Insertion Reactions of (Benzyne)nickel(0) Complexes with Carbon Monoxide: X-ray Structure of a (Phthalato)nickel(II) Complex Formed by Oxidation of an η^1:η^1-Phthaloyl Intermediate

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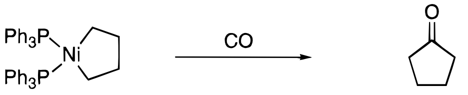
Received September 5, 1995⊗

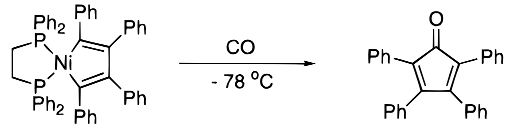
The reaction of (benzyne)nickel(0) complexes $Ni(\eta^2-C_6H_4)(dcpe)$ (**1**) and Ni((1,2-η)-4,5-$F_2C_6H_2$)(dcpe) (**2**) [dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$] with carbon monoxide at low concentration gives $Ni(CO)_2(dcpe)$ (**3**) and, as the main organic products, 9*H*-fluoren-9-one (**4**) and 2,3,6,7-tetrafluoro-9*H*-fluoren-9-one (**5**), 2,3,6,7-$X_4C_{12}H_4$-CO (X = H, F), respectively, resulting from monoinsertion into the nickel−benzyne bond. Higher concentrations of CO give rise to bis(acyl) intermediates, one of which, Ni(CO-4,5-$F_2C_6H_2$CO-2)(dcpe) (**9**), has been observed by ^{31}P and ^{19}F NMR spectroscopy. These intermediates reversibly form **3** and the corresponding benzocyclobutenediones OC-4,5-$X_2C_6H_2$CO [X = H (**12**), F (**13**)] by reductive elimination and react readily with oxygen to form the stable (phthalato)nickel(II) complexes $Ni(OCOC_6H_4COO$-2)(dcpe) (**6**) and Ni(OCO-4,5-$F_2C_6H_2COO$-2)(dcpe) (**7**). On treatment with iodine, the latter give the corresponding phthalic anhydrides $C_6H_4C_2O_3$ (**10**) and 4,5-$F_2C_6H_2C_2O_3$ (**11**), respectively. According to a single-crystal X-ray study, **7** is a planar nickel(II) complex containing a seven-membered chelate ring with monodentate carboxylato groups, the average Ni−O and Ni−P distances being 1.904(4) and 2.152(2) Å, respectively.

Introduction

The insertion of carbon monoxide into nickel−carbon σ-bonds to form nickel acyls is a key step in many organic reactions catalyzed or promoted by $Ni(CO)_4$.[1,2] Acylnickel(II) complexes $NiY(COR)L_2$ have been isolated by carbonylation of mono(alkyl)nickel(II) complexes $NiY(R)L_2$ (R = σ-alkyl; Y = various monoanionic ligands; L = various tertiary phosphines).[3] In contrast, carbonylation of bis(alkyls) NiR_2L_2 gives $Ni(CO)_2L_2$ and organic carbonyl compounds as a result of successive mono- or diinsertions and subsequent reductive eliminations. For example, $NiMe_2L_2$ gives 2,3-butanedione and acetone in proportions that depend on the temperature, pressure of CO, and the nature of L.[4] Similarly, nickelacycles react with CO to give cyclic ketones (eqs 1 and 2).[5,6]



(1)



(2)

Since nickel−carbon σ-bonded species are likely to be intermediates in the $Ni(CO)_4$-catalyzed formation of α,β-unsaturated acids from alkynes, CO, and H_2O,[1,2,7] the isolation of intermediates from the reaction of CO with nickel−alkyne complexes has attracted interest. The complexes Ni(η^2-alkyne)(bipy) (alkyne = PhC_2H, PhC_2Ph, MeC_2Me; bipy = 2,2′-bipyridine) undergo double insertion of CO to give bis(acyl)nickel(II) complexes, which reversibly eliminate the corresponding cyclobutenediones or form the corresponding anhydrides by reaction with oxygen (Scheme 1).[8−10]

The bonds in (benzyne)- and (naphthalyne)nickel(0) complexes probably have considerable nickel−carbon

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⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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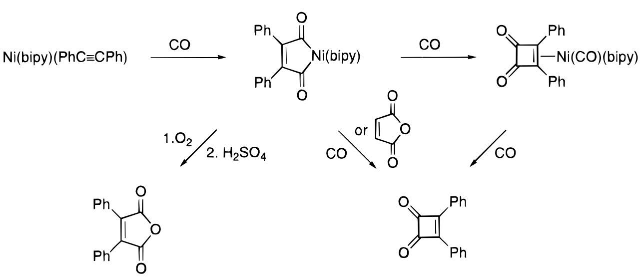
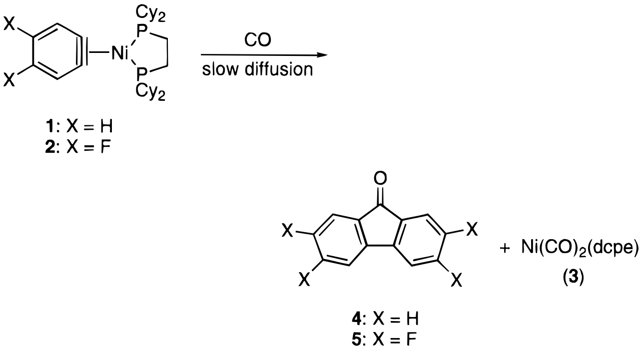
Scheme 1



Scheme 2



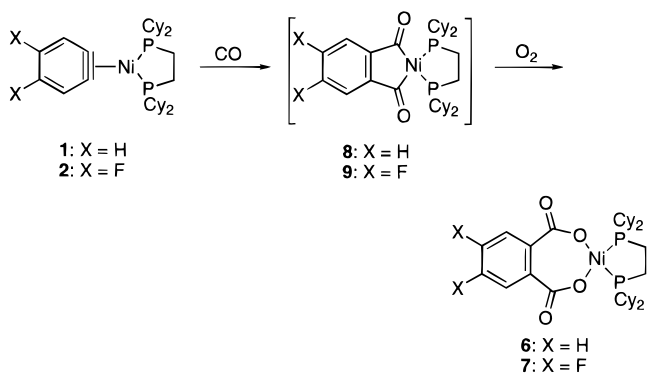
σ-bond character, and these molecules readily undergo insertion of small molecules into the nickel-aryne bond.[11-13] For example, Ni(η^2-C_6H_4)(dcpe) (**1**) [dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$] reacts with CO_2 or C_2H_4 to give the five-membered ring metallacycles $\overline{\mathrm{Ni(C_6H_4COO}}\mathrm{\text{-}2)(dcpe)}$ or $\overline{\mathrm{Ni(C_6H_4CH_2CH_2}}\mathrm{\text{-}2)(dcpe)}$, respectively.[11] Insertions of **1** with alkynes proceed via similar metallacycles, but these react readily with a second molecule of the alkyne to form, after reductive elimination, a substituted naphthalene.[12]

We therefore expected that **1** and its η^2-4,5-difluorobenzyne analogue Ni((1,2-η)-4,5-$F_2C_6H_2$)(dcpe) (**2**) would react readily with CO, and we describe here the results of this study.

Results

The reactions of **1** and **2** with CO are very dependent on the concentration of CO. Gas uptake measurements showed that 2.5 mol/mol of complex were absorbed when CO was allowed to diffuse slowly into a dilute (0.05–0.15 M) solution of **1** in toluene. As the ^{31}P NMR signals of **1** and **2** at δ 78.9 and 79.4, respectively, decreased in intensity, a new species appeared having a singlet at δ 63.9 in the ^{31}P NMR spectrum and strong bands at 1980 and 1920 cm^{-1} in the IR spectrum. This was identified as Ni$(CO)_2$(dcpe) (**3**), which was prepared for comparison by treatment of Ni(η^2-C_2H_4)(dcpe) with CO. Complex **3** was removed by decomposition with HCl, and the organic products, extracted into hexane, were identified as 9*H*-fluoren-9-one (**4**) and 2,3,6,7-tetrafluoro-9*H*-fluoren-9-one (**5**), respectively (Scheme 2). The latter was formed in *ca.* 90% yield as estimated from the ^{19}F NMR spectrum of the reaction mixture, which showed a pair of five-line multiplets at δ −126.7 and −135.9. A small amount of a compound having a triplet at δ −123.3 in C_6D_6, probably 4,5-difluorophthalic anhydride, was also present (see below).

Scheme 3



When CO was added more rapidly to the (benzyne)nickel(0) solutions, e.g. by first evacuating and then refilling with CO, the fluorenones were still formed, but other compounds were also present. When the concentration of CO was increased further, e.g. by bubbling CO through the solution, no fluorenones were observed. The reaction of **2** under these conditions showed, in addition to **3**, signals in the $^{31}P\{^1H\}$ and ^{19}F NMR spectra at δ 58.9 and at δ −132.2 (triplet, J_{FH} = 9 Hz), respectively, suggesting the formation of a symmetrical complex. This species was highly air-sensitive and could not be isolated. In the presence of traces of air, a stable yellow solid precipitated, which was identified as the phthalato complex $\overline{\mathrm{Ni(OCOC_6H_2X_2COO}}\mathrm{)(dcpe)}$ (X = F) (**7**) (Scheme 3). The analogue **6** (X = H) was obtained similarly from **1**. Complexes **6** and **7** show a singlet in their $^{31}P\{^1H\}$ NMR spectra at δ 77.8 and 78.7, respectively, and **7** has a triplet at δ −137.8 (J_{FH} = 9 Hz) in its ^{19}F NMR spectrum. The $^{13}C\{^1H\}$ NMR spectra contain a signal for the carboxylate carbon at δ 174.2 for **6** and δ 171.8 for **7**, in agreement with the proposed structures. The IR spectra display typical strong C=O stretching bands at 1635 cm^{-1} (**6**) and 1637 cm^{-1} (**7**); *cf.* 1636 and 1622 cm^{-1} for $\overline{\mathrm{Ni(C_6H_4COO}}\mathrm{\text{-}2)(dcpe)}$.[11] The structure of **7** has been confirmed by X-ray analysis (see below).

The symmetrical intermediate that forms **7** in the presence of air is assumed to be the bis(acyl)nickel(II) complex **9**. The reaction of CO with **1** probably generates the corresponding intermediate **8**, but this was not observed directly. Similar bis(acyls) have been isolated from the reaction of Ni(η^2-alkyne)(bipy) with CO, and their reaction with oxygen to give, after treatment with H_2SO_4, a substituted maleic anhydride has been noted (Scheme 1).[8]

At an early stage of this work, it was thought that the isolated carboxylato complexes **6** and **7** were bis(acyls), and in an attempt to confirm this, they were treated with iodine in dichloromethane or methanol in the expectation of isolating phthalic acid or dimethyl phthalate. The organic products formed were phthalic anhydride (**10**) and 4,5-difluorophthalic anhydride (**11**), respectively, presumably resulting from cleavage of the Ni−O bonds of **6** and **7** by traces of HI and dehydration

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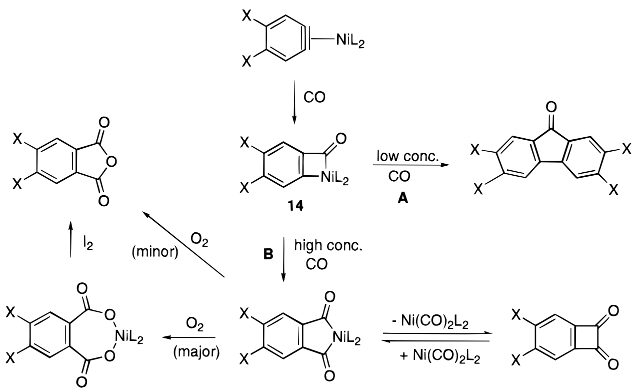
Scheme 4



of the resulting phthalic acid.[14] Small amounts of **11** were also formed during the reaction of intermediate **9** with air.

A second product detected together with **7** when CO was either bubbled through or applied at 25 bar to solutions of **2** showed a ^{19}F NMR triplet in C_6D_6 at δ -120.7 (J = 6.4 Hz). This species and its analogue obtained similarly from **1** show strong C═O stretching bands in their IR spectra at 1805 and 1780 cm^{-1} and are thought to be 4,5-difluorobenzocyclobutene-1,2-dione (**13**) and benzocyclobutene-1,2-dione (**12**), respectively; the values reported for the latter are 1808 and 1779 cm^{-1}.[15] However, these compounds could not be separated from Ni(CO)$_2$(dcpe), because they decomposed both on addition of HCl and on attempted chromatography on silica gel. The proposal is, however, supported by the observation that cyclobutenedione is formed reversibly by reductive elimination from the bis(acyl) complex $\overline{\text{Ni(COCR=CRCO}}$)(bipy) (R = Me, Ph) on treatment with CO (Scheme 1).[8−10]

During the reaction of the bis(acyl) intermediate **9** with oxygen to form the phthalato complex **7**, the ^{19}F NMR signal assigned to 4,5-difluorobenzocyclobutene-1,2-dione (**13**) also disappeared; hence, the formation of **13** also seems to be reversible.

Discussion

Scheme 4 provides a summary and rationalization of the observations. Initially, one molecule of carbon monoxide inserts into the nickel−benzyne bond to form a highly reactive monoacyl (**14**) containing a four-membered ring. A species of this type has been proposed as the first product of carbonylation of Ni(CO)$_3$(η^2-alkyne) in the Ni(CO)$_4$-catalyzed hydrocarbonylation of alkynes,[1,2,7] and a platinum analogue, $\overline{\text{Pt\{C(O)C(Ph)=C}}$(Ph)}(PPh$_3$)$_2$, has been isolated from the reaction of Pt(PPh$_3$)$_4$ or Pt(PPh$_3$)$_2$(*trans*-stilbene) with diphenylcyclopropenone.[16,17] If the concentration of CO is low, **14** reacts with another molecule of the benzyne complex to form, after reductive elimination, the corresponding fluorenone and Ni(CO)$_2$(dcpe) (pathway A). This process is represented by eq 3, which accounts for the observed

$$2Ni(C_6H_2X_2)(dcpe) + 5CO \rightarrow 2Ni(CO)_2(dcpe) + C_6H_2X_2COC_6H_2X_2 \quad (3)$$

$$X = H, F$$

gas uptake under these conditions. A similar process is thought to account for the formation of 9,10-bis(trifluoromethyl)-2,3,6,7-tetrafluorophenanthrene in the reaction of hexafluoro-2-butyne with **2**.[12]

In the presence of an excess of CO, e.g. when bubbled through the solution or applied under pressure, a second molecule of CO rapidly reacts with the monoacyl **14** to form the corresponding bis(acyl) complex, which has been detected in the case of **9** (pathway B). The bis(acyls) readily absorb oxygen to give the stable phthalato complexes **6** and **7** and traces of the phthalic anhydride. Aerial oxidation of monoacyls NiY(COR)L$_2$ has been reported to give paramagnetic monocarboxylato complexes NiY(OCOR)L$_n$, which have not been structurally characterized.[4] The bis(acyl) intermediate can also reductively eliminate benzocyclobutenedione, with formation of Ni(CO)$_2$(dcpe) (**3**); this reaction is probably induced by an excess of CO. The elimination is reversible; as the bis(acyl) is consumed by oxidation, it is re-formed by addition of benzocyclobutenedione to **3**. This type of addition has precedent. Reaction of 3,4-diphenylcyclobutenedione with Ni(bipy)(COD) at 100 °C in toluene gives the corresponding bis(acyl).[8] Cyclobutenediones or benzocyclobutenediones also add to Pt(PPh$_3$)$_2$ complexes to give bis(acyls), although these products are unsymmetrical and result from the insertion of platinum into one C−CO bond.[16−19] It is interesting that the unsymmetrical bis(acyl) of this type formed from benzocyclobutenedione and Pt(PPh$_3$)$_4$ is also oxidized with oxygen to form a symmetrical dicarboxylato (phthalato)platinum(II) complex similar to **6** and **7**.[16] However, since **9** shows only one resonance in both its ^{31}P and ^{19}F NMR spectra, an unsymmetrical structure can be ruled out.

Bis(carboxylato) complexes cannot be formed by double insertion of CO$_2$ into nickel−aryne bonds of **1** or Ni(2,3-η-C$_{10}$H$_6$)(dcpe); only the monoinsertion products $\overline{\text{Ni(C}_6\text{H}_4\text{COO}}$-2)(dcpe) and $\overline{\text{Ni(2-C}_{10}\text{H}_6\text{COO}}$-3)(dcpe) are observed.[11,13]

Crystal Structure of $\overline{\textbf{Ni(OCO-4,5-F}_2\textbf{C}_6\textbf{H}_2\textbf{COO}}$-2)-(dcpe) (7). The molecular geometry of $\overline{\text{Ni(OCO-4,5-F}_2\text{C}_6\text{H}_2\text{COO}}$-2)(dcpe) (**7**) is shown in Figure 1. Atomic coordinates, selected interatomic distances and angles, and experimental details are given in Tables 1−3, respectively.

The coordination geometry is close to square planar; the nickel atom lies 0.042 Å from the least-squares plane defined by the coordinated oxygen atoms (O1 and O3)

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[14] A reviewer has suggested that these products are formed by reductive elimination after one-electron oxidation of nickel; *cf.* the formation of 4,4-dimethyl-3,4-dihydrocoumarin by iodination of the oxanickelacycle $\overline{\text{Ni(CH}_2\text{CMe}_2\text{C}_6\text{H}_4\text{O}}$)(phen) (Koo, K.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 456). This seems to us unlikely, because reductive elimination after iodine oxidation of **6** and **7** would initially form energy-rich compounds such as the peroxides C$_6$H$_2$X$_2$COO−OCOC$_6$H$_2$X$_2$ or C$_6$H$_2$X$_2$COOI.

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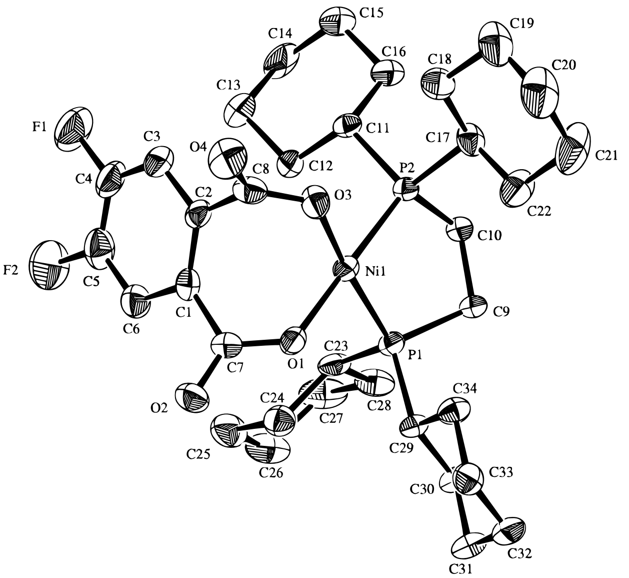

Figure 1. ORTEP diagram for $Ni(OCO\text{-}4,5\text{-}F_2C_6H_2COO\text{-}2)(dcpe)$ (7) with atom labeling and with 50% probability ellipsoids.

and the phosphorus atoms. The seven-membered ring has a boat-shaped conformation similar to that in $Ni(CH_2CMe_2C_6H_4COO)(PMe_3)_2$ (**15**).[20,21] The planes defined by Ni−O1−O3 and by C7−C1−C2−C8 form angles of 52 and 46°, respectively, with the plane defined by O3−C8−C7−O1. The average Ni−O distance of 1.904(4) Å is very similar to the distances of 1.900 and 1.877 Å found in the monocarboxylato complex $Ni(3\text{-}C_{10}H_6COO\text{-}2)(dcpe)$ (**16**)[13] and in **15**,[20,21] respectively. The Ni−P distances of **7**, 2.155(2) and 2.149(2) Å, are also similar to the Ni−P distance *trans* to the carboxylate group in **16** of 2.144(2) Å. These values are lower than typical Ni−P distances *trans* to σ-bonded carbon atoms of about 2.20 Å, which is consistent with the expected low *trans* influence of the oxygen donors.

Experimental Section

General Procedures. All experiments were performed under an inert atmosphere with use of standard Schlenk techniques, and all solvents were dried and degassed prior to use. All reactions involving benzyne complexes were carried out under argon. NMR spectra were recorded on a Varian XL-200E (^{1}H at 200 MHz, ^{13}C at 50.3 MHz, ^{19}F at 188.1 MHz, and ^{31}P at 80.96 MHz), a Varian Gemini-300 BB (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, and ^{31}P at 121.4 MHz), or a Varian VXR-300 instrument (^{1}H at 300 MHz and ^{13}C at 75.4 MHz). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvent and to external 85% H_3PO_4 for ^{31}P. The spectra of all nuclei (except ^{1}H and ^{19}F) were ^{1}H decoupled. The coupling constants (J) are given in Hz. Infrared spectra were measured in solution (KBr cells) or as KBr disks on a Perkin-Elmer 683 or a Perkin-Elmer FTIR 1800 instrument. Mass spectra of the complexes were obtained on a VG ZAB2-SEQ spectrometer by the fast-atom bombardment (FAB) technique. Solutions of the samples were prepared in CH_2Cl_2 and added to a matrix of tetraglyme or 3-nitrobenzyl alcohol. Mass spectra of the organic compounds were obtained by the electron impact (EI) method on a VG ZAB2-SEQ or a VG Micromass 7070F spectrometer. Microanalyses were done in-house.

Starting Materials. The benzyne complexes $Ni(\eta^2\text{-}C_6H_4)(dcpe)$ (**1**) and $Ni((1,2\text{-}\eta)\text{-}4,5\text{-}F_2C_6H_2)(dcpe)$ (**2**) were obtained by reduction of the corresponding (2-bromoaryl)nickel(II) bromides with lithium in ether.[11,12]

Preparation of $Ni(CO)_2(dcpe)$ (3). $Ni(\eta^2\text{-}C_2H_4)(dcpe)$[11] (80 mg, 0.16 mmol) in THF (10 mL) was exposed to an atmosphere of carbon monoxide. After the solution was stirred for 4 h at room temperature, the $^{31}P\{^1H\}$ NMR spectrum indicated that the reaction was complete. The solvent was removed by evaporation, and the residue was extracted with hexane. Evaporation of hexane gave **3** as a colorless solid (83 mg, 99%). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 23.0 (t, $J_{CP} = 20$), 26.7 (s), 27.5 (s), 28.5 (s), 29.3 (s, CH_2), 35.6 (t, $J_{CP} = 8$, CH), 204.9 (t, $J_{CP} = 4$, CO). $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 63.9. IR (KBr): 2930 (s), 2860 (s), 1980 (s, ν(CO)), 1915 (s, ν(CO)), 1450 (m), 960 (m) cm^{-1}. FAB-MS (3-nitrobenzyl alcohol, $C_{28}H_{48}NiO_2P_2$): *m/e* 508 (7, M − CO), 480 (47, M − 2CO), 371 (65), 355 (73), 289 (100).

Insertion Reactions with Carbon Monoxide. All the reactions were very dependent on the concentration of CO present in solution and especially on the speed of diffusion of CO into the solution. This parameter is hard to control reproducibly, and reactions for which the conditions seemed identical gave the products in varying proportions. Factors such as stirring speeds, diffusion of CO via a cannula or via a balloon, and evacuating the flask at room temperature or at −30 °C before adding CO appeared to be important. Some representative examples of the reactions carried out are given below.

Reaction of 1 with Carbon Monoxide. Method a. Carbon monoxide was allowed to slowly diffuse into a flask containing a solution of **1** (0.6 g, 0.83 mmol) in toluene (50 mL) via a cannula. The uptake of carbon monoxide (52 mL, 2.5 mol/mol of **1**) was measured at 293 K over a period of 60 min, after which time the $^{31}P\{^1H\}$ NMR spectrum indicated that the reaction was complete. The solvent was removed by evaporation. The $^{31}P\{^1H\}$ NMR signal at δ 63.9 indicated that the major phosphorus-containing product in the residue was $Ni(CO)_2(dcpe)$ (**3**). Several unsymmetrical phosphorus-containing compounds were also present in minor quantities. THF (5 mL) and concentrated hydrochloric acid (2 mL) were added, and the solvent was removed by evaporation. The residues from several experiments were combined. Extraction with hexane and removal of hexane from the extract allowed the isolation of an organic compound which was identified (^{1}H NMR, IR, and EI-MS) as 9*H*-fluoren-9-one (**4**).

Method b. Carbon monoxide (1 bar) was added from a balloon to a solution of **1** in toluene (90 mL), prepared in situ from $NiBr(2\text{-}BrC_6H_4)(dcpe)$ (2.3 g, 2.7 mmol). After 44 h the $^{31}P\{^1H\}$ NMR spectrum indicated that **1** had reacted completely, forming a yellow precipitate. The solution was decanted from the solid, which was dried *in vacuo* and identified as the phthalato complex $Ni(OCOC_6H_4COO\text{-}2)(dcpe)$ (**6**) (0.66 g, 38%), presumably formed by diffusion of air into the flask. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.20−2.00 (m, 40H, CH_2 of C_6H_{11}), 2.20−2.40 (m, 8H, CH_2 and CH of C_6H_{11}), 7.41 (AA′BB′ m, 2H, H^{arom}), 7.60 (AA′BB′ m, 2H, H^{arom}). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 20.7 (t, $J_{CP} = 30.2$), 26.0 (s), 27.0 (t, $J_{CP} = 7$), 27.3 (t, $J_{CP} = 9.8$), 28.6 (s), 29.3 (s, CH_2), 34.2 (t, $J_{CP} = 17$, CH), 128.5 (s, CH^{arom}), 128.8 (s, CH^{arom}), 139.0 (s, $C^{1,2}$), 174.2 (s, CO). $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 77.8 (s). IR (CH_2Cl_2): 2934 (s), 2854 (s), 1635 (s, ν(C=O)), 1448 (m), 1363 (s), 1273 (w). FAB-MS (tetraglyme, $C_{34}H_{52}NiO_4P_2$): *m/e* 645 (57, M + 1), 577 (100).

Reaction of 2 with Carbon Monoxide. Method a. A slight vacuum was applied at room temperature to a flask

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Table 1. Atomic Coordinates for Ni(OCO-4,5-$F_2C_6H_2$COO-2)(dcpe) (7)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ni1	0.19889(4)	0.03590(6)	0.04518(4)	C16	0.0887(3)	0.2851(4)	0.0211(3)
Cl1	0.2465(2)	0.2281(3)	0.7870(1)	C17	0.1196(3)	0.1625(4)	0.1381(3)
P1	0.29126(7)	0.09149(10)	0.04509(7)	C18	0.0528(3)	0.1280(4)	0.1364(3)
P2	0.16207(7)	0.1557(1)	0.06791(7)	C19	0.0208(3)	0.1393(6)	0.1954(3)
F1	0.0543(2)	0.0467(3)	−0.1844(2)	C20	0.0574(4)	0.0984(6)	0.2436(3)
F2	0.1705(2)	0.0002(3)	−0.2199(2)	C21	0.1237(4)	0.1318(6)	0.2466(3)
O1	0.2339(2)	−0.0687(3)	0.0237(2)	C22	0.1571(3)	0.1240(5)	0.1874(3)
O2	0.2567(2)	−0.1568(3)	−0.0469(2)	C23	0.3188(3)	0.1238(4)	−0.0287(3)
O3	0.1179(2)	−0.0129(3)	0.0540(2)	C24	0.3479(3)	0.0519(4)	−0.0624(3)
O4	0.0453(2)	−0.0984(3)	0.0191(2)	C25	0.3635(3)	0.0792(5)	−0.1254(3)
C1	0.1771(3)	−0.0595(4)	−0.0667(3)	C26	0.4059(3)	0.1546(5)	−0.1263(3)
C2	0.1162(3)	−0.0380(4)	−0.0492(3)	C27	0.3775(3)	0.2257(5)	−0.0919(3)
C3	0.0740(3)	−0.0040(4)	−0.0892(3)	C28	0.3620(3)	0.2010(4)	−0.0293(3)
C4	0.0934(4)	0.0099(5)	−0.1452(3)	C29	0.3501(3)	0.0216(4)	0.0774(2)
C5	0.1531(4)	−0.0120(5)	−0.1630(3)	C30	0.4155(3)	0.0607(4)	0.0860(3)
C6	0.1946(3)	−0.0487(4)	−0.1252(3)	C31	0.4612(3)	−0.0021(4)	0.1109(3)
C7	0.2258(3)	−0.0987(4)	−0.0273(3)	C32	0.4378(3)	−0.0382(4)	0.1680(3)
C8	0.0911(3)	−0.0525(4)	0.0124(3)	C33	0.3730(3)	−0.0770(4)	0.1597(3)
C9	0.2881(3)	0.1844(4)	0.0901(2)	C34	0.3259(3)	−0.0148(4)	0.1351(3)
C10	0.2268(3)	0.2311(4)	0.0753(3)	C35	0.3102(5)	0.2142(8)	0.7398(4)
C11	0.1100(3)	0.1954(4)	0.0102(3)	C36	0.3107(6)	0.1476(6)	0.7077(5)
C12	0.1416(3)	0.1867(4)	−0.0497(3)	C37	0.3602(8)	0.1369(7)	0.6713(5)
C13	0.0968(3)	0.2172(4)	−0.0983(3)	C38	0.4089(7)	0.194(1)	0.6692(6)
C14	0.0784(3)	0.3059(5)	−0.0861(3)	C39	0.4074(9)	0.259(1)	0.7038(7)
C15	0.0458(3)	0.3153(5)	−0.0271(3)	C40	0.3575(9)	0.2710(7)	0.7406(5)

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Ni(OCO-4,5-$F_2C_6H_2$COO-2)(dcpe) (7)

Bond Distances			
Ni−P1	2.155(2)	Ni−P2	2.149(2)
Ni1−O1	1.907(4)	Ni−O3	1.901(4)
F1−C4	1.359(7)	F2−C5	1.368(7)
O1−C7	1.274(7)	O2−C7	1.229(7)
O3−C8	1.278(7)	O4−C8	1.232(7)
C1−C2	1.396(8)	C1−C6	1.398(8)
C1−C7	1.510(8)	C2−C3	1.393(8)
C2−C8	1.524(8)	C3−C4	1.361(9)
C4−C5	1.378(9)	C5−C6	1.368(9)
Bond Angles			
P1−Ni−P2	87.50(7)	P1−Ni−O1	90.8(1)
P1−Ni−O3	174.0(1)	P2−Ni−O1	178.1(1)
P2−Ni−O3	91.0(1)	O1−Ni−O3	90.7(2)
Ni−O1−C7	121.3(4)	Ni−O3−C8	122.0(4)
O1−C7−O2	123.6(6)	O1−C7−C1	118.6(5)
O2−C7−C1	117.8(6)	O3−C8−O4	123.9(6)
O3−C8−C2	117.1(6)	O4−C8−C2	118.9(6)

Table 3. Crystal and Structure Refinement Data for Ni(OCO-4,5-$F_2C_6H_2$COO-2)(dcpe) (7)

(a) Crystal Data	
chem formula	$C_{34}H_{50}F_2NiO_4P_2 \cdot C_6H_5Cl$
fw	794.98
cryst syst	orthorhombic
unit cell dimens	
a (Å)	21.214(4)
b (Å)	16.131(5)
c (Å)	22.869(3)
V (Å^3)	7825(2)
space group	*Pbca* (No. 61)
D_c (g cm$^{-3)}$	1.349
Z	8
F(000)	3368
color, habit	yellow, prism
cryst dimens	0.10 × 0.14 × 0.12
μ (cm$^{-1)}$	25.16 (Cu Kα)
(b) Data Collection and Processing	
diffractometer	Rigaku AFC6R
X-radiation	Cu Kα (graphite monochromated)
scan mode	$\omega - 2\theta$
ω-scan width	$1.00 + 0.30 \tan \theta$
2θ limits (deg)	120.1
data collcd (*h,k,l*)	(−18,0,0) to (0,24,26)
no. of reflns	
tot	6431
obsd	3271 [$I > 3\sigma(I)$]
abs corr (transm factors)	azimuthal scans (0.884−1.000)
(c) Structure Analysis and Refinement[a]	
structure soln	Patterson methods (PATTY,[23] DIRDIF92[23])
refinement	full-matrix least squares
no. of params	452
weighting scheme	$w = 4F_o^2/[\sigma^2(F_o^2) + (0.007F_o^2)^2]$
R(obsd data) (%)	5.0
R_w (obsd data) (%)	4.7

[a] All calculations were performed by use of teXsan[24] with neutral atom scattering factors from Cromer and Waber,[25] Δf and $\Delta f'$ values from ref 26, and mass attenuation coefficients from ref 27. Anomalous dispersion effects were included in F_c.[28]

containing a solution of the benzyne complex **2**, prepared from NiBr(2-Br-4,5-$F_2C_6H_2$)(dcpe) (1.0 g, 1.3 mmol), in toluene (60 mL), which was then exposed to carbon monoxide (1 bar). After being stirred 16 h at room temperature, **2** had reacted completely and the $^{31}P\{^1H\}$ NMR spectrum indicated that the major phosphorus-containing product was $Ni(CO)_2$(dcpe). The solvent was removed by evaporation, and the products were extracted into hexane. The ^{19}F NMR spectrum of the solution showed two multiplets at δ −126.7 and δ −135.9, corresponding to 2,3,6,7-tetrafluoro-9*H*-fluoren-9-one (**5**), and two multiplets at δ −142.0 and δ −148.0 corresponding to 3,3′,4,4′-tetrafluorobiphenyl, formed by decomposition of **2**. The mixture was dissolved in THF (5 mL) and stirred with concentrated HCl (2 mL). Extraction with hexane gave 20 mg of **5** (12% based on nickel(II) precursor). ^1H NMR (200 MHz, CD_2Cl_2): δ 6.20 (dd, 1H, $J_{FH} = 10$, $J_{FH} = 7$, $H^{3,6}$), 6.90 (dd, 1H, $J_{FH} = 10$, $J_{FH} = 7$, $H^{2,7}$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 110.8 (d, $J_{CF} = 20$, CH), 114.4 (d, $J_{CF} = 20$, CH), 128.8 (d, $J_{CF} = 12$, C), 132.3 (d, $J_{CF} = 9$, C), 198.2 (s, CO); signals of CF were not located. ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ −126.7 (5-line m, $J_{FH} = 9$), −135.9 (5-line m, $J_{FH} = 9$). IR (CH_2Cl_2): 2850 (m), 1720 (m, ν(C=O)), 1500 (m) cm^{-1}. EI-MS ($C_{13}H_4F_4O$): *m/e* 252 (100, M), 224 (30, M − CO).

Method b. A vacuum was applied to a flask containing a solution of **2** in toluene (35 mL) that had been prepared from NiBr(2-Br-4,5-$F_2C_6H_2$)(dcpe) (1.0 g, 1.3 mmol), and the solution was then cooled to −30°C. Carbon monoxide (1 atm) was introduced, and the solution was allowed to warm to room temperature and was stirred for 16 h, forming a precipitate. The ^{19}F NMR spectrum in C_6D_6 of the supernatant solution contained signals corresponding to **5** and a signal at δ −123.3 due to 4,5-difluorophthalic anhydride (**11**), whereas the ^{31}P NMR spectrum showed the presence of **3**. The solid was washed with hexane and was identified as the phthalato complex $Ni(OCO\text{-}4,5\text{-}F_2C_6H_2COO\text{-}2)$(dcpe) (**7**), presumably formed from air in the reaction flask. Crystals suitable for X-ray analysis were grown from chlorobenzene. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.10−2.00 (m, 40H, CH_2 of C_6H_{11}), 2.10−2.20 (m, 4H, CH_2), 2.30−2.40 (m, 4H, CH of C_6H_{11}), 7.42 (t, 2H, $J_{FH} = 9$, H^{arom}). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 20.6 (t, $J_{CP} = 20$), 26.0 (t), 26.9−27.3 (m), 28.7 (s), 30.5 (s, CH_2), 34.3 (t, $J_{CP} = 11$, CH), 117.8 (t, $J_{HF} = 9$, C^{3,6}-H), 136.4 (s, C^{1,2}), 150.3 (dd, $J_{CF} = 249$, $J_{CF} = 14$, C^{4,5}-F), 171.8 (s, CO). ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ −137.8 (t, $J_{FH} = 9$). ^{31}P{^{1}H} NMR (80.96 MHz, CD_2Cl_2): δ 78.7 (s). IR (CH_2Cl_2): 2935 (s), 2856 (s), 1637 (s, ν(C═O)), 1504 (m) 1448 (m), 1368 (s), 1277 (w). FAB-MS (tetraglyme, $C_{34}H_{50}F_2NiO_4P_2$): *m/e* 681 (60, M + 1), 455 (100). Anal. Calcd for $C_{34}H_{50}F_2NiO_4P_2$: C, 59.9; H, 7.4. Found: C, 59.3; H, 7.7.

Method c. Under vigorous stirring, 150 mL of a toluene solution of **2**, prepared from NiBr(2-Br-4,5-$F_2C_6H_2$)(dcpe) (3.0 g, 4 mmol), was treated with carbon monoxide introduced from a balloon. After the mixture was stirred overnight, the ^{19}F NMR spectrum (C_6D_6) contained peaks at δ −126.7 and δ −135.9 due to 2,3,6,7-tetrafluoro-9*H*-fluoren-9-one (**5**), a very small peak at δ −123.3 due to 4,5-difluorophthalic anhydride (**11**) [lit. δ −123.7 in acetone-d^6],[22] a triplet at δ −120.7 ($J = 6.4$) which was attributed to 4,5-difluorobenzocyclobutenedione (**13**), and a peak at δ −137.8 due to the phthalato complex **7**. Another intense triplet at δ −132.2 ($J = 9$), corresponding to a ^{31}P NMR signal at δ 58.9 was assumed to be due to the bis(acyl) complex $Ni(OC\text{-}4,5\text{-}F_2C_6H_2CO\text{-}o)$(dcpe) (**9**). The proportions of the products changed on further stirring, the peak at δ −132.2 decreasing and that at δ −123.3 increasing in intensity. After 2 days the only components of the product mixture observed in the ^{19}F NMR spectrum were **11** and **5**, and **7** had precipitated. The mixture was decanted, and **7** was recovered in 25% yield.

Method d. A carbon monoxide pressure of 25 bar was applied to a solution of **2** in toluene (150 mL) that had been prepared as in method c. After 5 days, the ^{19}F NMR spectrum of the reaction mixture showed peaks corresponding to the bis(acyl) intermediate **9** and 4,5-difluorobenzocyclobutenedione (**13**). The IR spectrum contained ν(CO) bands at 1803 and 1782 cm^{-1} due to **13**, in addition to the ν(CO) bands of **3**. On exposure to air, the peaks due to **9** and **13** disappeared and only **11** remained, together with the yellow precipitate **7**.

Reaction of Phthalato Complexes 6 and 7 with Iodine. A solution of **7** (0.03 g, 0.05 mmol) in CD_2Cl_2 (0.5 mL) was treated with iodine (0.025 g, 0.1 mmol) at room temperature. The ^{19}F NMR spectrum (CD_2Cl_2) contained a signal at δ −121.2, while the ^{31}P{^{1}H} NMR spectrum contained only a broad peak at δ 82.0, corresponding to NiI_2(dcpe). The mixture was filtered through Celite, and 4,5-difluorophthalic anhydride (**11**) was isolated. ^{19}F NMR (188.1 MHz): CD_2Cl_2), δ −121.2 (t, $J = 6.2$); C_6D_6 δ −123.3 (t, $J = 7.5$); literature value in acetone-d_6, δ −123.7.[22] EI-MS ($C_8H_2F_2O_3$): *m/e* 183 (17, M − 1), 57 (100).

A similar reaction with **1** gave phthalic anhydride (**10**).

X-ray crystallography of $Ni(OCO\text{-}4,5\text{-}F_2C_6H_2COO\text{-}2)$(dcpe) (7). Crystal data and details of data collection, data processing, structure analysis, and structure refinement are in Table 3. The structure of **7** was solved by Patterson methods (PATTY)[23] and was expanded using Fourier techniques (DIRDIF92).[23] All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were included at calculated positions (C−H 0.95 Å) and held fixed. All calculations were performed using the teXsan Structure Analysis Software of Molecular Structure Corp.

Acknowledgment. M.G.H. thanks the ARC for an Australian Research Fellowship, and M.S. gratefully acknowledges the receipt of an RSC Honours Year Scholarship and a National Undergraduate Scholarship.

Supporting Information Available: For structure **7**, a packing diagram, text describing X-ray procedures, and tables of atomic coordinates with isotropic displacement parameters, bond lengths, bond angles, torsion angles, anisotropic displacement parameters, and data collection parameters (27 pages). Ordering information is given on any current masthead page.

OM950699V

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