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Dicationic Nickel(II) Carbonyl Complexes Containing Tetradentate Ligands

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This article describes the preparation and spectroscopic characterization of three dicationic Ni(II) carbonyl complexes containing tripodal tetradentate ligands. An X-ray diffraction study of $[Ni(PP_3E)(CO)](BF_4)_2$ (where PP_3E is tris(2-(diethylphosphino)ethyl)phosphine) has been completed and confirms a trigonal bipyramidal structure with an apical carbonyl ligand. The binding of CO is weak and reversible. The stability of these complexes is enhanced by the small chelate bite imposed by the tetradentate ligands. The electrochemical behavior of these complexes depends on the nature of the donor atom trans to CO. The $[Ni(NP_3E)(CO)]^{2+}$ (where NP_3E is tris(2-(diethylphosphino)ethyl)amine) cation undergoes two reversible one-electron reductions, whereas the corresponding tetraphosphine cations undergo irreversible two-electron reductions.

Introduction

There is currently considerable interest in Ni(II) carbonyl complexes because of their role as models for nickel-containing CO dehydrogenase enzymes.[1−4] Several Ni(II) carbonyl complexes are known, and a few have been structurally characterized.[5−7] All of these complexes are uncharged, and generally the carbonyl ligand is bound in the equatorial plane of a trigonal bipyramid, although Ni(II) complexes with apical carbonyl ligands have been characterized. Stable Ni(I) carbonyl complexes that contain CO in the apical position of a trigonal bipyramid have also been reported and structurally characterized.[3,8] The latter complexes are expected to contain an unpaired electron in the d_{z^2} orbital, which should contain some Ni−CO σ antibonding character.[9] This suggested that the synthesis of related Ni(II) dicationic species should be possible. Removal of an electron from this σ antibonding orbital should strengthen Ni−C σ bonding, while Ni−C π backbonding should be weakened because of the higher positive charge on the Ni atom.

In this paper we describe the synthesis and spectroscopic characterization of three dicationic Ni(II) carbonyl complexes, $[Ni(PP_3)(CO)](BPh_4)_2$, $[Ni(PP_3E)(CO)](BF_4)_2$, and $[Ni(NP_3E)(CO)](BF_4)_2$ [where PP_3 is $P(CH_2CH_2PPh_2)_3$, PP_3E is $P(CH_2CH_2PEt_2)_3$, and NP_3E is $N(CH_2CH_2PEt_2)_3$]. An X-ray diffraction study of $[Ni(PP_3E)(CO)](BF_4)_2$ has been completed that confirms the presence of a bound CO in this complex. The electrochemical behavior of these complexes is dependent on the nature of the apical donor ligand. $[Ni(NP_3E)(CO)](BF_4)_2$ exhibits two reversible one-electron reductions, whereas $[Ni(PP_3)(CO)](BPh_4)_2$ and $[Ni(PP_3E)(CO)](BF_4)_2$ undergo irreversible two-electron reductions. Qualitative molecular orbital calculations are used to explore the relationship between chelate bite size and the Ni−C bond strength.

Results

Synthesis and Characterization of Ligands and Complexes. The ligand PP_3E can be prepared by the free radical addition of diethylphosphine to trivinylphosphine with slight modifications of the procedure used to prepare tris[2-(dimethylphosphino)ethyl]phosphine.[10] NP_3E was synthesized from the nitrogen mustard tris(2-chloroethyl)amine and lithium diethylphosphide in a manner analogous to the procedure used for the preparation of tris[2-(diphenylphosphino)ethyl]amine.[11] ^{31}P and ^{1}H NMR spectral data for these ligands are given in the Experimental Section and are fully consistent with the proposed formulations.

The reaction of PP_3E with $[Ni(CH_3CN)_6](BF_4)_2$ in acetonitrile results in the formation of $[Ni(PP_3E)(CH_3CN)](BF_4)_2$. The ^{31}P NMR spectrum of this complex consists of a quartet at 149.9 ppm assigned to the central phosphorus atom (P_C) of the tetraphosphine ligand and a doublet at 56.8 ppm assigned to the terminal phosphorus atoms (P_T). The large downfield

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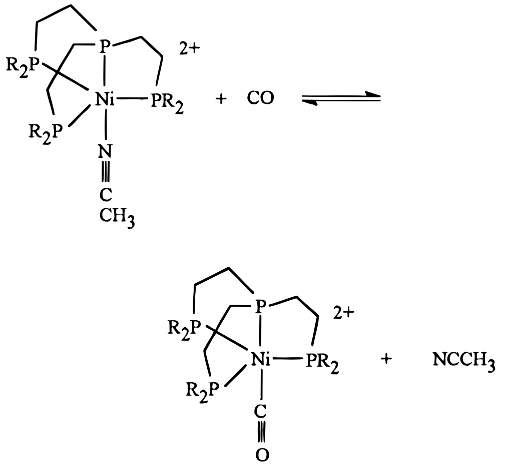
shift of the central phosphorus atom is typical for a phosphorus atom incorporated into three five-membered rings.[12] In noncoordinating solvents such as acetone-d_6, a quartet is observed for coordinated acetonitrile at 2.64 ppm in the ^{1}H NMR spectrum. This splitting is attributed to coupling between the coordinated acetonitrile and the terminal phosphorus atoms of the tetradentate ligand. A small cis-coupling is also observed between the terminal phosphorus atoms and the methyl group of acetonitrile for $[Ni(PP_3)(CH_3CN)](BF_4)_2$, as described previously.[13]

The reaction of CO (1 atm) with purple $[Ni(PP_3)(CH_3CN)]^{2+}$ to form orange $[Ni(PP_3)(CO)]^{2+}$ (reaction 1) is



(1)

reversible but proceeds to completion in weakly coordinating solvents such as dichloromethane and acetone containing no excess acetonitrile. Adding acetonitrile reverses the reaction. Qualitatively, the forward and reverse reactions shown in reaction 1 appear to have half-lives on the order of 10−15 min on the basis of the rate of color change. The loss of CO also appears to occur in the solid state for this complex, and a satisfactory elemental analysis was not obtained. However, the spectral data recorded under an atmosphere of CO are fully consistent with the proposed formulation. The ^{31}P NMR spectrum of the carbonyl complex consists of a quartet at 179.6 ppm assigned to the central phosphorus atom and a doublet at 64.4 ppm assigned to the terminal phosphorus atoms. Labeled ^{13}CO can be incorporated by exposing a dichloromethane solution of $[Ni(PP_3)(CH_3CN)](BF_4)_2$ to ^{13}CO. The ^{31}P NMR spectrum of $[Ni(PP_3)(^{13}CO)](BF_4)_2$ exhibits an additional doublet splitting for both the central and terminal phosphorus atoms caused by coupling between carbon and phosphorus (72 and 19 Hz, respectively). The resonance for the carbonyl ligand in the ^{13}C NMR spectrum is a doublet of quartets with the same coupling constants observed in the ^{31}P NMR spectrum. The presence of bound CO is also indicated by a strong CO stretching band at 2067 cm^{-1} in the infrared spectrum of dichloromethane solutions of $[Ni(PP_3)(CO)](BPh_4)_2$. This band shifts to 2016 cm^{-1} for $[Ni(PP_3)(^{13}CO)](BF_4)_2$, which is close to the value of 2020 cm^{-1} expected on the basis of the difference in mass between ^{12}C and ^{13}C.[14] Similar spectral data were obtained for $[Ni(PP_3E)(CO)](BF_4)_2$, and these are given in the Experimental Section.

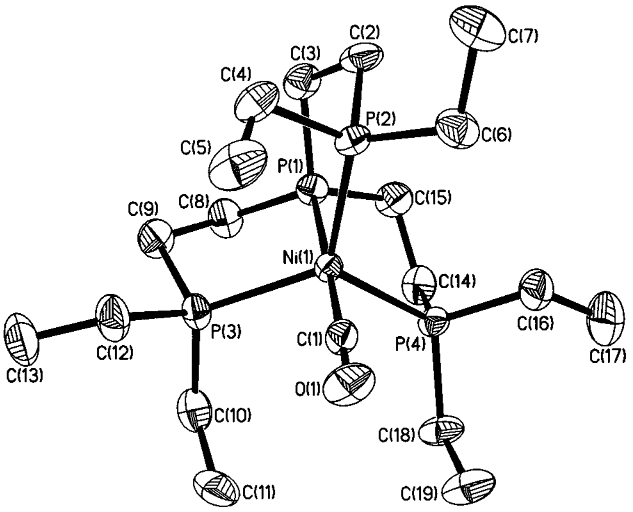


Figure 1. ORTEP showing the atom-numbering scheme for one of the $[Ni(PP_3E)(CO)]^{2+}$ cations. Hydrogen atoms are omitted for clarity, and the thermal ellipsoids are shown at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ni(PP_3E)(CO)](BF_4)_2$

Ni(1)−P(1)	2.168(3)	Ni(1)−P(2)	2.260(3)
Ni(1)−P(3)	2.253(3)	Ni(1)−P(4)	2.245(3)
Ni(1)−C(1)	1.780(11)	C(1)−O(1)	1.115(13)
P(1)−Ni(1)−P(2)	86.0(1)	P(1)−Ni(1)−P(3)	85.4(1)
P(2)−Ni(1)−P(3)	120.8(1)	P(1)−Ni(1)−P(4)	86.2(1)
P(2)−Ni(1)−P(4)	118.0(1)	P(3)−Ni(1)−P(4)	119.6(1)
P(1)−Ni(1)−C(1)	178.2(3)	P(2)−Ni(1)−C(1)	92.7(3)
P(3)−Ni(1)−C(1)	94.2(3)	P(4)−Ni(1)−C(1)	95.5(3)
Ni(1)−P(1)−C(3)	110.2(3)	Ni(1)−P(1)−C(8)	110.2(3)
C(3)−P(1)−C(8)	108.3(5)	Ni(1)−P(1)−C(15)	110.4(3)
C(3)−P(1)−C(15)	108.7(5)	C(8)−P(1)−C(15)	108.9(5)
Ni(1)−C(1)−O(1)	178.8(9)		

$[Ni(NP_3E)(CO)](BF_4)_2$ can be prepared directly from NP_3E and $[Ni(CH_3CN)_6](BF_4)_2$ in the presence of CO, which illustrates that isolation of the acetonitrile complexes as intermediates is not necessary. The ^{31}P NMR spectrum of this complex is a singlet at 59.8 ppm assigned to the terminal phosphorus atoms; this resonance splits into a doublet for the ^{13}C labeled isotopomer. The resonance assigned to the carbonyl ligand in the ^{13}C NMR spectrum is a quartet with the same coupling constant. The IR band assigned to the carbonyl stretch shifts from 2050 cm^{-1} for the ^{12}CO complex to 2002 cm^{-1} for the ^{13}CO complex (compared to a calculated value of 2004 cm^{-1}).

X-ray Structure Determination of $[Ni(PP_3E)(CO)](BF_4)_2$. Crystals of this complex were obtained from a mixture of dichloromethane and ethanol under an atmosphere of CO. The crystals consist of two independent $[Ni(PP_3)(CO)]^{2+}$ cations and their associated BF_4^- anions. One of the cations contains a disordered ethyl group, and the BF_4^- anions are disordered as well. Selected bond distances and bond angles for one of the $[Ni(PP_3E)(CO)]^{2+}$ cations are given in Table 1. A drawing of this cation is shown in Figure 1. The cation has a trigonal bipyramidal structure with the central phosphorus atom of the tetradentate ligand and CO occupying the apical positions, while the three terminal phosphorus atoms occupy equatorial positions. The largest deviations from an ideal trigonal bipyrami-

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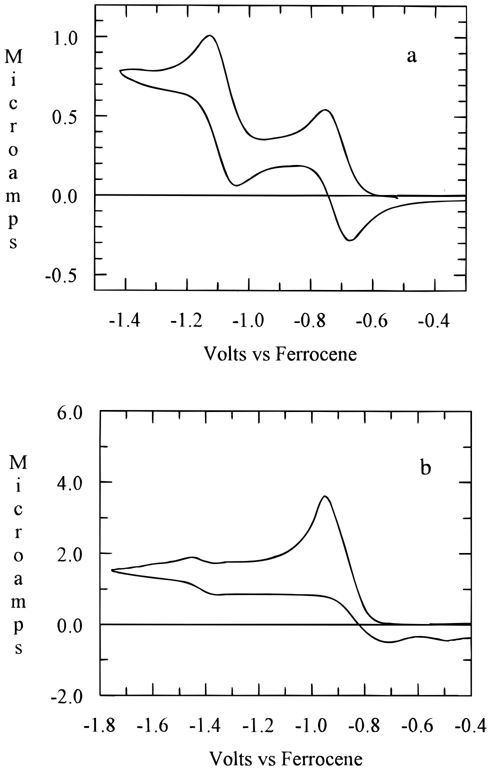


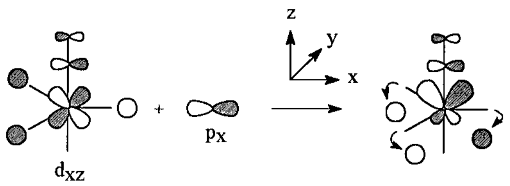
Figure 2. Cyclic voltammograms of (a) 1.0 × 10^{-3} M solution of $[Ni(NP_3E)(CO)](BF_4)_2$ (0.02 V/s) and (b) 2.4 ×10^{-3} M solution of $[Ni(PP_3E)(CO)](BPh_4)_2$ (0.05 V/s) in tetrahydrofuran. Both solutions were saturated with CO.

dal geometry are observed for the bond angles between the apical phosphorus atom and the equatorial phosphorus atoms. These angles are approximately 5° less than the ideal 90°, and the corresponding C(1)−Ni−P(eq) bond angles are 3−5° larger than the ideal 90°. This distortion is a result of the small chelate bite of the tetraphosphine ligand, and similar bond angles are observed for $[Ni(PP_3)(Br)](PF_6)_2$ and $[Ni(PP_3)P(OMe)_3](AsF_6)_2$.[15,16] The Ni−C(1) distance of 1.780(11) Å is within the range observed for other Ni(II) carbonyl complexes (1.73−1.83 Å), and it is shorter than the Ni−C bond distances observed for the Ni(I) complexes $[Ni(NS_3t\text{-}Bu)(CO)]^+$ (1.85(1) Å) and $[Ni(NP_3)(CO)]^+$ (1.90(5) Å), respectively (where NS_3t-Bu is $N(CH_2CH_2St\text{-}Bu)_3$ and NP_3 is $N(CH_2CH_2Ph_2)_3$).[3,8] These results are consistent with a significant lengthening of the Ni−C bond upon reduction from Ni(II) to Ni(I), but more definitive evidence would be provided by structures of a single complex in both Ni(I) and Ni(II) oxidation states.

Electrochemical Studies. A cyclic voltammogram of $[Ni(NP_3E)(CO)](BF_4)_2$ is shown in Figure 2 (trace a). Two reversible one-electron reductions are observed for this complex at −0.71 and −1.08 V vs the ferrocene/ferrocenium couple. The waves are diffusion controlled as indicated by a linear dependence of the peak current on the square root of the scan rate between 0.05 and 1.0 V/s for both waves.[17] A controlled-potential electrolysis carried out at −0.87 V in tetrahydrofuran (THF) resulted in the passage of 0.9 Faradays/mol of complex, which is consistent with a one-electron reduction. The peak-to-peak separations of the waves at 0.02 V/s are approximately 80 mV, which is within experimental error of the value observed for ferrocene under the same conditions and supports reversible one-electron processes for these two waves.

A cyclic voltammogram of $[Ni(PP_3)(CO)](BPh_4)_2$ is shown by trace b of Figure 2. It consists of an irreversible two-electron reduction wave with a peak at −0.95 V (for a scan rate of 0.05 V/s) and two associated oxidation waves at −0.74 and −0.50 V. There is also a small reversible wave at −1.42 V that is unassigned. The potential of the reduction wave at −0.95 V in Figure 2 exhibits a strong dependence on the scan rate, which indicates that the electron transfer step is slow.[18] The passage of 1.9 Faradays of charge/mol of complex during a bulk electrolysis experiment carried out at −1.15 V is consistent with a two-electron reduction process. Similarly, $[Ni(PP_3E)(CO)](BF_4)_2$ undergoes an irreversible two-electron reduction at −1.33 V with an associated irreversible anodic wave at −0.95 V (for a scan rate of 0.05 V/s).

Extended Hückel Molecular Orbital Calculations. Extended Hückel molecular orbital calculations[19] were carried out on $[Ni(PH_3)_4(CO)]^{2+}$ as a function of the P(a)−Ni−P(eq) bond angle. Of particular interest was the relationship between this angle and the Ni−C bond order. For P(a)−Ni−P(eq) bond angles of 80, 90, and 100°, the calculated bond orders using the parameter set given in the Supporting Information are 1.19, 1.06, and 0.91, respectively. Similar results were obtained using other parameter sets. The increase in the Ni−C bond strength for small P(a)−Ni−P(eq) angles can be largely attributed to greater π back-bonding. This arises from two factors. As the angle decreases from 90° the ligands move from a nonbonding position with respect to the d_{xz} and d_{yz} orbitals to antibonding positions. This destabilizes these orbitals and produces a better energy match between these d orbitals and the π^* orbital of CO. A second feature that contributes to better back-bonding is the result of mixing p_x and p_y orbitals with the d_{xz} and d_{yz} orbitals, respectively, as the effective symmetry of the complex is lowered. This mixing, shown qualitatively in eq 2, results in better overlap between these d orbitals and the π^* orbitals of CO. The increased Ni−C bond order is a result of both a better energy match and better overlap resulting from an acute P−Ni−P bond angle.



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Discussion

Although a number of five-coordinate Ni(II) carbonyl complexes are known,[5−7] none of those reported previ-

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ously are dicationic. One approach to stabilizing such a complex is to destabilize the product formed upon CO loss. Loss of CO from the equatorial position of a trigonal bipyramid or the axial position of a square pyramid leads naturally to the formation of stable square-planar 16-electron complexes. Loss of CO from the axial position of a trigonal bipyramid leads to a much more energetic and rare trigonal pyramidal complex.[9,20] By using tripodal tetradentate ligands, it is possible to impose steric constraints on Ni(II) complexes, which would require formation of trigonal pyramidal intermediates. As a result, binding of a fifth ligand to the apical site should be favored over formation of a four-coordinate species. In addition, the Ni(I) carbonyl complexes, $[\mathrm{Ni(NP_3)(CO)}]^+$ and $[\mathrm{Ni(NS_3}t\text{-}\mathrm{Bu)(CO)}]^+$, have been previously reported.[3,8] On the basis of simple molecular orbital considerations, it would be expected that the unpaired electron in these complexes would reside in a molecular orbital that possesses some degree of Ni−C antibonding character. This would suggest that oxidation of complexes of this type could result in stable dicationic Ni(II) complexes. In agreement with these expectations, the dicationic Ni(II) carbonyl complexes, $[\mathrm{Ni(PP_3)(CO)}]^{2+}$, $[\mathrm{Ni(PP_3E)(CO)}]^{2+}$, and $[\mathrm{Ni(NP_3E)(CO)}]^{2+}$, were prepared by the reaction of CO with the corresponding acetonitrile complexes in noncoordinating solvents.

Another feature which contributes to the stability of these dicationic Ni(II) carbonyl complexes is the relatively acute P(a)−Ni−P(eq) bond angles, such as those observed in the structure of $[\mathrm{Ni(PP_3E)(CO)}]^{2+}$. This small angle enhances the Ni−C π back-bonding by polarizing and increasing the energy of the d_{xy} and d_{xz} orbitals, leading to a stronger Ni−C bond. It is interesting to note that the carbonyl-stretching frequencies of $[\mathrm{Ni(PP_3)(CO)}]^{2+}$, $[\mathrm{Ni(PP_3E)(CO)}]^{2+}$, and $[\mathrm{Ni(NP_3E)(CO)}]^{2+}$, 2067, 2052, and 2050 cm^{-1}, respectively, are similar to those of the neutral Ni(II) carbonyl complex $[\mathrm{Ni(fdma)(CO)I_2}]$ (2053 cm^{-1}, where fdma is 1,1′-ferrocenyldimethylarsine). This suggests that the more acute angles of $[\mathrm{Ni(PP_3E)(CO)}]^{2+}$, compared to those observed for $[\mathrm{Ni(fdma)(CO)I_2}]$, partially compensate for the increased positive charge.

The existence of the stable Ni(I) and Ni(II) complexes, $[\mathrm{Ni(NP_3)(CO)}]^+$ and $[\mathrm{Ni(NP_3E)(CO)}]^{2+}$, suggested that the reduction of the latter complex should be chemically and electrochemically reversible. The electrochemical studies described above demonstrate that this is true. The structures of $[\mathrm{Ni(NP_3)(CO)}]^+$ and $[\mathrm{Ni(NP_3)(CO)}]$ show a lengthening of the Ni−N bond from 2.31 to 3.25 Å upon reduction.[8,21] This suggests that the reduction of $[\mathrm{Ni(NP_3E)(CO)}]^{2+}$ proceeds by a progressive lengthening of the Ni−N bond. In contrast the tetraphosphine complexes, $[\mathrm{Ni(PP_3)(CO)}]^{2+}$ and $[\mathrm{Ni(PP_3E)(CO)}]^{2+}$, undergo irreversible two-electron reductions. Possible reasons for the difference in behavior between these two complexes and $[\mathrm{Ni(NP_3E)(CO)}]^{2+}$ are the difference in the Ni−N(a) and Ni−P(a) bond strengths and the much easier inversion process for nitrogen compared to phosphorus. As the bond distance between Ni and the axial ligand lengthens, there is a tendency to invert the apical ligand. The relatively easy inversion at nitrogen for the $\mathrm{NP_3}$ ligand is manifested in rather large C−N−C bond angles in the trigonal pyramidal complex $[\mathrm{Pd(NP_3)}]$ (average C−N−C = 113.4(19)°).[22] The stronger Ni−P(a) bond and decreased ability to invert at phosphorus for $[\mathrm{Ni(PP_3)(CO)}]^{2+}$ and $[\mathrm{Ni(PP_3E)(CO)}]^{2+}$ may result in cleavage of either a Ni−CO bond or a Ni−P(eq) bond. Breaking either of these two bonds would account for the irreversibility of the two-electron reduction processes observed for these two complexes. The irreversible nature of these reductions precludes the possibility of isolating the Ni(I) complexes $[\mathrm{Ni(PP_3)(CO)}]^+$ and $[\mathrm{Ni(PP_3E)(CO)}]^+$ that are analogous to $[\mathrm{Ni(NP_3)(CO)}]^+$.

Summary and Conclusions

Tripodal tetradentate ligands were used to impose structural constraints that favor formation of five-coordinate complexes with an apical ligand. Qualitative molecular orbital calculations suggested that acute angles trans to the apical ligand should favor M−L π back-bonding. Tripodal tetradentate ligands with two-carbon chains between the central and terminal donor atoms result in acute angles between the apical and equatorial positions in trigonal bipyramidal Ni(II) complexes, which should make them ideal candidates for binding small pi-acceptor ligands. Advantage was taken of these properties to prepare stable dicationic Ni(II) carbonyl complexes. These complexes were characterized by spectroscopic and electrochemical techniques, and an X-ray diffraction study of one complex is reported. Electrochemical studies indicate that $[\mathrm{Ni(NP_3R)(CO)}]^+$ complexes are stable but the analogous $[\mathrm{Ni(PP_3R)(CO)}]^+$ complexes are not.

Experimental Section

Physical Measurements and General Procedures. ^{1}H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer at 299.95 and 121.42 MHz, respectively. ^{1}H chemical shifts are reported relative to tetramethylsilane using residual solvent protons as a secondary reference. ^{31}P chemical shifts are reported relative to external phosphoric acid. Infrared spectra were recorded on a Nicolet 510P spectrometer as Nujol mulls or dichloromethane solutions. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, NY. All syntheses were carried out using standard Schlenk and drybox techniques.

Single-crystal X-ray data for $[\mathrm{Ni(PP_3E)(CO)}](\mathrm{BF_4})_2$ were collected at 23 °C on a Siemens P3 diffractometer. Mo Kα radiation (monochromatized by diffraction off a highly oriented graphite crystal) was used in this study. Programs in the Siemens X-ray package were used for data collection and structure solution and refinement. Details of the experimental conditions are given in the Supporting Information. Table 2 summarizes the crystal data, data collection conditions, and solution and refinement details for $[\mathrm{Ni(PP_3E)(CO)}](\mathrm{BF_4})_2$.

All electrochemical experiments for the carbonyl complexes were carried out under an atmosphere of CO in 0.1 M $\mathrm{NBu_4BF_4}$ solutions in THF. Cyclic voltammetry experiments were

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Table 2. Crystal Data, Data Collection Conditions, and Solution and Refinement Details for $[Ni(PP_3E)(CO)](BF_4)_2$

empirical formula	$C_{19}H_{42}B_2F_8NiOP_4$
color, habit	orange prism
cryst size	0.38 × 0.62 × 0.28 mm
cryst syst	monoclinic
space group	$P2_1/c$
a	19.456(4) Å
b	10.485(2) Å
c	29.174(6) Å
β	94.75(3)°
V	5931(2) Å^3
Z	8
fw	642.7
d_{calcd}	1.440 g/cm^3
abs coeff	0.932 mm^{-1}
radiation	Mo Kα (λ = 0.710 73 Å)
temp	296
monochromator	highly oriented graphite crystal
2θ range	4.0−55.0°
scan type	Wycoff
scan speed	variable; 4.0−30.0°/min in ω
scan range (ω)	2.00°
index ranges	$0 \leq h \leq 16$, $-12 \leq k \leq 0$, $-34 \leq l \leq 34$
rflcns collcd	9557
indepdt reflcns	9224 (R_{int} = 1.70%)
obsd reflcns	4845 ($F > 6.0\sigma(F)$)
abs corr	semi-empirical
no. of params refined	601
final R indices (obs data)	R = 6.72%, wR = 8.78%
R indices (all data)	R = 12.11%, wR = 9.84%
data to param ratio	8.1:1

carried out on a Cypress Systems computer-aided electrolysis system. The working electrode was a glassy carbon disk (1-mm diameter, Cypress Systems EE005). The counter electrode was a glassy carbon rod (1-mm diameter), and a platinum wire immersed in a permethylferrocene/permethylferrocenium solution was used as a pseudoreference electrode to fix the potential.[21] Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.[22] Controlled-potential experiments were performed with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. Working electrodes were constructed from reticulated vitreous carbon cylinders with a diameter of 1 cm and a length of 3 cm (60 pores/in., Electrosynthesis Corp.). The electrode compartments were separated by vycor frits (7-mm diameter, 1-mm thick).

Syntheses. The following chemicals were purchased from commercial suppliers and used without further purification: vinylmagnesium bromide, tris(2-chloroethyl)amine hydrochloride, diethylphosphine, 2,2′-azobis(2-methylproprionitrile) (AIBN), and phosphorus trichloride. Trivinylphosphine,[10] lithium diethylphosphide,[23] and $[Ni(CH_3CN)_6](BF_4)_2$[24] were prepared by literature methods.

Tris[2-(diethylphosphino)ethyl]phosphine, PP_3E. Trivinylphosphine (3.9 g, 35 mmol), diethylphosphine (10 g, 110 mmol), and AIBN (100 mg) were dissolved in THF (25 mL) and irradiated for 18 h in a Rayonet reactor containing 254 and 350 nm wavelength bulbs. The solvent and volatile materials were removed *in vacuo* to produce a clear viscous oil (approximately 85% yield). $^{31}P\{^1H\}$ NMR (toluene-d_8): AB_3 pattern, P_A, 17.2 ppm; P_B, 17.7 ppm; $^3J_{AB}$ = 19 Hz. ^1H NMR (toluene-d_8): PCH_2CH_2P, 1.47 ppm (m); PCH_2CH_3, 1.24 ppm (q, $^3J_{HH}$ = 7 Hz); PCH_2CH_3, 0.99 ppm (dt, $^3J_{PH}$ = 14 Hz).

Tris[2-(diethylphosphino)ethyl]amine, NP_3E. A solution of tris(2-chloroethyl)amine (3.55 g, 0.017 mol) in THF (30 mL) was added via canula to a cold (−80 °C) solution of lithium diethylphosphide (5.0 g, 0.052 mol) in THF (50 mL). *Caution! Lithium diethylphosphide is pyrophoric.* This yellow solution was warmed to room temperature and stirred for 1 h. Degassed water (0.5 mL) was added to the reaction mixture, and the solvent was removed in vacuo to produce a mixture of a white solid in a clear oil. Hexane (100 mL) was added to this mixture, and the resulting suspension was filtered. A clear oil was obtained (3.75 g, 60%) from the filtrate by removing the solvent in vacuo at room temperature. $^{31}P\{^1H\}$ NMR (toluene-d_8): Et_2P, 24.0 ppm (s). ^1H NMR (toluene-d_8): NCH_2CH_2P, 2.67 ppm (m); NCH_2CH_2P, 1.54 ppm (m); PCH_2CH_3, 1.28 (q, $^3J_{HH}$ = 7.5 Hz); PCH_2CH_3, 1.02 (dt, $^3J_{PH}$ = 14 Hz).

$[Ni(PP_3E)(CH_3CN)](BF_4)_2$. This complex was prepared in a manner analogous to that described for $[Ni(PP_3)(CH_3CN)](BF_4)_2$.[13] ^{31}P NMR (acetone-d_6): P_C, 149.9 ppm (q, $^2J_{PP}$ = 28 Hz); P_T, 56.8 ppm (d). ^1H NMR (acetone-d_6): CH_3CN, 2.64 ppm (q, $^5J_{PH}$ = 3 Hz); CH_2CH_3 and PCH_2CH_2P, 2.2−2.6 ppm (m's); CH_2CH_3, 1.28 ppm (m).

$[Ni(PP_3)(CO)](BPh_4)_2$. Carbon monoxide was bubbled through a dichloromethane solution (25 mL) containing $[Ni(PP_3)(CH_3CN)](BF_4)_2$ (0.20 g, 0.215 mmol) for 15 min. The color of the solution changed from deep purple to red-orange. The reaction vessel was sealed, and the reaction mixture was stirred overnight at room temperature. Absolute ethanol (20 mL) was added to the reaction mixture, and then the volume of the resulting solution was reduced to approximately 20 mL under a stream of CO. A yellow-orange precipitate formed upon adding a solution of $NaBPh_4$ (0.64 g) in ethanol (4.0 mL). The precipitate was collected by filtration and washed with 2 aliquots of ethanol (10 mL each) and 2 aliquots of diethyl ether (10 mL each). The resulting orange solid (0.21 g, 71%) was dried in vacuo for 1.5 h. A satisfactory elemental analysis was not obtained for this compound because of the loss of CO. ^{31}P NMR (acetone-d_6): P_C, 179.6 ppm (q, $^2J_{PP}$ = 22 Hz); P_T, 64.4 ppm (d). ^1H NMR (acetone-d_6): Ph, 6.6−7.6 ppm (m's); PCH_2CH_2P, 2.8−3.4 ppm (m's). ν(CO) = 2067 cm^{-1} (dichloromethane solution). The ^{13}CO-labeled analogue can be prepared in a similar manner. ^{31}P NMR (acetone-d_6): P_C, 179.6 ppm (dq, $^2J_{PC}$ = 72 Hz); P_T, 64.4 ppm (dd, $^2J_{PC}$ = 19 Hz). ^{13}C NMR (acetone-d_6): CO, 200.5 ppm (dq). $\nu(^{13}CO)$ = 2016 cm^{-1} (dichloromethane solution).

$[Ni(PP_3E)(CO)](BPh_4)_2$ and $[Ni(PP_3E)(CO)](BF_4)_2$. These compounds can be prepared in a manner analogous to that described in the preceding paragraph by either including or deleting metathesis with $NaBPh_4$. X-ray-quality crystals of $[Ni(PP_3E)(CO)](BF_4)_2$ were grown by dissolving $[Ni(PP_3E)(CH_3CN)](BF_4)_2$ (0.050 g) in dichloromethane (2.0 mL) in a small test tube capped with a septum. The solution was placed under 1 atm CO for 0.5 h, and then ethanol (3 mL) was added. The volume of the resulting solution was reduced by approximately one-half in a stream of CO. Clusters of orange crystals grew over a 2-week period. The crystals were isolated by decanting the solvent, washing the crystals with a small amount of ethanol, and drying them under a stream of nitrogen. Anal. Calcd for $C_{19}H_{42}B_2F_8NiP_4O$: C, 35.51; H, 6.59. Found: C, 35.83; H, 6.62. ^{31}P NMR (acetone-d_6): P_C, 175.6 ppm (q, $^2J_{PP}$ = 25 Hz), P_T, 75.1 ppm (d). ν(CO) = 2052 cm^{-1} (dichloromethane).

$[Ni(NP_3E)(CO)](BF_4)_2$. Acetone (30 mL) was added to a Schlenk flask containing a mixture of $[Ni(CH_3CN)_6](BF_4)_2 \cdot 0.5CH_3CN$ (0.25 g, 0.5 mmol) and NP_3E (0.18 g, 0.5 mmol). The resulting reaction mixture was stirred for 1 h to form a deep purple solution. CO (60 mL) was added via syringe to the sealed flask, and the solution was stirred overnight. Ethanol (30 mL) was added to the resulting red

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solution, and then the volume of the solution was reduced to approximately 30 mL by applying a vacuum. CO was bubbled through the solution until a red solid precipitated. The solid (0.10 g) was collected by filtration and dried in vacuo for 1 h. A second fraction was obtained by adding diethyl ether to the filtrate (0.12 g, 70% total yield). Anal. Calcd for $C_{19}H_{42}B_2F_8N_1NiP_3O$: C, 36.47; H, 6.77; N, 2.24; P, 14.86. Found: C, 36.03; H, 6.68; N, 2.16; P, 15.07. ^{31}P NMR (acetone-d_6): P_T, 59.8 ppm (s). ^{1}H NMR (acetone-d_6): NCH_2CH_2P, 3.1 ppm (m), NCH_2CH_2P, 2.65 ppm (m); PCH_2CH_3, 2.47 ppm (m); PCH_2CH_3, 1.30 ppm (m). $\nu(CO) = 2050\ cm^{-1}$ (dichloromethane). $[Ni(NP_3E)(^{13}CO)](BF_4)_2$ can be prepared in a similar manner using ^{13}CO. ^{13}C NMR (acetone-d_6): CO, 187.9 ppm (q, $^2J_{PC} =$ 26 Hz). $\nu(^{13}CO) = 2002\ cm^{-1}$.

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Supporting Information Available: Tables 1s−3s, containing crystal data, data collection conditions, and solution and refinement details for $[Ni(PP_3E)(CO)](BF_4)_2$, Tables 4s−8s, giving atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic parameters, and Table 9s, listing parameters used in extended Hückel calculations (14 pages). Ordering information is given on any current masthead page.

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