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Journal of Organometallic Chemistry 679 (2003) 65–71

Journal of Organometallic Chemistry

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# (Fluoroalkyl)phosphine complexes of nickel(0) and cobalt(I)

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Received 15 May 2003; received in revised form 29 May 2003; accepted 29 May 2003

**Abstract**

The synthesis of a series of (fluoroalkyl)phosphine complexes of nickel is reported. Treatment of $(cod)_2Ni$ with dfepe (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) yields (dfepe)Ni(cod) (**1**), which has been structurally characterized. Treatment of **1** with CO or bipy results in the formation of $(dfepe)Ni(CO)_2$ (**2**) and (dfepe)Ni(bipy) (**3**), respectively. Addition of excess dfepe to **1** results in incomplete cod displacement to form $(dfepe)_2Ni$ (**4**). The homoleptic complex **4** may be independently prepared in high yield by reduction of $(acac)_2Ni$ with $(^iBu)_3Al$ in the presence of butadiene and excess dfepe. Solvation of (dfepe)Ni(cod) in acetonitrile gives a new complex tentatively identified as $(dfepe)Ni(MeCN)_2$ (**6**), whereas dissolution of $(dfepe)_2Ni$ in acetonitrile leads to a mixture of **6** and the partial displacement product (dfepe)($\eta^1$-dfepe)Ni(MeCN) (**5**). In contrast to $(R_3P)_4Ni(0)$ phosphine and phosphite complexes, which undergo protonation by strong anhydrous acids such as HCl, $H_2SO_4$ and $CF_3CO_2H$ to give $(R_3P)_4Ni(H)^+$ products, Treatment of $(dfepe)_2Ni$ with neat $CF_3CO_2H$ or excess HOTf in dichloromethane gave no spectroscopic evidence for $(dfepe)_2Ni(H)^+$. Exposure for extended periods leads to dfepe loss and decomposition to Ni(II) products. The synthesis of the first cobalt complex of dfepe, $(dfepe)Co(CO)_2H$, is also reported.

*Keywords:* Nickel; Phosphine; Carbonyl; Organometallic; Hydride

## 1. Introduction

A wide range of nickel(0) phosphine derivatives $(R_3P)_nNi(CO)_{4-n}$ have been prepared which provide useful benchmark standards for phosphine steric and electronic properties [1], and also serve as catalysts and catalyst precursors for many useful coupling processes [2,3]. Similarly, the parent tetracarbonyl $(CO)_4Co(H)$ and its phosphine substitution products $(R_3P)_n(CO)_{4-n}Co(H)$ have found extensive use as catalysts for hydroformylation and other transformations, and thus also constitute an important class of compounds for fundamental and applied studies. In our previous investigations of fundamental (fluoroalkyl)phosphine coordination chemistry, we have defined the electronic and steric effects of the perfluoroethyl chelate $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ ('dfepe') relative to other phosphines in a number of metal systems, including $(dfepe)M(CO)_4$ (M = Cr, Mo, W) [4], $(dfepe)Ru(CO)_3$ [5], and $(dfepe)Ir(CO)_2H$ [6]. The latter two systems serve as useful models for monomeric late transition metal carbonyl complexes. Due to the recent interest in electrophilic Group 10 metal chemistry, we have also been developing the (fluoroalkyl)phosphine chemistry of the nickel triad [7]. Here we report the synthesis of several nickel(0) complexes of dfepe, as well as the structural characterization of (dfepe)Ni(cod). Comparisons of structural and spectroscopic properties with known phosphine systems lend further insight into the bonding properties of $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$. We also report herein the synthesis of the related fluoroalkylphosphine cobalt hydride complex $(dfepe)(CO)_2Co(H)$.

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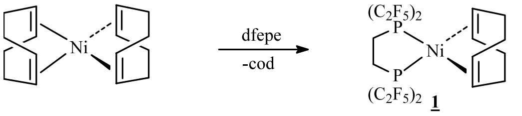
doi:10.1016/S0022-328X(03)00511-4

## 2. Results and discussion

### 2.1. Synthesis and crystal structure of (dfepe)Ni(cod) (1)

(cod)$_2$Ni serves as a convenient precursor to a wide range of Ni(0) complexes [8]. While no reaction was observed between (cod)$_2$Ni and the bis(perfluoroethyl)arylphosphine (C$_2$F$_5$)$_2$PPh [9], treatment of (cod)$_2$Ni with chelating dfepe in toluene at ambient temperature afforded (dfepe)Ni(cod) (**1**) in high yield as a crystalline yellow air-stable solid (Eq. (1)). The presence of a symmetrically-coordinated η$^4$-1,5-cyclooctadiene ligand in **1** was confirmed by $^1$H-NMR, which shows only one vinylic resonance at $\delta$ 4.74 (br. s), shifted downfield from the vinylic resonance for (cod)$_2$Ni at $\delta$ 4.29, which integrates 1:1 with the dfepe backbone multiplet at $\delta$ 1.63.



(1)

Metal–olefin complex bond length data often provide a relative measure of dπ→π* backbonding for related systems. Accordingly, the crystal structure of **1** has been determined to provide comparison with other (cod)Ni(0) complexes. Data collection parameters and selected bond length and angle data are summarized in Tables 1 and 2. As shown in Fig. 1, (dfepe)Ni(cod) adopts a pseudo-tetrahedral geometry distorted by chelate restrictions, with inter-ligand angles of 90.2° (P(1)–Ni–P(2)), 89.7° (C$_1$–Ni–C$_2$), 120.4 (C$_1$–Ni–P(1)), 120.5 (C$_1$–Ni–P(2)), 119.2 (C$_2$–Ni–P(1)), and 120.0 (C$_2$–Ni–P(2)), where C$_1$ and C$_2$ are the center points of the C(11)–C(12) and C(15)–C(16) olefinic bonds, respectively. Overall the molecule has essentially C$_2$ symmetry along an axis which bisects the dfepe chelate backbone and runs through nickel and the center of the cyclooctadiene ligand, which adopts a typical twist–boat conformation. The average C=C and Ni–C bond distances observed for **1** are 1.365 and 2.152 Å, respectively. These values differ significantly from values reported for the nitrogen-donor complex (bipy)Ni(cod) (C=C(ave): 1.382 Å, Ni–C(ave): 2.052 Å) [10] and are consistent with the anticipated reduced backbonding for the (dfepe)Ni moiety relative to (bipy)Ni. Although the C=C values for **1** fall within the general reported range for (cod)Ni(0) complexes (1.35–1.39 Å) [10–15], the metal–cod distance for **1** is the largest yet reported and may reflect a combination of steric repulsion between the cyclooctadiene and dfepe ligands and reduced Ni–cod π interactions (Table 3). The observed Ni–P bond distances (2.104(1), 2.103(1) Å) are 0.06 Å shorter than the average metal–phosphine bond distance reported for other Ni(0) complexes and are in accord with bond shortening generally observed for dfepe complexes [7].

Table 1
Crystallographic data for (dfepe)Ni(cod) (**1**)

| | |
|---|---|
| Chemical formula | $C_{18}H_{16}F_{20}NiP_2$ |
| Formula weight | 732.96 |
| Crystal system | Monoclinic |
| Color | Yellow |
| Space group | $P2_1/c$ (No. 14) |
| Size (mm) | 0.29 × 0.32 × 0.42 |
| $a$ (Å) | 14.145(3) |
| $b$ (Å) | 10.358(2) |
| $c$ (Å) | 16.856(3) |
| $\beta$ (°) | 90.37(3) |
| $V$ (Å$^3$) | 2469.6(8) |
| $Z$ | 4 |
| $T$ (°C) | −100 |
| $\lambda$ (Å) | 0.71073 |
| $D_{calc}$ (g cm$^{-3}$) | 1.971 |
| $\mu$ (cm$^{-1}$) | 19.71 |
| *Data collection* | |
| Scan method | Omega |
| Scan limits (°) | 4.6–50 |
| Data collected ($h$, $k$, $l$) | ±16, +12, +20 |
| Reflections collected | 4500 |
| Independent reflections | 4338 |
| Observed reflections | 3281 ($I_0 > 2\sigma(I_0)$) |
| *Refinement* [a] | |
| $R_1(F)$, % | 3.87 |
| $R_1(wF)$, % | 8.91 |
| GOF | 1.045 |
| $\Delta/\sigma$(max) | 0.001 |
| $\Delta(\rho)$, e Å$^{-3}$ | 0.366, −0.465 |

[a] $R_1 = \Sigma(|F^{o}| - |F_c|)/\Sigma|F^{o}|$.

### 2.2. Ligand displacement reactions of (dfepe)Ni(cod)

A brief survey of ligand substitution chemistry for (dfepe)Ni(cod) was undertaken (Scheme 1). Only ~50% displacement of cod was noted by $^1$H-NMR after warming **1** to 80 °C in the presence of excess dfepe (~10 equivalent) for 6 h. No significant cod displacement was observed in the presence of 1 atm tetrafluoroethylene. Attempts to sequester cyclooctadiene in the presence of excess dfepe by the addition of 1 atm H$_2$, excess LiBEt$_3$H, or HBF$_4$(Me$_2$O) were also unsuccessful. Treatment of **1** with 1 atm CO, however, resulted in an immediate bleaching of yellow **1** and formation of the colorless dicarbonyl (dfepe)Ni(CO)$_2$ (**2**). Removal of volatiles gave **2** as an oil contaminated with free cod. Carbonyl bands for **2** of roughly equal intensity appear at 2081 and 2038 cm$^{-1}$, values which are lower than those reported for (F$_3$P)$_2$Ni(CO)$_2$ (2101, 2064 cm$^{-1}$) and [(CF$_3$)$_2$PCH$_2$CH$_2$P(CF$_3$)$_2$]Ni(CO)$_2$ (2092, 2060 cm$^{-1}$) [16], but significantly higher than $\nu$(CO) data reported for [(PhO)$_3$P]$_2$Ni(CO)$_2$ (2043, 1996 cm$^{-1}$) [17], (Ph$_3$P)$_2$Ni(CO)$_2$ (1997, 1936 cm$^{-1}$) [18], and (Cy$_3$P)$_2$Ni(CO)$_2$ (1980, 1912 cm$^{-1}$) [19].

Table 2
Bond lengths (Å) and angles (°) for (dfepe)Ni(cod) (**1**)

| *Bond length* | |
|---|---|
| Ni–P(1) | 2.104(1) |
| Ni–P(2) | 2.103(1) |
| Ni–C(11) | 2.159(4) |
| Ni–C(12) | 2.147(4) |
| Ni–C(15) | 2.165(4) |
| Ni–C(16) | 2.143(4) |
| Ni–$C_1$ | 2.039 |
| Ni–$C_2$ | 2.043 |
| P(1)–C(1) | 1.854(4) |
| P(1)–C(3) | 1.910(4) |
| P(1)–C(5) | 1.923(4) |
| P(2)–C(2) | 1.864(4) |
| P(2)–C(7) | 1.909(4) |
| P(2)–C(9) | 1.914(4) |
| C(11)–C(12) | 1.364(6) |
| C(12)–C(13) | 1.520(6) |
| C(13)–C(14) | 1.535(6) |
| C(14)–C(15) | 1.514(5) |
| C(15)–C(16) | 1.366(5) |
| *Bond angles* | |
| P(1)–Ni–P(2) | 90.14(4) |
| C(11)–Ni–C(16) | 84.2(2) |
| C(12)–Ni–C(15) | 83.9(2) |
| $C_1$–Ni–$C_2$ | 89.7 |
| P(1)–Ni–$C_1$ | 120.4 |
| P(1)–Ni–$C_2$ | 119.2 |
| P(2)–Ni–$C_1$ | 120.5 |
| P(2)–Ni–$C_2$ | 120.0 |

$C_1$ = midpoint of C(11)–C(12); $C_2$ = midpoint of C(15)–C(16).

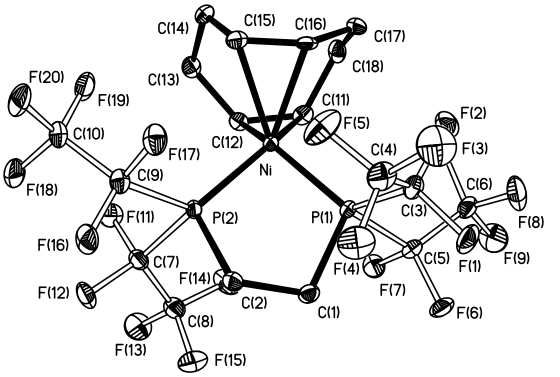


Fig. 1. Molecular structure of (dfepe)Pt(cod) (**1**) with atom labeling scheme (30% probability ellipsoids).

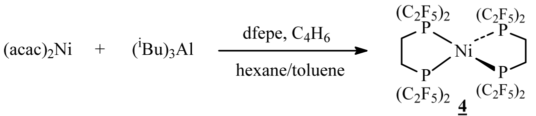
Table 3
Structural comparison of $L_nNi(\eta^4\text{-}1,5\text{-cyclooctadiene})$ complexes

| Complex | C=C (ave), Å | Ni–C (ave), Å | Reference |
|---|---|---|---|
| (dfepe)Ni(cod) | 1.365 | 2.152 | This paper |
| (bipy)Ni(cod) | 1.382 | 2.052 | [10] |
| $(\eta^5\text{-}2,3,5\text{-}C_3B_3R_6)Ni(cod)^+$ | 1.363 | 2.105 | [11] |
| $(cod)_2Ni$ | 1.39 | 2.12 | [12] |
| $(MeO_2CCH{=}CHSO_2Ph)Ni(cod)$ | 1.351 | 2.115 | [13] |
| $(\eta^4\text{-}C_4Ph_4Al(Et_2O))Ni(cod)$ | 1.374 | 2.11 | [14] |
| (PhC≡CPh)Ni(cod) | 1.356 | 2.096 | [15] |

Prior studies have suggested that $(bipy)Pt(R_3P)_2$ complexes are stable provided that the phosphine is a π-acceptor phosphine or a phosphite [20]. Accordingly, cyclooctadiene displacement from **1** is observed in the presence of excess 2,2′-bipyridine, affording dark violet (dfepe)Ni(bipy) (**3**). The visible maximum for **3** occurs at 562 nm (ε = 7700), which is at higher energy than maxima observed for (bipy)(cod)Ni ($\lambda_{max}$ = 578 nm; ε = 6500) and $(bipy)_2Ni$ ($\lambda_{max}$ = 624 nm; ε = 3900), consistent with the effect of reduced metal dπ electron density on this presumed dπ → π* MLCT transition.

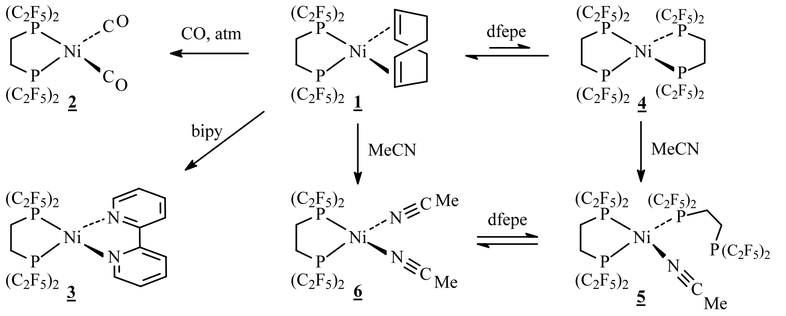
### 2.3. Synthesis of $(dfepe)_2Ni$ (4)

Direct reaction of $(cod)_2Ni$ with dfepe resulted in incomplete substitution; therefore, an alternative synthetic route was required to cleanly produce $(dfepe)_2Ni$. Following Schunn's synthetic procedure for the preparation of $(cod)_2Ni$ [21], $(dfepe)_2Ni$ (**4**) was obtained in high yield as a white solid from the reduction of $Ni(acac)_2$ with $(^iBu)_3Al$ in the presence of butadiene and excess dfepe (Eq. (2)). The role of butadiene is apparently to stabilize metal reduction intermediates. No isolable product was obtained from an identical synthetic procedure using $(C_2F_5)_2PPh$ as the trapping phosphine ligand. Complex **4** exhibits a single phosphorus resonance at 64.1 ppm with unresolved $^2J_{PF}$ fine structure. A single $^{19}F$ trifluoromethyl resonance observed at −77.5 ppm is consistent with the equivalence of the two dfepe ligands.



(2)

Solvation properties of (dfepe)Ni(cod) (**1**) and $(dfepe)_2Ni$ (**4**) in acetonitrile have also been examined (Scheme 1). Dissolution of **4** in $CD_3CN$ gave a bright yellow solution which exhibited $^{31}P$-NMR resonances at 58.8 and 55.0 ppm (2:1 ratio), 35.4, 9.6 (free dfepe) and a shoulder at ~11 ppm. We tentatively assign the resonances at δ 58.8, 55.0 and 11 to the partially solvated complex $(dfepe)(\eta^1\text{-dfepe})Ni(CD_3CN)$ (**5**), and the δ 35.2 resonance to the bis-solvate $(dfepe)Ni(CD_3CN)_2$ (**6**). The identity of complex **6** is supported by the solvation behavior of **1**: upon dissolution in $CD_3CN$, a golden yellow solution was obtained which $^{31}P$-NMR indicated to be a mixture of unreacted **1** at δ 69.6 (20%) and a single species at δ 35.4 (80%) assigned as **6**. No change in this ratio was observed after 24 h. The formulation of **6** as the cod displacement



Scheme 1.

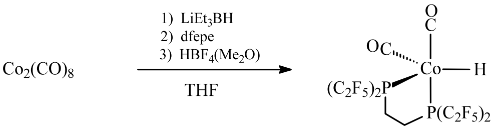
product was confirmed by $^1$H-NMR, which displayed resonances due to free cod and a new dfepe backbone multiplet at $\delta$ 1.79. These data are consistent with a competitive coordination of cod and acetonitrile under neat solvent conditions. In the case of **4**, the presence of an additional equivalent of dfepe results in an equilibrium between the partially displaced chelate product **5** and **6**.

### 2.4. (dfepe)$_2$Ni protonation studies

The protonation of $(R_3P)_4Ni(0)$ phosphine and phosphite complexes by strong anhydrous acids such as HCl, $H_2SO_4$ and $CF_3CO_2H$ to give $(R_3P)_4Ni(H)^+$ products has been reported [22]. Cationic nickel phosphine hydride complexes are involved in a variety of catalytic processes. For instance, $[(RO)_3P]_3NiH^+$, generated *in situ* from $[(RO)_3P]_4Ni$ and methanolic HCl, is a highly active olefin isomerization catalyst, albeit with limited stability [23]. We have previously reported that (dfepe)$_2$Pd is a catalyst for ethylene dimerization in trifluoroacetic acid, presumably via the intermediacy of active (dfepe)Pd(H)(X)$^+$ species [24]. Thus, we were interested in the acid–base properties of (dfepe)$_2$Ni and sought evidence for the formation of (dfepe)$_2$Ni(H)$^+$ or (dfepe)Ni(H)(X)$^+$. $^{31}$P- and $^1$H-NMR spectra of (dfepe)$_2$Ni in neat trifluoroacetic acid at ambient temperature showed no evidence for protonation to form (dfepe)$_2$Ni(H)$^+$ at ambient temperatures. No color change or evolution of hydrogen was observed. After several days, however, the $^{31}$P resonance for (dfepe)$_2$Ni at 62.9 ppm was completely replaced by that of the unbound dfepe ligand at 6.5 ppm. Addition of 1–10 equivalents triflic acid to dichloromethane solutions of **4** similarly did not produce (dfepe)$_2$Ni(H)$^+$. In neat triflic acid, a white precipitate was initially observed which dissolved within 20 min to form a yellow solution displaying free dfepe (80%) as well as two minor dfepe-containing nickel products at 50.0 ppm (6%) and 43.1 ppm (14%). The observations in trifluoroacetic acid are consistent with an unfavorable protonation pre-equilibrium followed by irreversible dfepe loss (Scheme 2). In the case of the stronger acid HOTf, the initial precipitate is likely the protonation product [(dfepe)$_2$Ni(H)]$^+$OTf$^-$ which is also unstable with respect to dfepe loss. These observations are in accord with our unsuccessful efforts to prepare stable (dfepe)Ni(II) compounds [25], and suggest that nickel(II) centers provide insufficient π-backbonding to stabilize dfepe coordination.

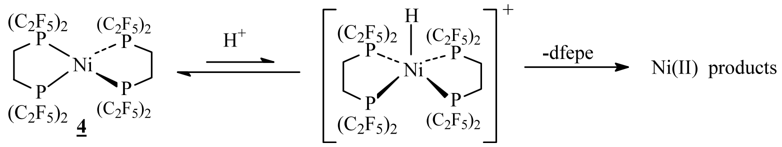
### 2.5. Synthesis of (dfepe)(CO)$_2$Co(H) (7)

The dicarbonyl complex (dfepe)(CO)$_2$Co(H) was prepared by treatment of the $(CO)_4Co^-$ anion, formed in situ by reduction of $Co_2(CO)_8$ with $LiEt_3BH$ [26], with dfepe followed by acidification with $HBF_4(Me_2O)$ (Eq. (3)). Removal of volatiles, extraction of the residues by hexanes and cooling the filtrate afforded yellow solid (dfepe)(CO)$_2$Co(H) (**7**), which melted at ambient temperature. $^1$H-NMR spectra in benzene-$d_6$ of this oil showed a clean spectrum with a dfepe backbone resonance at $\delta$ 1.77 and a hydride triplet at $\delta$ −10.88 ($^2J_{PH} = 16$ Hz). IR spectra of the neat oil showed two $\nu$(CO) bands at 2061 and 2017 cm$^{-1}$, at significantly higher energy than the CO modes reported for $(Ph_3P)_2Co(CO)_2H$ (1990 and 1920 cm$^{-1}$) [27]. An IR band assignable to the hydride ligand was not identified. Benzene solutions of **7** are stable at ambient temperatures, but as a neat oil this complex began to darken and decompose after several hours.



(3)

In summary, prototypical examples of low-valent late-transition metal complexes incorporating the dfepe ligand have been prepared. These systems serve as sterically-encumbered analogues of $(CO)_4Ni$ and $(CO)_4Co(H)$, and thus provide the starting point for future reactivity studies which explore the comparative reactivity and possible catalytic behavior of these new systems.



Scheme 2.

## 3. Experimental

### 3.1. General procedures

All manipulations were conducted under an atmosphere of nitrogen using Schlenk, high vacuum line, and/ or glovebox techniques. Dry, oxygen-free solvents were vacuum-distilled prior to use. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on a Mattson Cygnus 100, Perkin–Elmer 1600, or Bomem MB100 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were obtained with a JEOL JMN-FX270 or GSX-400 instrument. $^{19}$F spectra were referenced to $CF_3CO_2Et$ as an internal standard (−75.32 ppm vs. $CFCl_3$ with downfield chemical shifts taken to be positive). $^{31}$P spectra were referenced to a 85% $H_3PO_4$ external standard. UV–vis spectra were taken as benzene solutions under nitrogen at ambient temperature on a Perkin–Elmer Lambda 9 instrument. $(cod)_2Ni$ was prepared following published procedures [21].

### 3.2. (dfepe)Ni(cod) (*1*)

To a solution of $(cod)_2Ni$ (0.100 g, 0.363 mmol) in 30 mL toluene at ambient temperature was added dfepe (0.450 g (0.23 ml), 0.795 mmol) via syringe. After stirring the reaction mixture for 24 h, the toluene was removed and 20 ml of methanol was added. The resulting slurry was filtered and dried under vacuum, affording 0.212 g (80%) of crystalline yellow **1**. Anal. Calc. for $C_{18}H_{16}F_{20}NiP_2$: C, 29.50; H, 2.20. Found: C, 29.50; H, 1.96%. IR (Nujol, $cm^{-1}$): 1300 (s), 1209 (s), 1125 (m), 1105 (m), 1082 (m), 956 (s), 745 (w). $^1$H-NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ 4.74 (br. s, 4H; vinylic cod protons), 2.22 and 1.89 (m, 8H; aliphatic cod protons), 1.63 (m, 4H; $PCH_2$). $^{31}$P-NMR (161.7 MHz, $C_6D_6$, 25 °C): $\delta$ 68.5 (m).

### 3.3. $(dfepe)_2Ni$ (*4*)

$Ni(acac)_2$ (0.500 g, 1.95 mmol) was suspended in 15 ml of hexane/toluene (1:1) and excess dfepe (5.250 g, 9.27 mmol) was added via syringe. The reaction mixture was cooled to −78 °C and butadiene (1.35 ml, 4.04 mmol) was added by vacuum transfer. 1.48 ml of $Al(^iBu)_3$ was then added via syringe and the reaction mixture was slowly warmed to ambient temperature. Over a period of 24 h a white solid precipitated from the yellow solution. The volatiles were then removed and ca. 15 ml of petroleum ether was added to the residue. Trituration yielded a white solid, which was filtered off and washed with two 5 ml portions of petroleum ether. The isolated yield of **4** was 2.110 g (82%). Anal. Calc. for $C_{20}H_8F_{40}NiP_4$: C, 20.17; H, 0.67. Found: C, 20.33; H, 0.50%. IR (Nujol, $cm^{-1}$): 1430 (w), 1306 (s), 1296 (sh), 1210 (vs), 1134 (s), 1117 (sh), 1096 (s), 974 (m), 957 (s), 874 (m), 828 (m), 748 (s). $^1$H-NMR (270 MHz, $C_6D_6$, 25 °C): $\delta$ 1.82 (m, $PCH_2$). $^{31}$P-NMR (161.7 MHz, $C_6D_6$, 25 °C): $\delta$ 64.1 (m). $^{19}$F-NMR (376.5 MHz, $C_6D_6$, 27 °C): $\delta$ −77.5 (s, $CF_3$), −104.6 (m, $CF_2$).

### 3.4. Reaction of (dfepe)Ni(cod) with CO

A 5 mm NMR tube was charged with 10 mg of **1** and 0.5 ml $C_6D_6$ under nitrogen. The head space of the NMR tube was flushed several times with CO via syringe and the NMR tube was shaken to aid gas mixing. Upon initial contact with CO, the yellow solution became colorless. NMR spectra at this time revealed free cyclooctadiene and resonances attributable to $(dfepe)Ni(CO)_2$ (**2**). Removal of volatiles gave a colorless oil consisting of the dicarbonyl and free cod. Spectral data for **2**: IR (neat oil, $cm^{-1}$): 2081 (s), 2038 (s), 1305 (s), 1210 (vs), 1125 (s), 962 (m). $^1$H-NMR (400 MHz, $C_6D_6$, 27 °C): $\delta$ 1.67 (m, $PCH_2$). $^{31}$P-NMR (161.7 MHz, $C_6D_6$, 27 °C): $\delta$ 71.5 (m). $^{19}$F-NMR (376.5 MHz, $C_6D_6$, 27 °C): $\delta$ −78.0 (s, $CF_3$), −110.5 (m, $CF_2$).

### 3.5. (dfepe)Ni(2,2′-bpy) (*3*)

To a 50-ml flask charged with 68.5 mg (dfepe)Ni(cod) (0.0935 mmol) was added 25 ml of diethyl ether and 15.6 mg of 2,2′-bipyridine (0.0993 mmol) at −78 °C. After slow warming, the reaction mixture was allowed to stir at ambient temperature. The reaction mixture was sampled and reaction progress was evaluated by $^{31}$P-NMR at 12 h intervals. After 24 h two additional equivalents of bipyridine were added, and the reaction was deemed complete after a total of 72 h had elapsed. Ether was removed and 10 ml of dichloromethane was added to the dark residue. Cooling to −78 °C and filtering afforded 44 mg (60%) of dark violet (**3**). Anal. Calc. for $C_{20}H_{12}F_{20}N_2NiP_2$: C, 30.76; H, 1.55. Found: C, 30.78; H, 1.35%. IR (benzene, $cm^{-1}$): 1467 (m), 1441 (m), 1271 (sh), 1308 (m), 1292 (s), 1271 (m), 1213 (vs), 1121(s), 1102 (s), 1075 (m), 948 (s). $^1$H-NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ 8.77 (d, $^3J_{HH} = 5.4$ Hz, 2H; bipy H(3)), 6.87 (d, $^3J_{HH} = 8.0$ Hz, 2H; bipy H(6)), 6.76 (dd, $^3J_{HH} =$ 8.0, 7.2 Hz, 2H; bipy H(5)), 6.42 (dd, $^3J_{HH} = 7.2$, 5.4 Hz, 2H; bipy H(4)), 1.97 (m, 4H; $PCH_2$). $^{31}$P-NMR (161.7 MHz, $C_6D_6$, 25 °C): $\delta$ 39.5 (m). $^{19}$F-NMR (376.5 MHz, $C_6D_6$, 25 °C): $\delta$ −78.5 (s, $CF_3$), −109.5 (m, $CF_2$). UV–vis (benzene): $\lambda_{max} = 562$ nm ($\varepsilon = 7700$).

### 3.6. (dfepe)$Co(CO)_2(H)$ (**6**)

To a stirred solution of 0.480 g (0.00140 mmol) $Co_2(CO)_8$ in ca. 20 ml THF was added 3.50 ml of 1.0 M $LiBEt_3H$ in THF (0.0035 mmol). Initially orange, the solution became dark red-purple. After 4 h the volatiles were removed, giving a purple oily solid. IR of this crude material confirmed the presence of $Co(CO)_4^-$. The mixture was redissolved in 20 ml THF and 0.50 g (0.0028 mmol) dfepe was added, whereupon the solution became red. After 12 h the solvent was removed and the red–brown residue was triturated with hexanes and a green–gray solid was obtained which was washed with hexanes. IR of this material (Nujol) showed $\nu$(CO) bands due to unreacted $(CO)_4Co^-$ as well as two new strong bands at 1890 and 1815 cm$^{-1}$ which are tentatively assigned to (dfepe)$(CO)_2Co^-$. This solid was taken up in hexanes, 0.093 g (0.00069 mmol) $HBF_4(Me_2O)$ was added, and the solution was filtered. Concentration of the filtrate and cooling to −78 °C afforded a yellow solid which melted upon warming. Complex **5** may be stored indefinitely at −30 °C, but decomposes slowly at ambient temperatures. IR (neat oil, cm$^{-1}$): 2061 (s), 2017 (vs), 1417 (w), 1306 (s), 1218 (vs), 1128 (s), 967 (s), 874 (w), 805 (m), 749 (m). $^1$H-NMR (270 MHz, $C_6D_6$, 27 °C): $\delta$ 1.77 (m, 4H; $PCH_2$), −10.88 ($^2J_{PH} = 16$ Hz, 1H; Co(H)). $^{31}$P-NMR (161.7 MHz, $C_6D_6$, 27 °C): $\delta$ 119.8 (m). $^{19}$F-NMR (376.5 MHz, $C_6D_6$, 27 °C): $\delta$ −77.7 (s, $CF_3$), −111.7 (m, $CF_2$).

### 3.7. Crystal structure of (dfepe)Ni(cod) (**1**)

X-ray data were collected at −100 °C on a Siemens P4 automated diffractometer system using Mo–$K_\alpha$ radiation. Crystal, data collection and refinement parameters are summarized in Table 1. All computations used the SHELXTL/IRIS (version 5.04) program library (Siemens Corp., Madison, WI) [28]. A suitable crystal of **1** was grown from a warm methanol solution. Monoclinic unit cell dimensions were derived from a least-squares fit of 39 random reflections ($19° < 2\theta < 30°$). Data were collected using the omega scan technique with a variable scan rate of 4.2–30.0° min$^{-1}$. Three standard reflections monitored after every 100 data collected showed no systematic variation; the residual for averaging 162 redundant data was 3.28%. Data were not corrected for absorption. $P2_1/c$ space group symmetry was deduced from a statistical analysis of all collected data.

The structure of **1** was solved using the SHELXTL Direct Methods program; all non-hydrogen atoms were located on a series of difference Fourier maps. After all non-hydrogen atoms were refined anisotropically, a difference map revealed hydrogen atom positions, which were added to the model and were refined with fixed isotropic thermal parameters set at 1.2 times the isotropic equivalent of the attached carbon atom. Full-matrix least-squares refinement gave an $R$ value of 3.87% ($R_w = 8.91\%$) for 3281 data with $I > 2\sigma(I)$. The final difference Fourier map showed residual peaks of 0.37 and −0.47 e Å$^{-3}$.

## 4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 210468 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

This work has been supported by the National Science Foundation (Grants CHE-9615985 and CHE-0093049).

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