4 to regenerate **5a** and presumably H_2. The mechanism shown in Scheme I differs significantly from that proposed for other catalysts in which the reduced metal complexes interact directly with CO_2 and no ligand dissociation step is required.[8-13]

The cycle shown in Scheme I is consistent with the observed products and kinetic data; however, further studies are needed before the mechanistic details of the last two steps are known. Since reaction of the metal hydride intermediate with CO_2 is the rate-limiting step in this proposed cycle, the formation of the

Scheme I



metallocarboxylic acid, **9**, is inferred from the nature of the product, CO. All previously reported insertions of CO_2 into metal–hydride and metal–carbon bonds which have been investigated in detail have resulted in the formation of metal formates and carboxylates.[1,25,26] Because of this, the formation of [Pd(triphos)(COOH)](BF_4), **9**, as an intermediate must be regarded with some circumspection. However, similar intermediates have been proposed for the water gas shift reaction,[27] and metallocarboxylic acids can be prepared by the addition of OH^- or water to metal carbonyls.[28] The isolation of the metal hydride, **8**, and its reaction with CO_2 are important goals which remain to be achieved before this system can be fully understood.

In summary, a series of isoelectronic and isostructural complexes of the type [M(triphos)(PR_3)](BF_4)$_2$ have been prepared and characterized. When M is Pd, these complexes mediate the electrochemical reduction of CO_2 in acidic acetonitrile solutions. Kinetic studies have been carried out for this reaction, and a mechanism has been proposed in which the rate-limiting step is the reaction of a coordinatively unsaturated palladium hydride intermediate with CO_2.

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