DALTON

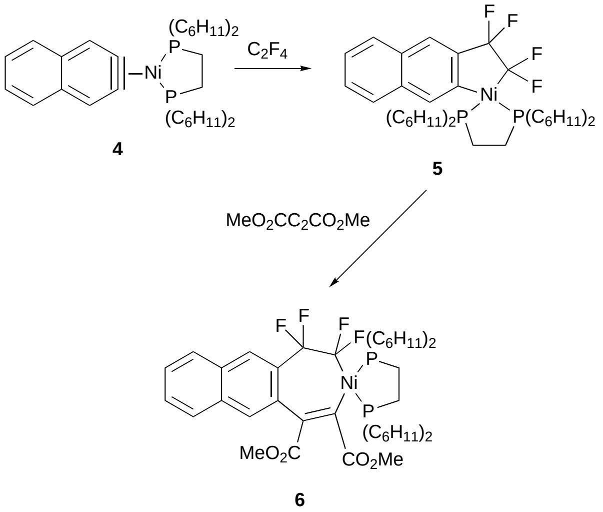
Successive insertion of tetrafluoroethylene and CO and of tetrafluoroethylene and acetylenes into aryne–nickel(0) bonds†

Martin A. Bennett,* Margaret Glewis, David C. R. Hockless and Eric Wenger

Research School of Chemistry, Australian National University, GPO Box 414, Canberra,
A.C.T. 2601, Australia

Aryne–nickel complexes [Ni(η^2-C_6H_4)L_2] [L_2 = 2PEt$_3$ or dcpe; dcpe = $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$] and [Ni($\eta^2$-$C_{10}H_6$)$(PEt_3)_2$] reacted readily with C_2F_4 to form the corresponding five-membered tetrafluoro-substituted nickelacycles [Ni($C_6H_4CF_2CF_2$-2)L_2] (L_2 = dcpe or 2PEt$_3$) and [Ni(2-$C_{10}H_6CF_2CF_2$-3)$(PEt_3)_2$], respectively. The complex [Ni($C_6H_4CF_2CF_2$-2)(dcpe)] is very stable towards air, whereas the PEt$_3$ analogues react readily to give μ-aryloxo dimers. The naphthalene-based dimer [{Ni(μ-2-$OC_{10}H_6CF_2CF_2$-3)(PEt_3)}$_2$] has been structurally characterized. The complexes [Ni($C_6H_4CF_2CF_2$-2)L_2] insert CO into their aryl–nickel bonds to form six-membered acyl complexes [Ni{C(O)$C_6H_4CF_2CF_2$-2}L_2] (L_2 = dcpe or 2PEt$_3$) and, after CO-induced reductive elimination, 2,2,3,3-tetrafluoroindanone. The dcpe acyl complex has also been shown to undergo reaction with air to form the carboxylato complex [Ni{OC(O)$C_6H_4CF_2CF_2$-2}(dcpe)], whose structure has been confirmed by X-ray crystallography. Some insertions of acetylenes into the aryl–nickel bonds of [Ni($C_6H_4CF_2CF_2$-2)L_2] are also reported.

Arynenickel(0) bis(tertiary phosphine) complexes, Ni(η^2-aryne)L_2, which are generated by alkali-metal reduction of the corresponding (2-bromoaryl)nickel(II) halide compounds, react readily with unsaturated molecules.[1–4] For example, the benzyne complexes [Ni(η^2-C_6H_4)L_2] [L_2 = 2PEt$_3$ **1** or dcpe **2**; dcpe = $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$] undergo double insertion with acetylenes to form, after reductive elimination, a substituted naphthalene,[2,4] and the 2,3-didehydronaphthalene complexes [Ni(2,3-η-$C_{10}H_6$)L_2] (L_2 = 2PEt$_3$ **3** or dcpe **4**) similarly give substituted anthracenes.[3] We have shown that tetrafluoroethylene reacts with **4** to form the five-membered tetrafluoro-substituted nickelacycle [Ni(2-$C_{10}H_6CF_2CF_2$-3)(dcpe)] **5**, which in turn undergoes insertion with dimethyl acetylenedicarboxylate under vigorous conditions (50 °C, 16 h) to give the seven-membered ring nickelacycle [Ni{3-C(CO_2Me)=C(CO_2Me)$C_{10}H_6CF_2CF_2$-2}(dcpe)] **6** (Scheme 1). Double insertions of this type seemed to offer a route to novel fluoro-substituted indanones and dihydronaphthalenes. We report here on the reaction of C_2F_4 with **1**–**3** and on the reactions of the resulting tetrafluoronickelaindanes with CO and with acetylenes.

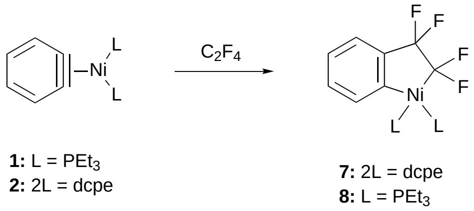


Scheme 1

Results

Insertion of C_2F_4

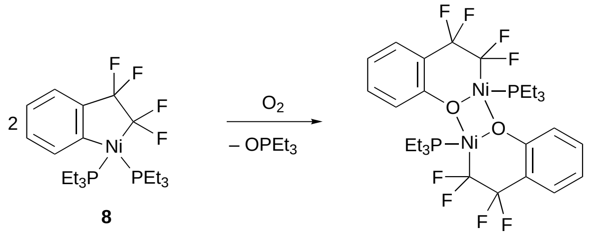
Reaction of the benzynenickel(0) complex [Ni(η^2-C_6H_4)(dcpe)] **2** with C_2F_4 at −20 °C and subsequent warming to room temperature gave the nickelaindane complex [Ni($C_6H_4CF_2CF_2$-2)(dcpe)] **7**, which was isolated in 61% yield as an air-stable, yellow solid (Scheme 2). The ^{19}F NMR spectrum contains a doublet of triplets at δ −103.84 [*J*(FP) 6, *J*(FF) 11 Hz] for the benzylic CF_2 group and a doublet of doublets of triplets at δ −93.35 [*J*(FP) 32, 21, *J*(FF) 11 Hz] corresponding to the CF_2 attached to the nickel. The ^{31}P NMR spectrum shows two signals, a doublet of triplets of triplets at δ 64.47 [*J*(PP) 12, *J*(FP), 32, 5 Hz] and a doublet of triplets at δ 68.38 [*J*(PP) 12, *J*(FP) 21 Hz]. The magnitude of the P−P coupling shows that the phosphorus atoms are mutually *cis*; the more shielded resonance, which shows coupling to both CF_2 groups, probably corresponds to the phosphorus atom *trans* to CF_2. These data are similar to those for [Ni(2-$C_{10}H_6CF_2CF_2$-3)(dcpe)] **5**.[3] In one reaction, the nickelacycle [Ni($CF_2CF_2CF_2CF_2$)(dcpe)] was also isolated as a by-product, possibly arising from the reaction of C_2F_4 with [Ni(dcpe)$_2$] present as an impurity in **2**. Similar products have been obtained from the reaction of C_2F_4 with nickel(0) complexes such as [Ni(η^4-1,5-C_8H_{12})$_2$] and [Ni(PEt$_3$)$_4$].[5]



Scheme 2

---

† In memoriam: Geoff Wilkinson, pioneer of organotransition metal chemistry.



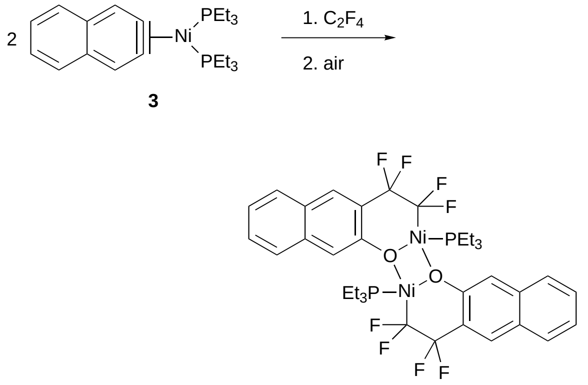
9a (*syn*-isomer)
9b (*anti*-isomer)

Scheme 3

Complex **1** also reacted readily with C_2F_4 to give the corresponding yellow nickelaindane $[\overline{\mathrm{Ni}(C_6H_4CF_2C}F_2\text{-}2)(PEt_3)_2]$ **8** in 83% yield (Scheme 2), which shows ^{19}F NMR signals at δ −105.24 and −94.58 due to the CF_2 groups. The ^{31}P NMR spectrum contains a doublet of triplets of triplets at δ 7.75 [*J*(PP) 22, *J*(FP) 35, 5 Hz] for the phosphorus *trans* to the CF_2 unit and an apparent quartet at δ 11.48 (separation = 23 Hz), indicative of mutually *cis*-PEt_3 ligands. In contrast with its dcpe analogue, complex **8** is very sensitive to traces of air. Under those conditions, two new species, **9a** and **9b**, were formed in almost equal amounts (Scheme 3). They were characterized in their ^{31}P-{^{1}H} NMR spectra by a triplet at δ 28.07 [*J*(FP) 30.5 Hz] and a doublet of doublets at δ 29.12 [*J*(FP) 31, 16 Hz], respectively. The ^{19}F NMR spectrum of **9a** shows only a very broad singlet at δ −98.65, whereas that of **9b** consists of complex signals for each of the four inequivalent fluorines. Although the proportions of **9a** and **9b** did not change when the solution was heated, passage through a silica gel column afforded only **9b**; the quantity recovered suggested that **9a** had isomerized to **9b**, not that it had merely undergone selective decomposition. During the reaction of **8** with air an intermediate having two multiplets at δ 23.0 and 31.3 in its ^{31}P NMR spectrum was detected.

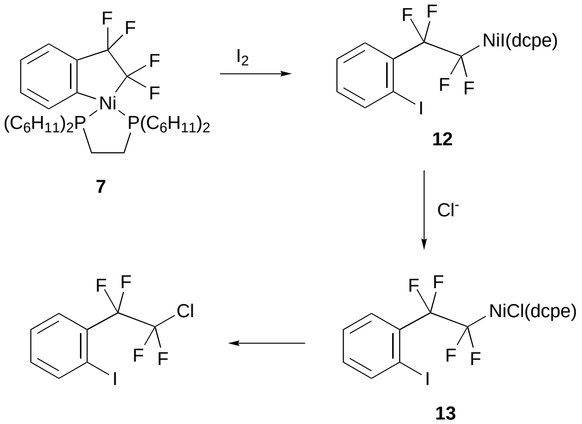
Reaction of the 2,3-didehydronaphthalene complex $[Ni(\eta^2\text{-}C_{10}H_6)(PEt_3)_2]$ **3** with C_2F_4 in the presence of air gave a similar pair of compounds, **10a** and **10b**, which showed in their ^{31}P NMR spectra a triplet at δ 28.23 and a doublet of doublets at δ 29.05, respectively. Compound **10b** was isolated in 51% yield by recrystallization from dichloromethane and was shown by X-ray crystallography (see below) to be the μ-aryloxo dimer $[\{\overline{\mathrm{Ni}(\mu\text{-}2\text{-}OC_{10}H_6CF_2C}F_2\text{-}3)(PEt_3)\}_2]$. This is presumably formed from the initial insertion product $[\overline{\mathrm{Ni}(2\text{-}C_{10}H_6CF_2C}F_2\text{-}3)(PEt_3)_2]$ (analogous to the dcpe compound **5**) by loss of PEt_3, insertion of an oxygen atom into the nickel–aryl bond, and dimerization of the resulting three-co-ordinate $\overline{\mathrm{Ni}(2\text{-}OC_{10}H_6CF_2C}F_2\text{-}3)(PEt_3)$ units (Scheme 4).

The crystal structure of **10b** (see below) shows that the two naphthalene rings are on the same side of the Ni_2O_2 plane, *i.e.* they adopt a *syn* arrangement having a C_2 axis; we assume that in **10a** they are in the alternative centrosymmetric *anti* disposition. The similarity of the ^{31}P NMR parameters strongly suggests that **9a** and **9b** are the corresponding *syn* and *anti* isomers of $[\{\overline{\mathrm{Ni}(\mu\text{-}OC_6H_4CF_2C}F_2\text{-}2)(PEt_3)\}_2]$. Closely related to our observations are the reported reactions of the metallacycle $[\overline{\mathrm{Ni}(C_6H_4CMe_2C}H_2\text{-}2)(PMe_3)_2]$ **11** with formaldehyde[6] and nitrous oxide.[7] In the first case, insertion occurs at the nickel–alkyl, not the nickel–aryl, bond.[6] The dimeric μ-alkoxo product, $[\{\overline{\mathrm{Ni}(C_6H_4CMe_2CH_2O}\text{-}2)(PMe_3)\}_2]$, also exists as two isomers in solution, which were proposed to be *syn* and *anti* isomers arising from the *meso* and *rac* arrangements of the two nickelacycloheptene rings. In the second case, a di-μ-aryloxo-nickel(II) complex $[\{\overline{\mathrm{Ni}(\mu\text{-}OC_6H_4CMe_2C}H_2)(PMe_3)\}_2]$ is formed by transfer of an oxygen atom to the nickel–aryl bond,[7] but apparently only one isomer of this compound was observed.



10a (*syn*-isomer)
10b (*anti*-isomer)

Scheme 4

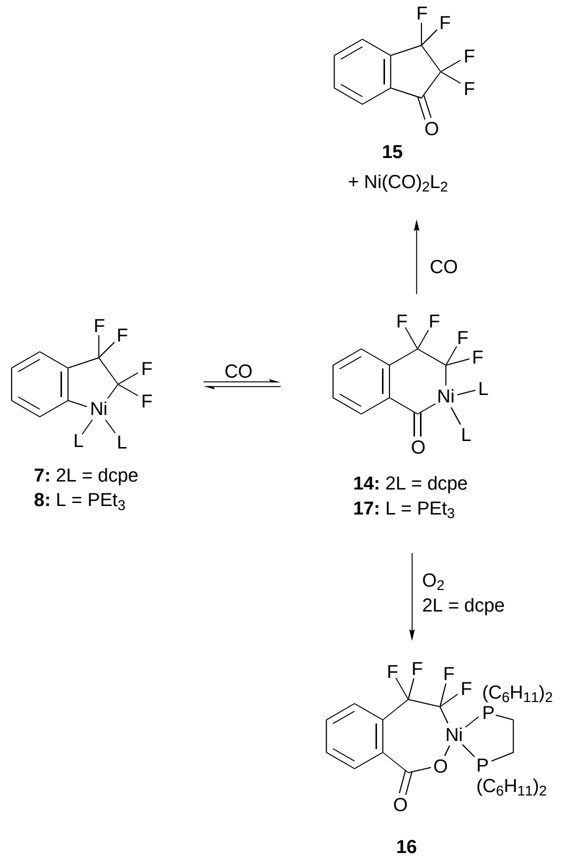


Scheme 5

The nickel–aryl bond of compound **7** is cleaved by iodine to give $[NiI(CF_2CF_2C_6H_4I\text{-}2)(dcpe)]$ **12** (Scheme 5), which was identified tentatively on the basis of its NMR spectroscopic data. The ^{31}P NMR spectrum in CD_2Cl_2 shows two doublets of triplets, at δ 65.5 [*J*(PP) 38, *J*(FP) 27 Hz] (P *trans* to CF_2) and δ 84.6 [*J*(PP) 38, *J*(FP) 27 Hz] (P *trans* to I). The ^{19}F NMR spectrum has a singlet at δ −92.4 and a triplet at δ −76.3 [*J*(FP) 27 Hz], and the fragment $Ni(CF_2CF_2C_6H_4I)(dcpe)$ (*m*/*z* 783) appears in the electron impact (EI) mass spectrum. Complex **12** is not very stable; in $CDCl_3$ the ^{31}P NMR signals broaden and new doublets of triplets appear at δ 63.5 [*J*(PP) 45, *J*(FP) 28 Hz] and 81.1 [*J*(PP) 45, *J*(FP) 23 Hz]. The shift upfield of the phosphorus *trans* to the halogen is consistent with the formation of the corresponding chloro-complex $[NiCl(CF_2CF_2C_6H_4I\text{-}2)(dcpe)]$ **13**. This decomposed on attempted chromatography on silica gel to give an organic species having singlets in its ^{19}F NMR spectrum at δ −99.3 and −56.7. The latter signal is in the range expected for a CF_2X group, indicating that $2\text{-}IC_6H_4CF_2CF_2Cl$ may have been formed, but the reaction was not investigated further.

Reactions with CO

The dcpe complex **7** reacts slowly with CO under atmospheric pressure at 50 °C (Scheme 6). Monitoring by IR and NMR spectroscopy showed the formation of a complex believed to be the chelate acyl $[\overline{\mathrm{Ni}\{C(O)C_6H_4CF_2C}F_2\text{-}2\}(dcpe)]$ **14**, in addition to $[Ni(CO)_2(dcpe)]$. The IR spectrum shows a strong ν(C=O) band at 1615 cm^{-1}, which shifts to 1570 cm^{-1} for the species **14a** generated by use of ^{13}CO, and the ^{13}C NMR spectrum of **14a** contains a doublet of doublets of triplets at δ 256.6 [*J*(CP) 76, 18, *J*(CF) 5.5 Hz], which is assigned to the acyl carbon atom. The IR and chemical shift data are similar to those reported for acylnickel(II) complexes,[8–12] *e.g.* for *trans*-$[NiCl(COPh)(PMe_3)_2]$ the ν(C=O) is at 1600 cm^{-1} and

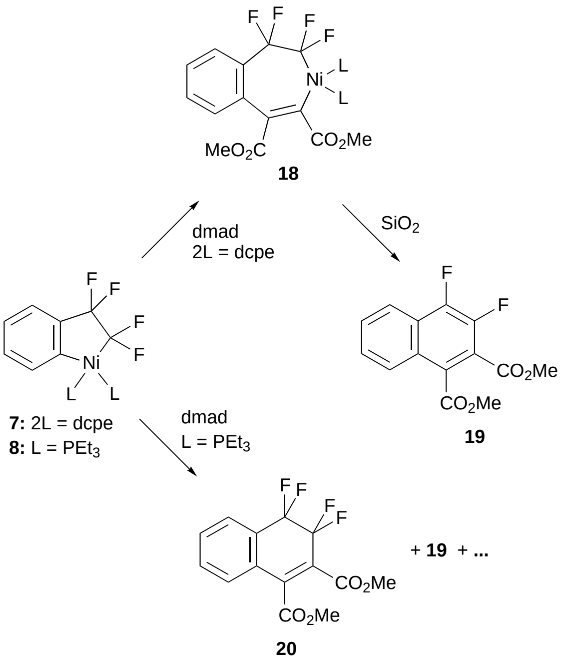


Scheme 6

δ_C(*C*OPh) is 253.0 [*J*(PC) 26.5 Hz].[10] The ^{31}P NMR spectrum of **14** contains triplets at δ 58.8 [*J*(FP) 37] and 56.8 [*J*(FP) 29.5 Hz], these chemical shifts being similar to that of the phthaloylnickel(II) complex $[\overline{Ni\{4,5\text{-}F_2\text{-}C(O)C_6H_2C}(O)\text{-}2\}(dcpe)]$ (δ 58.9).[12] These signals appear as doublets of triplets in the ^{31}P NMR spectrum of **14a** [*J*(CP) 76 and 19 Hz, respectively], the smaller coupling being to the phosphorus atom *cis* to the acyl carbon {*cf.* the value for *trans*-$[NiCl(COPh)(PMe_3)_2]$[10]}. Unfortunately, there appear to be no literature values of *J*(CP) for *trans*-[P–Ni–COR] complexes for comparison, but for related platinum(II) complexes *J*(PC) for *trans* and *cis* arrangements have been reported as 107 and 7 Hz, respectively.[13] The ^{19}F NMR spectrum of **14** consists of a broad singlet at δ −102.1 and a broad triplet of triplets at δ −94.7, the separation due to P–F coupling ['*J*(FP)'] being 33 Hz. In **14a**, the second resonance appears as a doublet of triplets of triplets with '*J*(FP)' 33, *J*(FF) 9 and *J*(CF) 5.5 Hz. The small magnitude of *J*(FC) is consistent with the expected *cis* C(O)–Ni–CF_2 arrangement. When a sample containing **14** was left under nitrogen for 16 h its ^{31}P NMR spectrum showed that the amount of **14** had decreased and the starting complex **7** had reformed. This observation can be accounted for if the insertion of CO into the nickel–aryl bond is reversible.

Work-up of the air-sensitive reaction mixtures obtained from complex **7** and CO (3–4 bar; bar = 101 325 Pa) at 50 °C gave mixtures, in varying proportions, of two compounds: 2,2,3,3-tetrafluoroindanone **15**, identified by the band at 1759 cm^{-1} in its IR spectrum and by its ^{19}F NMR and mass spectra, and the chelate carboxylato complex $[\overline{Ni\{OC(O)C_6H_4CF_2C}F_2\text{-}2\}\text{-}(dcpe)]$ **16**, whose structure has been confirmed by X-ray crystallography (see below). Both arise from **14**, the former by CO-induced reductive elimination, the latter by aerial oxidation. The presence of the monodentate carboxylato function in **16** is evident from a ν(C=O) band at 1630 cm^{-1} in the IR spectrum and a signal at δ 172.10 in the ^{13}C NMR spectrum. Similar values have been recorded for the phthalatonickel(II) complex $[\overline{Ni\{4,5\text{-}F_2\text{-}OC(O)C_6H_2C(O)O}\text{-}2\}(dcpe)]$ formed by aerial oxidation of the bis(acyl) $[\overline{Ni\{4,5\text{-}F_2\text{-}C(O)C_6H_2C}(O)\text{-}2\}(dcpe)]$.[12] The ^{31}P NMR spectrum of **16** shows two multiplets at δ 63.7 (P *trans* to CF_2) and 77.8 (P *trans* to carboxylate), the chemical shift of the latter being identical with that of the phthalato complex. The magnitude of the *J*(PP) (40 Hz) confirms that the phosphorus atoms are mutually *cis*.

The PEt_3 complex **8** reacts rapidly with CO (1 bar) at room temperature, giving an inseparable mixture of **15** and $[Ni(CO)_2(PEt_3)_2]$. An intermediate, probably the acyl $[\overline{Ni\{C(O)C_6H_4CF_2C}F_2\text{-}2\}(PEt_3)_2]$ **17**, was observed; it showed two singlets in the ^{19}F NMR spectrum at δ −96.84 and −105.23 and a broad singlet at δ 7.75 in the ^{31}P NMR spectrum.

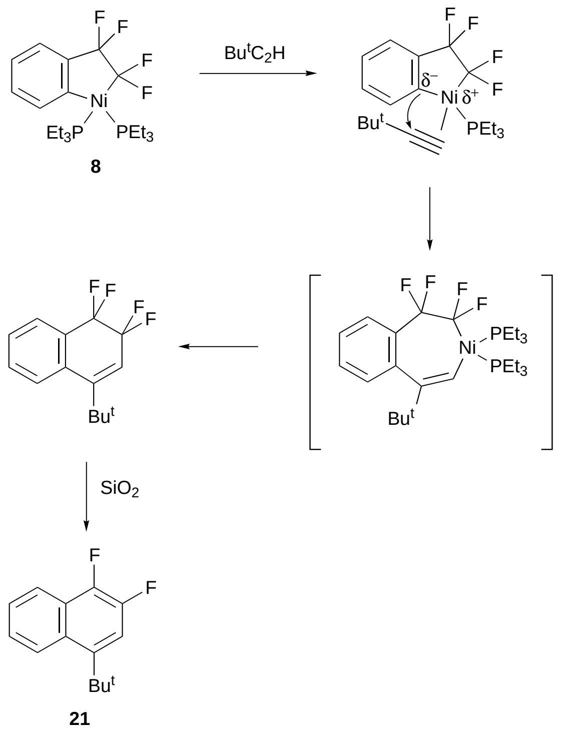


Scheme 7

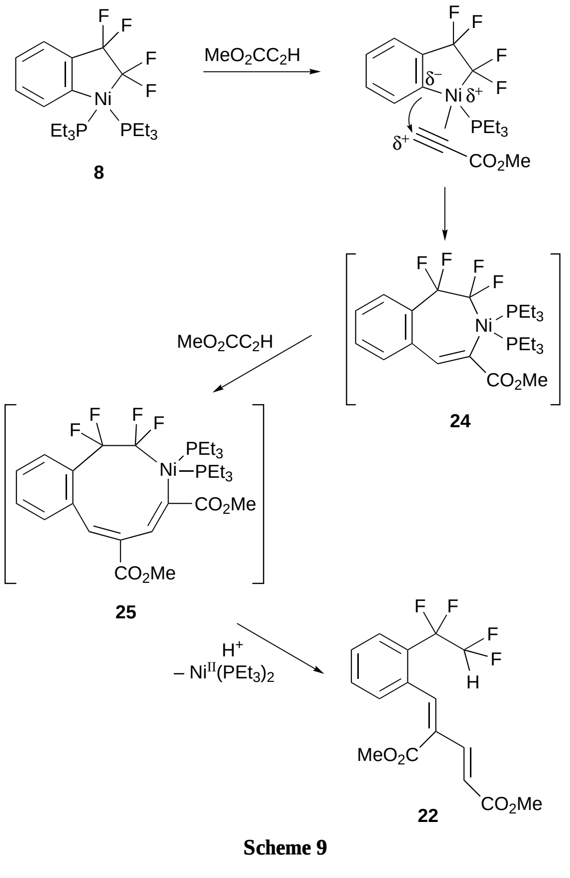
Reactions with acetylenes

The dcpe nickelaindane **7** failed to react with *tert*-butylacetylene, even after several days in refluxing tetrahydrofuran (thf), but with dimethyl acetylenedicarboxylate (dmad) the expected insertion product $[\overline{Ni\{2\text{-}C(CO_2Me){=}C(CO_2Me)C_6H_4CF_2C}F_2\}(dcpe)]$ **18** was formed in >80% yield as estimated by ^{31}P NMR spectroscopy (Scheme 7). Complex **18** was identified from the similarity of its NMR parameters (see Experimental section) with those of the naphthalene analogue **6**.[3] Unfortunately, it proved impossible to separate **18** from an unidentified red polymeric oil. Attempted chromatography on silica gel gave small amounts of a substituted naphthalene having two doublets at δ −144.1 and −144.7 [*J*(FF) 19 Hz] in its ^{19}F NMR spectrum, probably dimethyl 3,4-difluoronaphthalene-1,2-dicarboxylate **19**. This could be formed by the reductive elimination of Ni(dcpe) and subsequent aromatization, with loss of two atoms of fluorine, on silica gel.

The PEt_3 complex **8** is considerably more reactive than **7** towards acetylenes, as is true for the reactions with CO. Reaction with dmad gave immediately a complex mixture that appeared to contain the dihydronaphthalene 3,3,4,4-F_4-1,2-$(CO_2Me)_2C_{10}H_4$ **20** in addition to **19** and other unidentified species (Scheme 7). *tert*-Butylacetylene gave, after silica gel chromatography, 4-*tert*-butyl-1,2-difluoronaphthalene **21**, presumably formed by insertion of the acetylene into the nickel–aryl bond as for **6** and **18** and subsequent reductive elimination and aromatization on silica (Scheme 8). The alternative regio-



Scheme 8



Scheme 9

isomer, 3-*tert*-butyl-1,2-difluoronaphthalene, was not detected. The complicated ^{1}H NMR spectrum of **21** was simulated by LAOCOON[14] as an ABCDMXY spin system and the position of the Bu^t group at C^4 was confirmed by nuclear Overhauser experiments (see Experimental section).

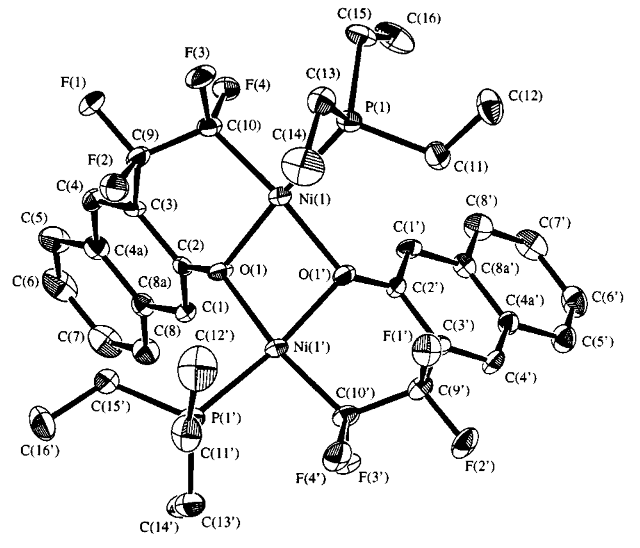


Fig. 1 An ORTEP[15] diagram for [{$\overline{\text{Ni}(\mu\text{-2-OC}_{10}\text{H}_6\text{CF}_2\text{C}}\text{F}_2$-3)(PEt$_3$)}$_2$] **10b** with atom labelling and 20% probability ellipsoids

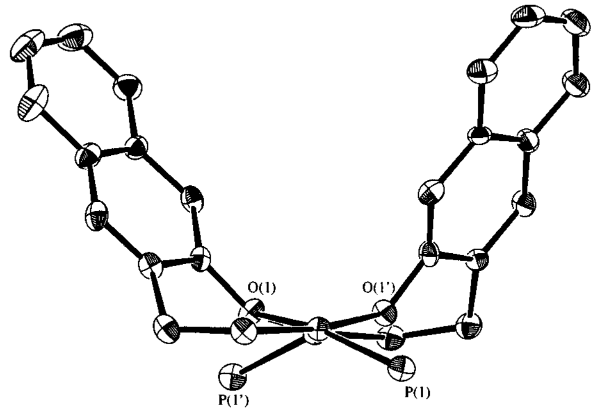


Fig. 2 Side view of dimer **10b** showing the *cis* configuration of the two naphthalene rings. Hydrogen atoms, fluorine atoms, and ethyl groups of the PEt$_3$ ligands have been omitted for clarity

Surprisingly, reaction of complex **8** with an excess of methyl propiolate did not give a naphthalene or dihydronaphthalene, but rather the tetrafluoroethylbenzene derivative 2-(HCF$_2$CF$_2$)-C$_6$H$_4$CH=C(CO$_2$Me)CH=C(CO$_2$Me) **22**, arising from the insertion of two methyl propiolate molecules (Scheme 9). The structure was assigned on the basis of its EI-mass and NMR (^{1}H, ^{19}F, ^{13}C) spectra. The presence of the CF$_2$CF$_2$H group is evident from a one-proton triplet of triplets in the ^{1}H NMR spectrum at δ 5.90 [^2J(HF) 54, ^3J(HF) 2.8 Hz] and a pair of resonances at δ −134.22 [dt, J(FH) 54, J(FF) 4 Hz, CF$_2$H] and −110.45 (quintet, J 4 Hz) in the ^{19}F NMR spectrum. The ^{1}H NMR spectrum also contains a pair of 3 H singlets at δ 3.69 and 3.87 due to the OMe groups, a pair of 1 H doublets at δ 6.65 and 7.28 [J(HH) 16 Hz] due to a *trans*-CH=CH group, and a broad triplet at δ 8.07 due to the remaining vinylic proton.

Molecular structures of [{$\overline{\text{Ni}(\mu\text{-2-OC}_{10}\text{H}_6\text{CF}_2\text{C}}\text{F}_2$-3)(PEt$_3$)}$_2$] 10b and [$\overline{\text{Ni}\{\text{OC(O)C}_6\text{H}_4\text{CF}_2\text{C}}\text{F}_2$-2}(dcpe)] 16

The molecular geometry of [{$\overline{\text{Ni}(\mu\text{-2-OC}_{10}\text{H}_6\text{CF}_2\text{C}}\text{F}_2$-3)(PEt$_3$)}$_2$] **10b** is shown in Figs. 1 and 2. Selected interatomic distances and angles are given in Table 1. The molecule occupies a general position in the unit cell. The two nickel atoms Ni(1) and Ni(1′) have a distorted square-planar geometry and are 0.133 and 0.062 Å, respectively, from the least-squares plane defined by the oxygen atoms O(1) and O(1′), the phosphorus atom and the carbon atom of the co-ordinated CF$_2$ group. The dihedral angle between the co-ordination planes intersecting at O(1) and O(1′) is 36.4°. The Ni(1)–Ni(1′)–O(1)–O(1′) unit is slightly bent, the two oxygen atoms being 0.32 Å out of the plane defined by these atoms. The two naphthalene rings are in a *syn* arrangement with angles of

Table 1 Selected bond distances (Å) and angles (°) for $[\{\text{Ni}(\mu\text{-}2\text{-OC}_{10}\text{H}_6\text{CF}_2\text{CF}_2\text{-}3)(\text{PEt}_3)\}_2]$ **10b**

Ni(1′)–P(1′)	2.183(2)	Ni(1′)–O(1)	1.934(4)
Ni(1′)–O(1′)	1.919(4)	Ni(1′)–C(10′)	1.911(7)
Ni(1)–P(1)	2.170(2)	Ni(1)–O(1)	1.894(4)
Ni(1)–O(1′)	1.940(4)	Ni(1)–C(10)	1.914(6)
O(1)–C(2)	1.357(6)	O(1′)–C(2′)	1.367(6)
P(1′)–Ni(1′)–O(1)	97.8(1)	P(1′)–Ni(1′)–O(1′)	168.4(1)
P(1′)–Ni(1′)–C(10′)	92.7(2)	O(1)–Ni(1′)–O(1′)	78.3(2)
O(1)–Ni(1′)–C(10′)	168.2(2)	O(1′)–Ni(1′)–C(10′)	92.4(2)
P(1)–Ni(1)–O(1)	168.2(1)	P(1)–Ni(1)–O(1′)	96.7(1)
P(1)–Ni(1)–C(10)	92.5(2)	O(1)–Ni(1)–O(1′)	78.7(2)
O(1)–Ni(1)–C(10)	93.1(2)	O(1′)–Ni(1)–C(10)	169.7(2)
Ni(1′)–O(1)–Ni(1)	98.5(2)	Ni(1′)–O(1)–C(2)	129.5(4)
Ni(1)–O(1)–C(2)	118.9(4)	Ni(1′)–O(1′)–Ni(1)	97.5(2)
Ni(1′)–O(1′)–C(2′)	115.7(4)	Ni(1)–O(1′)–C(2′)	126.7(4)

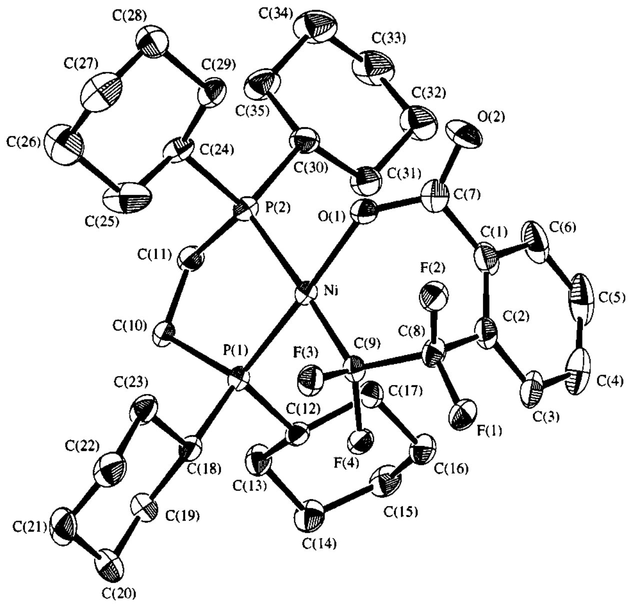


Fig. 3 An ORTEP diagram for $[\text{Ni}\{\text{OC(O)C}_6\text{H}_4\text{CF}_2\text{CF}_2\text{-}2\}(\text{dcpe})]$ **16** with atom labelling and 20% probability ellipsoids

121.4 and 63.4° between the planes defined by C(1)–C(2)–C(3)–C(4)–C(4a)–C(8a) and C(1′)–C(2′)–C(3′)–C(4′)–C(4a′)–C(8a′), respectively, and the Ni–O plane (Fig. 2), so that there is almost a C_2 symmetry axis at right angles to the Ni(1)–Ni(1′) axis. The two six-membered rings Ni–CF_2–CF_2–C(2)–C(3)–O have a boat-shaped conformation. The average Ni–O distance in the six-membered ring [Ni(1)–O(1) and Ni(1′)–O(1′)] of 1.907 Å is slightly shorter than the other Ni–O distance [Ni(1)–O(1′) and Ni(1′)–O(1)] of 1.937 Å. These distances are comparable with those found in other nickel(II) aryloxides, *e.g.* $[\text{Ni}(\text{OC}_6\text{H}_4\text{CMe}_2\text{CH}_2\text{-}2)(\text{dmpe})]$ (dmpe = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) [1.872(3) Å][7] and *trans*-$[\text{Ni(OPh)Me(PMe}_3)_2]\cdot\text{PhOH}$ [1.932(5) Å],[16] and in the binuclear di-μ-hydroxo complex $[\text{Ni}_2(\mu\text{-OH})_2(\text{CH}_2\text{C}_6\text{H}_4\text{Me-}2)_2(\text{PMe}_3)_2]$ [1.920(4), 1.917(4) Å].[17]

Table 2 Selected bond distances (Å) and angles (°) for $[\text{Ni}\{\text{OC(O)C}_6\text{H}_4\text{CF}_2\text{CF}_2\text{-}2\}(\text{dcpe})]$ **16**

Ni–P(1)	2.155(3)	Ni–P(2)	2.221(3)
Ni–O(1)	1.902(7)	Ni–C(9)	1.97(1)
P(1)–Ni–P(2)	87.2(1)	P(1)–Ni–O(1)	173.8(3)
P(1)–Ni–C(9)	91.6(3)	O(1)–Ni–C(9)	94.1(4)
P(2)–Ni–C(9)	176.7(3)	P(2)–Ni–O(1)	87.3(2)

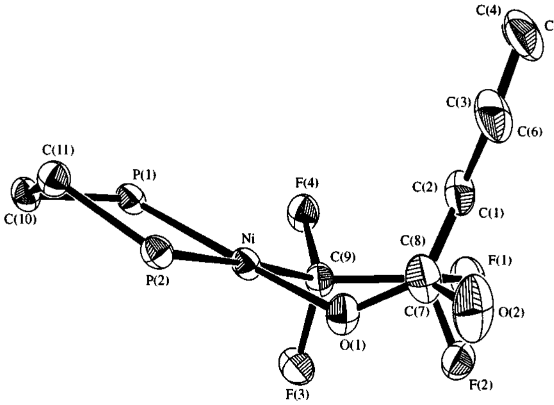


Fig. 4 Side view of complex **16** showing the boat-shaped conformation of the seven-membered nickelacycle. Hydrogen atoms and cyclohexyl groups of the dcpe ligand have been omitted for clarity

The molecular geometry of $[\text{Ni}\{\text{OC(O)C}_6\text{H}_4\text{CF}_2\text{CF}_2\text{-}2\}(\text{dcpe})]$ **16** is shown in Figs. 3 and 4; selected interatomic distances and angles are given in Table 2. The seven-membered nickelacycle has a boat-shaped conformation and the coordination geometry about the nickel is close to square planar. The Ni–P(1) distance *trans* to the carboxylate [2.155(3) Å] is significantly less than that *trans* to CF_2 [2.221(3) Å], consistent with the larger *trans* influence of the σ-bonded carbon atom. The Ni–CF_2 distance in **16** [1.97(1) Å] seems to be greater than those in **10b** [1.911(7), 1.914(6) Å], **5** [1.926(3) Å][3] and **6** [1.955(4) Å],[3] possibly reflecting the relative *trans* influences of the aryloxide and tertiary phosphine ligands, but the range in all these complexes fits well with the reported values for $[\text{Ni}(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2)(\text{PEt}_3)_2]$ [1.948(6) Å][18] and $[\text{Ni}(\text{CF}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ [mean 1.948(22) Å].[19] The Ni–O (carboxylate) distance [1.902(7) Å] and other bond lengths in **16** are unexceptional.

Discussion

Pioneering work, especially by Stone and co-workers,[5,20–23] has shown that two molecules of tetrafluoroethylene readily undergo C–C coupling on reaction with nickel(0)–tertiary phosphine complexes to form octafluoronickelacyclopentanes, but there are relatively few examples of the coupling of C_2F_4 with a η^2-alkene or η^2-alkyne on nickel(0). They include the reaction of $[\text{Ni(tmen)}(\eta^2\text{-C}_2\text{F}_4)]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) with acetylene to give the nickelacyclopentane $[\text{Ni(CH=CHCF}_2\text{CF}_2)(\text{tmen})]$[24] and the similar reaction of $[\text{NiL}^1(\eta^2\text{-C}_2\text{F}_4)]$ (L^1 = 2,6-$\text{Pr}^i{}_2\text{C}_6\text{H}_3\text{NCH=CHNC}_6\text{H}_3\text{Pr}^i{}_2$-2,6) with ethylene to give the nickelacyclopentene $[\text{Ni}(\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2)\text{L}^1]$; the latter compound can also be made from $[\text{NiL}^1(\eta^2\text{-C}_2\text{H}_4)]$ and C_2F_4.[25] We have extended these observations by showing that C_2F_4 readily couples with η^2-2,3-didehydronaphthalene and η^2-benzyne on nickel(0) to give chelate σ-bonded nickel(II) complexes $[\text{Ni}(2\text{-C}_{10}\text{H}_6\text{CF}_2\text{CF}_2\text{-}3)(\text{dcpe})]$ **5** (Scheme 1) and $[\text{Ni}(\text{C}_6\text{H}_4\text{CF}_2\text{CF}_2\text{-}2)\text{L}_2]$ (L_2 = dcpe **7** or 2 PEt_3 **8**) (Scheme 2), respectively.

An interesting feature of complex **8** is its ready loss of PEt_3 in the presence of air to form the *syn* and *anti* isomers of the μ-aryloxo-nickel(II) complexes, **9a** and **9b**, as a result of insertion of an oxygen atom into the nickel–aryl bond. The formation of the analogous compounds **10a** and **10b** from $[\text{Ni}(\eta^2\text{-C}_{10}\text{H}_6)(\text{PEt}_3)_2]$ **3** and C_2F_4 in the presence of air (Scheme 4) probably proceeds *via* the insertion product $[\text{Ni}(2\text{-C}_{10}\text{H}_6\text{CF}_2\text{CF}_2\text{-}3)(\text{PEt}_3)_2]$ analogous to **5**, though we did not attempt to isolate it.

The behaviour of complex **8** with oxygen contrasts with that of the bis(σ-bonded) complexes *trans*-$[\text{Ni}(2\text{-MeC}_6\text{H}_4)\text{Me}(\text{PEt}_3)_2]$[26] and *trans*-$[\text{Ni}(4\text{-MeC}_6\text{H}_4)(\text{C}_6\text{Cl}_5)(\text{PMe}_2\text{Ph})_2]$,[27] which undergo reductive elimination of *o*-xylene and *p*-$\text{MeC}_6\text{H}_4\text{C}_6\text{Cl}_5$, respectively, on heating in air. There may be an analogy with the formation of $[\{\overline{\mathrm{Ni}(\mu\text{-}\mathrm{OC_6H_4CMe_2C}}\mathrm{H_2})(\mathrm{PMe_3})\}_2]$ from **11** and N_2O,[7] in which the latter is believed to add as a heterocumulene similarly to CO_2, CS_2, COS, PhNCS, PhNCO and *p*-MeC_6H_4-$NCNC_6H_4Me$-*p*.[28,29] Oxygen-atom insertions into the Pd–C σ bonds of arylpalladium(II) complexes are induced by reaction with *m*-chloroperbenzoic acid[30,31] or *tert*-butyl hydroperoxide;[32] in the latter case the rate of oxygenation increases with the nucleophilicity of the metal centre. It is also well known that alkyls of main-group elements (especially those in Groups 1–3),[33,34] of titanium and zirconium (MR_4),[35] and of molybdenum and tungsten (M_2R_6)[35] undergo autoxidation to form unstable peroxides, which react rapidly with the initial alkyl to give finally metal alkoxides (Scheme 10). Several stable peroxoplatinum(II)[36,37] and -palladium(II)[38] complexes have been characterized. The selective oxidation of terminal olefins by oxygen to methyl ketones in the presence of palladium(0) and platinum(0) complexes proceeds *via* a five-membered peroxometallacycle formed by a 1,3-dipolar reaction of a dioxygen complex $ML_2(O_2)$ with the olefin.[38–40] This decomposes to give the ketone and an oxo-metal species. In the light of these observations we suggest that the tetrafluoronickelaindane **8** inserts oxygen into the nickel–aryl bond to give a six-membered peroxonickel(II) species **23** (Scheme 11); this may be the intermediate observed by ^{31}P NMR spectroscopy. It could then react with unco-ordinated PEt_3 to give Et_3PO and the final isomeric aryloxonickel(II) complexes **9a**, **9b**.

The fact that CO and dmad insert exclusively into the nickel–aryl bond of complex **5**, not the $Ni-CF_2$ bond, is consistent with the well known reluctance of transition metal–fluoroalkyl bonds (and, more generally, bonds to electron-withdrawing alkyl groups) to undergo insertion of CO.[41] The same regioselectivity undoubtedly applies in the case of **8**, whose tendency to lose PEt_3 causes it to be far more reactive than **5** towards insertion of acetylenes such as *tert*-butylacetylene and methyl propiolate. Surprisingly, in the former case, the nickel–aryl bond must attack exclusively the sterically more hindered alkyne carbon atom bearing the *tert*-butyl group. This contrasts with the reactions of *tert*-butylacetylene with $[Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2]$ **1**, which gives exclusively 1,3-di-*tert*-butylnaphthalene.[2] In the first step of this reaction the nickel–carbon bond is believed to attack the sterically less hindered alkyne carbon atom to give a nickelaindene intermediate in which the *tert*-butyl group is adjacent to the metal atom. A second difference is that the insertion of the second molecule of *tert*-butylacetylene into this intermediate occurs at the nickel–vinyl bond, not the nickel–aryl bond.[2,4] Presumably, in the reaction of **8** with *tert*-butylacetylene steric hindrance between the tertiary phosphine and the *tert*-butyl group of the alkyne as it approaches the nickel–aryl bond determines the regioselectivity. For comparison, the reaction between $[\overline{\mathrm{Ni}(\mathrm{C_6H_4CMe_2C}}\mathrm{H_2}\text{-}2)(\mathrm{PMe_3})_2]$ **11** and *tert*-butylacetylene gives a 2.2 to 1 mixture of dihydronaphthalenes, the isomer having the *tert*-butyl group in the 3 position being favoured.[42] Thus, assuming that insertion occurs into the nickel–aryl bond, attack at the sterically less hindered alkyne carbon atom is preferred, as in the corresponding insertions with **1**. It is not clear whether the difference in behaviour between **8** and **11** towards *tert*-butylacetylene is caused mainly by the change from PEt_3 to the less bulky PMe_3.

$$R{-}M \xrightarrow{O_2} R{-}O{-}O{-}M \xrightarrow{R-M}$$

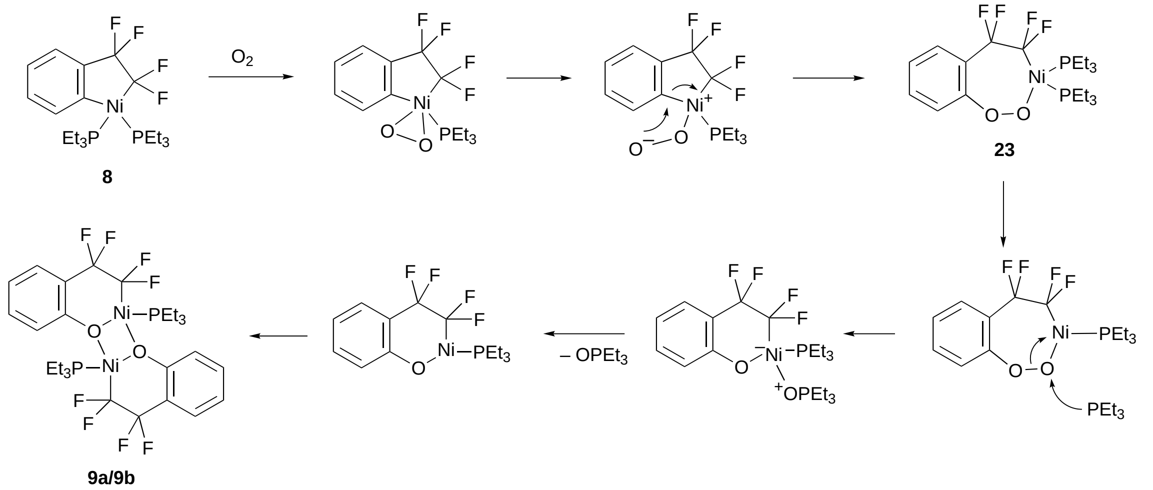
$$2\,R{-}O{-}M \xrightarrow{H_2O} R{-}OH$$

Scheme 10

The formation of the tetrafluoroethylbenzene derivative **22** from **8** and methyl propiolate (Scheme 9) can be accounted for by assuming a double insertion of methyl propiolate under electronic control into the nickel–aryl bond of **8**, giving successively intermediate nickelacycles **24** and **25** in which a CO_2Me group is on the carbon atom bound to nickel. Subsequent protonation then gives **22**. The source of the proton is not known, however, and it is not clear why protonation should take precedence over ring closure in this case.

Experimental

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. The NMR spectra were recorded on the following Varian instruments: 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), Gemini-300 BB (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, ^{19}F at 282.2 MHz and ^{31}P at 121.4 MHz), VXR-300 (^{1}H at 300 MHz and ^{13}C at 75.4 MHz) and VXR-500 (^{1}H at 500 MHz). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvent, to external 85% H_3PO_4 for ^{31}P and to $CFCl_3$ for ^{19}F. The spectra of all nuclei (except ^{1}H and ^{19}F) were ^{1}H or ^{19}F decoupled. Infrared spectra were measured in solution (KBr cells) on Perkin-Elmer 683 or 2000 FT-IR spectrometers. 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 (2,5,8,11,14-pentaoxapentadecane), 3-nitrobenzyl alcohol or 3-nitrophenyl octyl ether. Mass spectra of the organic compounds were obtained by the EI method on a VG



Scheme 11

Micromass 7070F or a Fisons Instruments VG AutoSpec spectrometer.

The aryne complexes [Ni(η^2-C_6H_4)L_2] (L_2 = 2 PEt_3 **1**[1] or dcpe **2**[2]) and [Ni(2,3-η-$C_{10}H_6$)(PEt_3)$_2$] **3**[3] were prepared as described previously; usually they were made *in situ* and reactions were carried out directly. Carbon monoxide (99% ^{13}C) was obtained from Monsanto Research Corporation.

Preparation of $[\overline{Ni(C_6H_4CF_2C}F_2)(dcpe)]$ 7

A solution of [Ni(η^2-C_6H_4)(dcpe)] **2** in toluene (60 cm^3) at −20 °C, prepared by lithium reduction of [NiBr(2-BrC_6H_4)-(dcpe)] (1.34 g, 1.87 mmol), was stirred under C_2F_4 (1 bar) at room temperature overnight. The dark orange-brown solution was dried *in vacuo* and filtered through a silica gel column (CH_2Cl_2). Evaporation of the solvent and washing with hexane yielded complex **7** as a yellow powder (754 mg, 61%) which could be recrystallized from CH_2Cl_2 (Found: C, 61.8; H, 7.9. $C_{34}H_{52}F_4NiP_2$ requires C, 62.1; H, 8.0%); $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 2940s, 2860s, 1610w, 1590m, 985s, 955s, 865s and 535m; δ_H(200 MHz, C_6D_6) 0.85–1.80 (40 H, m, CH_2 of cyclohexyl), 1.80–2.05 (2 H, m, CH_2), 2.10–2.40 (4 H, m, CH), 2.50–2.70 (2 H, m, CH_2), 7.10–7.30 (2 H, m, H^{arom}), 7.62 [1 H, t, *J*(HH) 6.0, H^4 or H^5] and 7.82 [1 H, d, *J*(HH) 7.2, H^3 or H^6]; δ_C(75.4 MHz, $CDCl_3$) 19.68 [dd, *J*(CP) 21.5, 16.9, CH_2], 20.28 [dd, *J*(CP) 22.0, 17.6, CH_2], 26.42, 26.60, 27.50, 27.53, 27.65, 27.86, 28.04 (CH_2), 29.60 [d, *J*(CP) 5.5, CH_2], 29.65 [d, *J*(CP) 3.3, CH_2], 30.93 [d, *J*(CP) 3.3, CH_2], 31.80 [d, *J*(CP) 5.5, CH_2], 35.83 [d, *J*(CP) 16.5, CH], 35.97 [d, *J*(CP) 18.6, CH], 122.89, 124.83 (CH), 127.88 [d, *J*(CP) 4.4, C^5H], 139.24 [dd, *J*(CP) 9.9, 3.3, C^6H], 143.88 [t, *J*(CF) 22.0, C^2] and 160.70–162.30 (m, C^1); δ_C(75.4 MHz, $CDCl_3$, ^{19}F-decoupled) 126.20 ($C_6H_4CF_2$), 143.92 (C^2) and 146.89 [dd, *J*(CP) 92.2, 22.0, NiCF_2]; δ_F(188.2 MHz, C_6D_6) −103.84 [dt, *J*(FP) 5.7, *J*(FF) 10.7] and −93.35 [ddt, *J*(FP) 32.0, 21.2, *J*(FF) 10.6]; δ_P(80.96 MHz, C_6D_6) 64.47 [dtt, *J*(PP) 12.1, *J*(FP) 32.0, 5.1] and 68.38 [dt, *J*(PP) 12.1, *J*(FP) 20.8 Hz]; *m*/*z* (FAB) 637 (*M* − F).

Preparation of $[\overline{Ni(C_6H_4CF_2C}F_2)(PEt_3)_2]$ 8

A solution of [Ni(η^2-C_6H_4)(PEt_3)$_2$] **1** in hexane (20 cm^3), prepared by reduction of [NiBr(2-BrC_6H_4)(PEt_3)$_2$] (1.02 g, 1.92 mmol) with lithium, was cooled to −78 °C and stirred for 16 h under dry C_2F_4 (1 bar) while being allowed to warm up to room temperature. The resulting suspension was decanted and the residue washed with hexane to give complex **8** as a yellow solid {750 mg, 83% based on [NiBr(2-BrC_6H_4)(PEt_3)$_2$]}. δ_H(200 MHz, C_6D_6) 0.77–1.10 (18 H, m, CH_3), 1.10–1.27 (6 H, m, CH_2), 1.42–1.58 (6 H, m, CH_2), 7.04–7.08 (2 H, m, $H^{4,5}$), 7.36 (1 H, br s, H^3 or H^6) and 7.61 [1 H, br d, *J*(HH) 6.0, H^6 or H^3]; δ_C(75.4 MHz, C_6D_6) 8.17, 8.26 (CH_3), 16.32 [d, *J*(CP) 19.8, CH_2], 17.67 [d, *J*(CP) 18.6, CH_2], 122.67, 124.42, 136.76, 136.91 (CH), 143.41 [t, *J*(CP) 21.9, C^1] and 162.70–164.20 (m, C^2); δ_F(188.2 MHz, C_6D_6) −105.24 (br s) and −94.58 (m); δ_P(80.96 MHz, C_6D_6) 7.75 [dtt, *J*(PP) 22.3, *J*(FP) 35.1, 4.9] and 11.48 (apparent q, *J* 22.9 Hz).

Reaction of complex 8 with air

In a qualitative NMR experiment, a solution of complex **8** in CD_2Cl_2 was left in contact with air for 48 h at room temperature to give a 1:1.3 mixture of the oxo-dimer $[\{\overline{Ni(\mu\text{-}OC_6H_4CF_2C}F_2\text{-}2)(PEt_3)\}_2]$ **9a**, having a ^{31}P triplet at δ 28.07 [*J*(FP) 30.5 Hz] and a broad ^{19}F singlet at δ −98.65, and its isomer **9b**. After filtration through silica gel only **9b** remained. δ_F(188.2 MHz, CD_2Cl_2) −133.11 [d, *J*(FF) 249.9], −101.71 [dm, *J*(FF) 245.1], −100.10 [dd, *J*(FF) 249.2, *J* 21.1] and −95.36 [dm, *J*(FF) 245.8]; δ_P(80.96 MHz, CD_2Cl_2) 29.12 [dd, *J*(FP) 31.2, 15.6 Hz].

Preparation of $[\{\overline{Ni(\mu\text{-}2\text{-}OC_{10}H_6CF_2C}F_2\text{-}3)(PEt_3)\}_2]$ 10a, 10b

A solution of [Ni(2,3-η-$C_{10}H_6$)(PEt_3)$_2$] **3** in hexane (40 cm^3), prepared by reduction of [NiBr(3-Br$C_{10}H_6$-2)(PEt_3)$_2$] (0.539 g, 0.92 mmol) with 1% Na/Hg in thf (30 cm^3), was stirred under C_2F_4 (1 bar) containing oxygen for 16 h. The yellow solid formed was decanted and dried *in vacuo*. The ^{31}P NMR spectrum showed a doublet of doublets at δ 29.05 due to **10b** and a triplet at δ 28.23 due to **10a**, the latter predominating. Recrystallization from CH_2Cl_2 gave only **10b** {198 mg, 51% based on [NiBr(3-Br$C_{10}H_6$-2)(PEt_3)$_2$]}; **10a** evidently rearranged to **10b** under these conditions. Complex **10b** (Found: C, 52.3; H, 5.0. $C_{36}H_{42}F_8Ni_2O_2P_2$ requires C, 51.6; H, 5.1%): $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 3050w, 2970m, 2940w, 2880w, 1635s, 1605m, 1500m, 1460s, 1340s, 1205s, 1170s, 1045m and 990s; δ_H(200 MHz, C_6D_6) 1.05–1.35 (15 H, m), 6.95 [1 H, t, *J*(HH) 7.9, H^6 or H^7], 7.11 [1 H, t, *J*(HH) 7.7, H^7 or H^6], 7.25 [1 H, d, *J*(HH) 8.2, H^5 or H^8], 7.38 [1 H, d, *J*(HH) 7.9, H^8 or H^5], 8.09 [1 H, d, *J*(HH) 2.6, H^1 or H^4] and 8.25 (1 H, s, H^4 or H^1); δ_C(75.4 MHz, CD_2Cl_2) 8.13 (CH_3), 13.44 [d, *J*(CP) 27.4, CH_2], 113.36, 123.75, 126.14 (CH), 126.65 [dd, *J* 10.9, 3.2, C^4H], 127.65 (C^{4a} or C^{8a}), 127.82, 128.92 (CH), 136.45 (C^{8a} or C^{4a}), 156.59 [d, *J*(CP) 7.7, C^2], signals due to C^3 and the two CF_2 groups were not observed; δ_F(188.2 MHz, CD_2Cl_2) −133.81 [dt, *J*(FF) 246.0, 8.8], −102.74 [dddd, *J*(FF) 251.8, 22.7, 7.5, *J*(FP) 32.0], −100.00 [dd, *J*(FF) 246.1, *J* 21] and −93.78 [dt, *J*(FF) 250.2, *J* 15.3]; δ_P(80.96 MHz, C_6D_6) δ 28.96 [dd, *J*(FP) 31.8, 16.8 Hz]. Complex **10a**: δ_H(200 MHz, C_6D_6) 1.00–1.50 (15 H, m), 7.00 [1 H, t, *J*(HH) 7.2, H^6 or H^7], 7.07 (1 H, s, H^1 or H^4), 7.25 [1 H, t, *J*(HH) 7.4, H^7 or H^6], 7.54 [1 H, d, *J*(HH) 8.2, H^5 or H^8], 7.64 [1 H, d, *J*(HH) 8.2, H^8 or H^5] and 8.23 (1 H, s, H^4 or H^1); δ_F(188.2 MHz, C_6D_6) −97.21 (br s); δ_P(80.96 MHz, C_6D_6) 28.23 [t, *J*(PF) 30.8 Hz].

Reaction of complex 7 with CO

In a typical experiment, a solution of complex **7** (0.215 g, 0.32 mmol) in thf (30 cm^3) was stirred under CO (1 bar) at room temperature. The course of the reaction was monitored by NMR (^{13}C, ^{31}P, ^{19}F) and IR spectroscopy. After 25 h, the acyl complex $[\overline{Ni\{C(O)C_6H_4CF_2C}F_2\text{-}2\}(dcpe)]$ **14** was the main species present, although there were traces of **7** and some 2,2,3,3-tetrafluoroindanone **15** had already formed. After 49 h the reaction mixture contained **14** (major), **15**, [Ni(CO)$_2$(dcpe)] (δ_P 64.0) and [Ni(dcpe)$_2$] (δ_P 47.4); no starting material was observed. When a sample of this reaction mixture was stirred for 16 h under nitrogen the amount of acyl complex **14** had decreased and the starting complex **7** had reformed, as shown by ^{31}P NMR spectroscopy. After 97 h all these compounds were still present, but the indanone **15** had become the major product. The ^{13}C-labelled compounds **14a** and **15a** were generated similarly.

In another experiment, a solution of complex **7** (0.183 g, 0.28 mmol) in thf (20 cm^3) was stirred at 50 °C under CO (3 bar) containing air. Monitoring showed rapid formation of intermediate **14** and of [Ni(CO)$_2$(dcpe)]. After 5 d the reaction was complete, as shown by ^{19}F NMR spectroscopy, which showed the presence of $[\overline{Ni\{OC(O)C_6H_4CF_2C}F_2\text{-}2\}(dcpe)]$ **16** and 2,2,3,3-tetrafluoroindanone **15** in a 2:1 ratio; ^{31}P NMR spectroscopy showed that there was some [Ni(dcpe)$_2$]. The compounds were difficult to separate as they seemed to react with the chromatography materials. Compound **15** could be extracted with hexane as a sticky solid (20 mg, 35%). Complex **16** was isolated as a yellow solid by preparative TLC (silica gel, hexane–acetone 1:1), but some decomposition occurred. The yield was 75 mg (38%). Single crystals of **16** suitable for X-ray analysis were obtained from acetone–diethyl ether. The ^{13}C-labelled carboxylate complex **16a** was generated similarly from ^{13}CO. $[\overline{Ni\{C(O)C_6H_4CF_2C}F_2\text{-}2\}(dcpe)]$ **14**: $\tilde{\nu}_{max}$/cm^{-1} (thf) 1615 (C=O); δ_F(188.2 MHz, C_6D_6–thf) −102.07 (br s, $C_6H_4CF_2$) and

−94.72 [br tt, *J*(FP) 33.0, *J*(FF) 8.9, $NiCF_2$]; δ_P(80.96 MHz, C_6D_6–thf) 56.77 [t, *J*(FP) 29.5] and 58.83 [t, *J*(FP) 37.1 Hz]. Complex **14a**: $\tilde{\nu}_{max}$/cm^{-1} (thf) 1570 (C=O); δ_C(75.4 MHz, C_6D_6–thf) 256.56 [ddt, *J*(CP) 75.8, 17.7, *J*(CF) 5.5, CO]; δ_F(188.2 MHz, C_6D_6–thf) −103.39 (br s) and −96.11 [dtt, *J*(CF), 5.5, *J*(FP) 33.0, *J*(FF) 8.8]; δ_P(80.96 MHz, C_6D_6–thf) 56.79 [dt, *J*(CP) 18.6, *J*(FP) 30.2] and 58.85 [dt, *J*(CP) 75.7, *J*(FP) 37.9 Hz]. Compound **15**: $\tilde{\nu}_{max}$/cm^{-1} ($CHCl_3$) 2963w, 2873w, 1759s (CO), 1608w, 1303m, 1292m, 1261m, 1200w, 1158m, 1125s, 1034m, 960m, 891m, 808w and 768w; δ_H(300 MHz, $CDCl_3$) 7.80–8.05 (4 H, m); δ_C(75.4 MHz, $CDCl_3$) 124.86, 124.88, 134.07 (CH), 134.90 (C^7), 138.32 (CH), the multiplets expected for CO, C^2F_2, C^3F_2 and C^4 were not visible; δ_F(188.2 MHz, $CDCl_3$) −126.48 (s) and −108.60 (s). Compound **15a**: δ_C(50.3 MHz, $CDCl_3$) 184.93 [t, *J*(CF) 25.3, CO]; δ_F(188.2 MHz, C_6D_6) −127.20 [dt, *J*(CF) 25.1, *J*(FF) 3.2, C^2F_2] and −109.2 [t, *J*(FF) 3.1 Hz, C^3F_2]; *m/z* (high resolution) 205.022 389; $C_8{}^{13}CF_4O$ requires 205.022 040. Complex **16**: $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 2940vs, 2860s, 1630s (C=O), 1605m, 1595m, 1570m, 1450m, 1365m, 1330w, 1290w, 1180m, 1090m, 990m, 870m and 535w; δ_H(300 MHz, [$^2H_6$]acetone) 1.25–2.35 (48 H, m, dcpe), 7.58–7.68 (3 H, m), 7.83 [1 H, br d, *J*(HH) 7.1, H^6]; δ_C(75.4 MHz, [$^2H_6$]acetone) 17.28 [dd, *J*(CP) 23.7, 7.9, CH_2], 21.71 [dd, *J*(CP) 30.0, 17.2, CH_2], 26.49, 26.51, 26.58, 26.59, 27.50, 27.62, 27.76, 27.92, 28.12, 28.31, 29.20, 29.40, 29.69, 29.93, 29.96 (CH_2 of C_6H_{11}), 31.86 [d, *J*(CP) 2.3, CH_2 of C_6H_{11}], 33.76 [d, *J*(CP) 18.2], 36.92 [d, *J*(CP) 23.2] (CH of C_6H_{11}), 126.05 (m, C^3H), 129.08 (CH), 129.54 (CH), 130.34 (C^6H), 132.65 [t, *J*(CF) 23.5, C^2], 141.64 [apparent d, *J*(CP) 63.9, C^1] and 172.10 (CO); δ_F(188.2 MHz, [$^2H_6$]acetone) −111.79 (br s), −95.81 [br t, *J*(FP) 28.2, $NiCF_2$]; δ_P(80.96 MHz, [$^2H_6$]acetone) 63.69 [dtt, *J*(PP) 39.7, *J*(FP) 30.9, 6.0] and 77.76 [dt, *J*(PP) 39.7, *J*(FP) 23.5 Hz]. Complex **16a**: $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 1595m (C=O) and 1570m; δ_H(300 MHz, [$^2H_6$]acetone) 1.25–2.35 (48 H, m, dcpe), 7.58–7.68 (3 H, m) and 7.83 [1 H, ddt, *J*(HH) 7.2, *J*(CH) 3.9, *J*(FH) 1.0, H^6]; δ_C(75.4 MHz, [$^2H_6$]acetone) 130.40 [d, *J*(CC) 3.2, C^6H], 132.61 [t, *J*(CF) 23.5, C^2], 140.84 [apparent dd, *J*(CP) 69.3, *J*(CC) 4.2 Hz, C^1] and 172.45 (CO); *m/z* ($C_{34}{}^{13}CH_{52}F_4NiO_2P_2$) 701 ($M^+$, 5), 480 (80), 289 (100) and 241 (38%).

Reaction of complex 8 with CO

A solution of complex **8** in thf (15 cm^3) was stirred for 16 h under CO (1 bar). The solvent was evaporated and the residue was purified by preparative TLC (hexane–ether 1 : 1). The only fluorine-containing compound isolated was 2,2,3,3-tetrafluoroindanone **15**.

Reaction of complex 7 with dmad

A mixture of complex **7** (401 mg, 0.6 mmol) and dmad (5 cm^3) in thf (40 cm^3) was refluxed for 48 h. The resulting orange solution was evaporated to give a deep red oil that contained $[\overline{\mathrm{Ni}\{C(CO_2Me)=C(CO_2Me)C_6H_4CF_2C}F_2\text{-}2\}(dcpe)]$ **18** in addition to polymeric material. All attempts to purify the complex by TLC or fractional crystallization proved unsuccessful. δ_P(80.96 MHz, C_6D_6) 54.95 [ddt, *J*(PP) 24.4, *J*(FP) 29.1, 9.2] and 63.24 [ddd, *J*(PP) 24.4, *J*(FP) 98.9, 3.9 Hz]. These data are similar to those of the corresponding naphthalene-based complex.[3]

Reaction of complex 8 with dmad

Dimethyl acetylenedicarboxylate (0.02 cm^3) was added to a solution of complex **8** (about 30 mg) in C_6D_6 (0.5 cm^3). Reaction occurred immediately to give a complicated mixture, as shown by ^{31}P and ^{19}F NMR spectroscopy. Attempted separation by preparative TLC (CH_2Cl_2) gave a mixture of 3,4-F_2-1,2-$(CO_2Me)_2C_{10}H_4$ **19** and dihydronaphthalene 3,3,4,4-F_4-1,2-$(CO_2Me)_2C_{10}H_4$ **20**, whose structures were assigned tentatively on the basis of NMR and mass spectroscopy. Compound **19**: δ_H(200 MHz, $CDCl_3$) 3.97 (3 H, s, OCH_3), 3.99 (3 H, s, OCH_3), 7.55–7.72 (3 H, m) and 8.09–8.14 (1 H, m); δ_F(188.2 MHz, $CDCl_3$) −143.61 [d, *J*(FF) 19.0] and −143.11 [d, *J*(FF) 19.0]. Compound **20**: δ_H(200 MHz, $CDCl_3$) 3.89 (3 H, s, OCH_3), 3.97 (3 H, s, OCH_3) and 7.20–7.85 (4 H, m, H^{arom}); δ_F(188.2 MHz, $CDCl_3$) −124.72 (br s) and −120.65 (br s); *m/z* ($C_{14}H_{10}F_4O_4$) 318 (M^+, 18), 286 (64), 249 (100), 190 (22), 162 (47) and 150 (28%).

Reaction of complex 8 with *tert*-butylacetylene

A solution of crude complex **8** (0.7 mmol) in thf (10 cm^3) at −50 °C was treated with *tert*-butylacetylene (0.25 cm^3, 2 mmol) and the mixture allowed to warm up to room temperature over 1 h. The ^{31}P NMR spectrum of the solution showed that **8** had completely disappeared. The solution was filtered through silica gel and the solvent evaporated. The residue was purified by preparative TLC (hexane) to give 4-*tert*-butyl-1,2-difluoronaphthalene **21** (58 mg, 38%): δ_H(500 MHz, $CDCl_3$) 1.58 (9 H, s, Bu^t), 7.32 [1 H, dd, *J*(HF) 13.3, 8.2, H^3], 7.41 (1 H, m, H^6), 7.46 (1 H, m, H^7), 8.07 (1 H, m, H^8) and 8.34 (1 H, m, H^5); this spectrum was simulated by LAOCOON as an ABCDMXY spin system with $^3J(F^1F^2)$ 20.2, $^3J(F^2H^3)$ 13.2, $^3J(H^5H^6)$ 8.6, $^3J(H^6H^7)$ 6.9, $^3J(H^7H^8)$ 8.5, $^4J(F^1H^8)$ 1.1, $^4J(F^1H^3)$ 7.9, $^4J(H^5H^7)$ 1.2, $^4J(H^6H^8)$ 1.5, $^5J(F^1H^5)$ 0.76, $^5J(H^5H^8)$ 0.75 and $^6J(F^2H^7)$ 1.1; the NOE spectrum showed a 24% response of H^3 (δ 7.32) and a 26% response of H^5 (δ 8.34) on irradiation of the Bu^t group at δ 1.58; δ_C(75.4 MHz, $CDCl_3$) 31.72 (CH_3), 35.88 (C), 114.55 [d, *J*(CF) 21.6, CH], 121.14 [t, *J*(CF) 6.6, CH], 124.56 [d, *J*(CF) 3.2, CH], 125.75 [d, *J*(CF) 2.2, CH], 126.11 [d, *J*(CF) 13.2, C], 126.82 (CH), 128.83 (C), 142.89 [dd, *J*(CF) 249.3, 12.1, CF], 143.92 [t, *J*(CF) 5.5, C] and 144.90 [dd, *J*(CF) 243.7, 11.0, CF]; δ_F(282.2 MHz, $CDCl_3$) −153.25 [ddd, *J*(FF) 20.3, *J*(FH) 7.9, 1.7] and −142.41 [dd, *J*(FF) 20.3, *J*(FH) 13.5 Hz]; *m/z* ($C_{14}H_{14}F_2$) 220 (M^+, 33), 205 (100), 188 (25), 177 (67) and 165 (32%).

Reaction of complex 8 with methyl propiolate

A solution of crude complex **8** (0.7 mmol) in thf (20 cm^3) at −15 °C was treated slowly with a solution of methyl propiolate (0.178 cm^3, 2 mmol) in thf (3 cm^3). The solution was allowed to warm to room temperature over 3 h and the solvent was evaporated. The ^{19}F NMR spectrum of the crude product showed the formation of 2-($HCF_2CF_2C_6H_4CH$=C(CO_2Me)-CH=CH(CO_2Me) **22** in an estimated yield of 70%. This compound did not migrate on silica gel and isolation by sublimation failed. A preparative TLC on alumina (ether–hexane 1 : 1) finally yielded 17 mg of **25** (7%). $\tilde{\nu}_{max}$/cm^{-1} (CH_2Cl_2) 3055w, 2955m, 2845w, 1725vs, 1630w, 1435s, 1290s and 1115s; δ_H(300 MHz, $CDCl_3$) 3.69 (3 H, s, OMe), 3.87 (3 H, s, OMe), 5.90 [1 H, tt, *J*(FH) 54.0, 2.8, CHF_2], 6.65 [1 H, d, *J*(HH) 15.9, H^{olefin}], 7.23 (1 H, m, H^{arom}), 7.28 [1 H, dd, *J*(HH) 15.9, 0.9, H^{olefin}] (becomes a doublet on irradiation of the triplet at δ 8.07), 7.46–7.59 (2 H, m, H^{arom}), 7.61 [1 H, dd, *J*(HH) 7.3, 1.9, H^{arom}] and 8.07 [1 H, br t, *J*(FH) 3.6, H^{olefin}]; δ_C(75.4 MHz, $CDCl_3$) 51.72, 52.46 (OMe), 110.25 [t, *J*(CF) 42.8], 128.23 [t, *J*(CF) 7.7, CH], 129.30, 131.36, 131.71 (CH), 133.78 (C), 135.92, 144.07 (CH), 166.21, 167.40 (*C*O_2Me), CHF_2 and several quaternary C not located; δ_F(282.2 MHz, $CDCl_3$) −134.22 [dt, *J*(FH) 54.0, *J*(FF) 4.4 Hz, CF_2H] and −110.45 (apparent qnt, *J* 4.0); *m/z* ($C_{16}H_{14}F_4O_4$) 346 (M^+, 20), 315 (25), 287 (100), 255 (64), 244 (32), 213 (47), 177 (42), 149 (51), 71 (61) and 57 (99%).

X-Ray crystallography of $[\{\overline{\mathrm{Ni}(\mu\text{-}2\text{-}OC_{10}H_6CF_2C}F_2\text{-}3)(PEt_3)\}_2]$ 10b and $[\overline{\mathrm{Ni}\{OC(O)C_6H_4CF_2C}F_2\text{-}2\}(dcpe)]$ 16

Selected crystal data, details of data collection, data processing, structure analysis and structure refinement are in Table 3. The structure of complex **10b** was solved by Patterson methods (PATTY)[43] and was expanded using Fourier tech-

Table 3 Crystal and structure refinement data for $[\{\overline{\mathrm{Ni}(\mu\text{-}2\text{-}\mathrm{OC_{10}H_6CF_2C}}\mathrm{F_2}\text{-}3)(\mathrm{PEt_3})\}_2]$ **10b** and $[\overline{\mathrm{Ni}\{\mathrm{OC(O)C_6H_4CF_2C}}\mathrm{F_2}\text{-}2\}(\mathrm{dcpe})]$ **16a***

	10b	**16**
Chemical formula	$C_{36}H_{42}F_8Ni_2O_2P_2$	$C_{35}H_{52}F_4NiO_2P_2 \cdot 0.5(C_2H_5)_2O$
M	838.06	738.50
Crystal system	Monoclinic	Triclinic
Space group (no.)	$P2_1/n$ (14)	$P\bar{1}$ (2)
a/Å	12.429(3)	9.696(6)
b/Å	16.175(3)	14.068(7)
c/Å	20.016(3)	15.405(9)
α/°		100.26(4)
β/°	106.47(2)	93.21(6)
γ/°		109.16(5)
U/Å^3	3858(1)	1938(2)
D_c/g cm^{-3}	1.442	1.265
Z	4	2
F(000)	1728	786
Crystal size/mm	0.13 × 0.14 × 0.20	0.28 × 0.16 × 0.20
μ/cm^{-1}	11.28 (Mo-Kα)	19.24 (Cu-Kα)
Diffractometer	Rigaku AFC6S	Rigaku AFC6R
X-Radiation (graphite monochromated)	Mo-Kα	Cu-Kα
ω-Scan width	$1.20 + 0.34 \tan\theta$	$1.40 + 0.30 \tan\theta$
2θ Limit/°	45.1	120.6
h, k, l Range	(0, 0, −24) to (15, 19, 24)	(−10, −16, 0) to (10, 16, 17)
Total reflections	5573	6006
Unique reflections (R_{int})	5290 (0.134)	5759 (0.043)
Used reflections [$I > 3\sigma(I)$]	2755	3357
Corrections (transmission factors)	Analytical[47] (0.753 to 0.902)	Azimuthal scans (0.412 to 1.000)
No. parameters	452	455
Weighting scheme, w	$4F_o^2/[\sigma^2(F_o^2) + (0.002F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.013F_o^2)^2]$
R, R' (used reflections)	0.035, 0.024	0.076, 0.092
Goodness of fit	1.75	3.01
ρ_{max}, ρ_{min}/e Å^{-3}	0.35, −0.24	0.68, −0.69

* Details in common: orange, prism; ω–2θ scans; all calculations were performed by use of TEXSAN[46] with neutral atom scattering factors from Cromer and Waber,[48] Δf and $\Delta f'$ values from ref. 49 and mass attenuation coefficients from ref. 50; anomalous dispersion effects were included in F_c.[51]

niques (DIRDIF 92),[43] whereas the structure of **16** was solved by direct methods (SIR 92)[44] and was expanded using Fourier techniques (DIRDIF 94).[45] The structure of **16** contains Et_2O as solvation molecule. All non-hydrogen atoms were refined anisotropically by full-matrix least squares, except for the C atoms of the minor component of a disordered cyclohexyl group in **16**. Hydrogen atoms were included at calculated positions (C–H 0.95 Å) and held fixed. For **16**, Et_2O and the minor disordered components of the cyclohexyl group were refined without hydrogens. All calculations were performed using the TEXSAN program.[46]

CCDC reference number 186/580.

Acknowledgements

Mr. Chris Blake from the Australian National University NMR centre is gratefully acknowledged for the LAOCOON simulations.

References

1 M. A. Bennett, T. W. Hambley, N. K. Roberts and G. B. Robertson, *Organometallics*, 1985, **4**, 1992.
2 M. A. Bennett and E. Wenger, *Organometallics*, 1995, **14**, 1267.
3 M. A. Bennett, D. C. R. Hockless and E. Wenger, *Organometallics*, 1995, **14**, 2091.
4 M. A. Bennett and E. Wenger, *Organometallics*, 1996, **15**, 5536.
5 C. S. Cundy, M. Green and F. G. A. Stone, *J. Chem. Soc. A*, 1970, 1647.
6 E. Carmona, E. Gutiérrez-Puebla, J. M. Marín, A. Monge, M. Paneque, M. L. Poveda and C. Ruiz, *J. Am. Chem. Soc.*, 1989, **111**, 2883.
7 K. Koo, G. L. Hillhouse and A. L. Rheingold, *Organometallics*, 1995, **14**, 456.
8 T. Yamamoto, T. Kohara and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2161.
9 E. Carmona, F. González, M. L. Poveda, J. L. Atwood and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1980, 2108.
10 E. Carmona, M. Paneque, M. L. Poveda, R. D. Rogers and J. L. Atwood, *Polyhedron*, 1984, **3**, 317.
11 E. Carmona, M. Paneque and M. L. Poveda, *Polyhedron*, 1989, **8**, 285.
12 M. A. Bennett, D. C. R. Hockless, M. G. Humphrey, M. Schultz and E. Wenger, *Organometallics*, 1996, **15**, 928.
13 E. R. Hamner, R. D. W. Kemmitt and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1977, 261.
14 L. Cassidei and O. Sciacovelli, LAOCOON-5 (QCPE Program no. 458), modified and included in NMRI Software Package, Version 1.1, New Methods Research, Inc., New York, 1990.
15 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
16 Y.-J. Kim, K. Osakada, A. Takenaka and A. Yamamoto, *J. Am. Chem. Soc.*, 1990, **112**, 1096.
17 E. Carmona, J. M. Marín, P. Palma, M. Paneque and M. L. Poveda, *Inorg. Chem.*, 1989, **28**, 1895.
18 R. R. Burch, J. C. Calabrese and S. D. Ittel, *Organometallics*, 1988, **7**, 1642.
19 M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 1970, 161.
20 A. Greco, M. Green, S. K. Shakshooki and F. G. A. Stone, *Chem. Commun.*, 1970, 1374.
21 F. G. A. Stone, *Pure Appl. Chem.*, 1972, **30**, 551.
22 P. K. Maples, M. Green and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1973, 388.
23 C. A. Tolman and W. C. Seidel, *J. Am. Chem. Soc.*, 1974, **96**, 2774.
24 W. Kaschube, W. Schröder, K. R. Pörschke, K. Angermund and C. Krüger, *J. Organomet. Chem.*, 1990, **389**, 399.
25 W. Schröder, W. Bonrath and K. R. Pörschke, *J. Organomet. Chem.*, 1991, **408**, C25.
26 D. G. Morrell and J. K. Kochi, *J. Am. Chem. Soc.*, 1975, **97**, 7262.
27 M. Wada, K. Kusabe and K. Oguro, *Inorg. Chem.*, 1977, **16**, 446.
28 E. Carmona, P. Palma, M. Paneque, M. L. Poveda, E. Gutiérrez-Puebla and A. Monge, *J. Am. Chem. Soc.*, 1986, **108**, 6424.
29 J. Cámpora, E. Gutiérrez, A. Monge, P. Palma, M. L. Poveda, C. Ruíz and E. Carmona, *Organometallics*, 1994, **13**, 1728.
30 A. K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay and A. Chakravorty, *Inorg. Chem.*, 1986, **25**, 2214.
31 C. Sinha, D. Bandyopadhyay and A. Chakravorty, *Inorg. Chem.*, 1988, **27**, 1173.

32 P. L. Alsters, H. T. Teunissen, J. Boersma, A. L. Spek and G. van Koten, *Organometallics*, 1993, **12**, 4691.
33 J. J. Eisch, *The Chemistry of Organometallic Compounds*, Macmillan, New York, 1967, p. 66.
34 J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978, p. 517.
35 P. B. Brindley and J. C. Hodgson, *J. Organomet. Chem.*, 1974, **65**, 57.
36 G. Strukul, R. A. Michelin, J. D. Orbell and L. Randaccio, *Inorg. Chem.*, 1983, **22**, 3706.
37 G. Ferguson, P. K. Monaghan, M. Parvez and R. J. Puddephatt, *Organometallics*, 1985, **4**, 1669.
38 H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 1980, **102**, 1047.
39 H. Mimoun, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 734.
40 R. A. Sheldon and J. A. Van Doorn, *J. Organomet. Chem.*, 1975, **94**, 115.
41 A. Yamamoto, *Organotransition Metal Chemistry: Fundamental Concepts and Applications*, Wiley, New York, 1986, p. 251.
42 J. Cámpora, A. Llebaria, J. M. Moretó, M. L. Poveda and E. Carmona, *Organometallics*, 1993, **12**, 4032.
43 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The PATTY and DIRDIF Program System, Technical Report of the Crystallographic Laboratory, University of Nijmegen, 1992.
44 A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
45 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF 94 Program System, Technical Report of the Crystallographic Laboratory, University of Nijmegen, 1994.
46 TEXSAN, Single Crystal Structure Analysis Software, Version 1.6c, Molecular Structure Corp., The Woodlands, TX, 1993.
47 J. de Meulenaer and H. Tompa, *Acta Crystallogr.*, 1965, **19**, 1014.
48 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
49 D. C. Creagh and W. J. McAuley, *International Tables for X-Ray Crystallography*, Kluwer, Boston, MA, 1992, vol. C, p. 219.
50 D. C. Creagh and J. H. Hubbell, *International Tables of X-Ray Crystallography*, Kluwer, Boston, MA, 1992, vol. C, p. 200.
51 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

Received 7th April 1997; *Paper* 7/02375H