341. *Chemistry of the Metal Carbonyls. Part XXV.*[1] *Fluorocarbon Derivatives of Nickel.*

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The compounds π-C_5H_5·Ni(CO)R_f [R_f = CF_3, C_2F_5, or n-C_3F_7] have been isolated from reactions between dicarbonyl-π-dicyclopentadienyldinickel and perfluoroalkyl iodides. The related complexes have also been obtained, namely π-C_5H_5·Ni(CO)Me, π-C_5H_5·Ni(Ph_3P)C_2F_5, and π-C_5H_5·Ni(Ph_3P)I. Treatment of the salt K[π-C_5H_5·Ni(CO)] with perfluoroallyl chloride yields a mixture of π-C_5H_5·Ni(CO)(CF_2·CF:CF_2) and π-C_5H_5·Ni(CO)(CF:CF·CF_3). The probable constitution is discussed of the C_4F_5 group in a new complex π-C_5H_5·Ni(Ph_3P)C_4F_5. Reactions between dicyclopentadienylnickel and ethylene, hexafluorobut-2-yne, and butadiene are described.

Nickel complexes wherein aryl groups are σ-bonded to nickel have been well characterized, but attempts to obtain analogous alkylnickel compounds have been unsuccessful.[2] In contrast, we have recently reported two stable perfluoroalkylnickel(II) complexes (Ph_2P·CH_2·CH_2·PPh_2)NiR_fI (R_f = C_2F_5 and n-C_3F_7).[3] This Paper describes several other perfluoroalkylnickel compounds, demonstrating the ability of fluoroalkyl groups to form stable carbon–nickel σ-bonds.

Treatment of dicarbonyl dicyclopentadienyldinickel in benzene at room temperature with perfluoroalkyl iodides affords complexes, π-C_5H_5·Ni(CO)R_f, *e.g.*, [π-C_5H_5·Ni(CO)]$_2$ + C_3F_7I $\longrightarrow$ π-C_5H_5·Ni(CO)C_3F_7 + π-C_5H_5·Ni(CO)I. The iodide, π-C_5H_5·Ni(CO)I, known to decompose at ambient temperatures,[4] was not isolated. It is remarkable that cleavage of dimeric [π-C_5H_5·Ni(CO)]$_2$ by perfluoroalkyl iodides requires only about 20 minutes for completion. The compounds π-C_5H_5·Ni(CO)R_f are deep red air-stable liquids, that can be slowly distilled in a high vacuum at room temperature.

Reaction between the derivative π-C_5H_5·Ni(CO)C_2F_5 and triphenylphosphine at ambient temperatures affords the complex π-C_5H_5·Ni(Ph_3P)C_2F_5. Similarly, π-C_5H_5·Ni(Ph_3P)I can be obtained from π-C_5H_5·Ni(CO)I. Both are air-stable.

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[1] Part XXIV, Massey, Park, and Stone, *J. Amer. Chem. Soc.*, 1963, **85**, 2021; Part XXIII, Treichel, Chaudhari, and Stone, *J. Organometallic Chem.*, 1963, **1**, 98.

[2] Chatt and Shaw, *J.*, 1960, 1718.

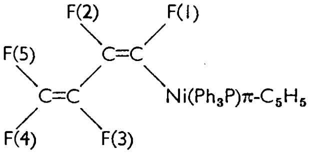
[3] McBride, Stafford, and Stone, *J.*, 1963, 723.

[4] Fischer and Palm, *Ber.*, 1958, **91**, 1725.

In an attempt to obtain the perfluorovinyl derivative, π-C_5H_5·Ni(CO)CF⁚CF_2, perfluorovinylmagnesium bromide was added to the unstable carbonyl-π-cyclopentadienylnickel iodide in tetrahydrofuran at low temperatures. After removal of the solvent, a volatile red-brown mixture was obtained. The infrared spectrum of this material showed an intense carbonyl absorption at 2080 cm.$^{-1}$ and a weak band at 1710 cm.$^{-1}$. Two intense bands were present at 1760 and 1680 cm.$^{-1}$, indicating the presence of additional fluorine-substituted double bonds.[5] Treatment of this liquid with triphenylphosphine gave dark green crystals, which still displayed the bands at 1760 and 1680 cm.$^{-1}$. The fluorine-19 n.m.r. spectrum of the phosphine complex contained 5 multiplets of roughly equal intensity; each multiplet consisted of sixteen equally intense lines. This is the pattern expected for five spin-coupled, non-equivalent fluorine atoms.[6] The three high-field resonances displayed chemical shifts and coupling constants (Table 1) similar to those observed for CF$_2$⁚CF·X groups.[7] The magnitude of the coupling between the remaining two fluorine atoms (42 c./sec.) indicated that they were *cis* to each other, since *trans* coupling constants are much larger.[7c] Combination of the i.r. and fluorine-19 n.m.r. spectral evidence leads to formulation of the complex as (I), a *cis*-perfluorobutadienyl derivative of nickel. A possible mechanism for the formation of (I) could involve initial formation of π-C_5H_5·Ni(CO)CF⁚CF_2, followed by an addition–elimination sequence:

TABLE 1.

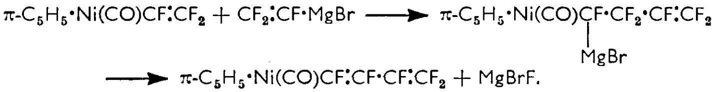
Fluorine-19 chemical shifts and spin coupling constants of π-C_5H_5·Ni(Ph_3P)·C_4F_5 and related compounds.



Compound	Shifts (p.p.m.) *				
	$\delta_{(1)}$	$\delta_{(2)}$	$\delta_{(3)}$	$\delta^{(4)}$	$\delta_{(5)}$
–-C_5H_5·Ni(Ph_3P)·C_4F_5 †	73	57	153	107	119
F_2C⁚CFCl ‡	—	—	145	105	121
F_2C⁚CF·CF_2Cl ¶	—	—	185	95	106
F_2C⁚CF·$SnBu_3$ ‡	—	—	193	88	123

	Spin coupling constants (c./sec.)									
	$J_{3,5}$	$J_{3,4}$	$J_{4,5}$	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{1,5}$	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$
π-C_5H_5·Ni(Ph_3P)·C_4F_5	113	23	82	42	5	6	7	15	6	20
F_2C⁚CF·CF_2Cl ¶	118	39	56	—	—	—	—	—	—	—
F_2C⁚CF·$SnBu_3$ ‡	115	34	79	—	—	—	—	—	—	—
F_2C⁚CFSiEt_3 **	115	27	71	—	—	—	—	—	—	—

* Relative to CCl_3F, increasing to high field. † In 15% CH_2Cl_2 solution, CCl_3F internal standard. ‡ Ref. 7*b*. ¶ Ref. 7*c*. ** Ref. 8*b*.



$$\pi\text{-}C_5H_5\cdot Ni(CO)CF{:}CF_2 + CF_2{:}CF\cdot MgBr \longrightarrow \pi\text{-}C_5H_5\cdot Ni(CO)\underset{\displaystyle MgBr}{\underset{|}{C}}F\cdot CF_2\cdot CF{:}CF_2$$

$$\longrightarrow \pi\text{-}C_5H_5\cdot Ni(CO)CF{:}CF\cdot CF{:}CF_2 + MgBrF.$$

Although this type of reaction has not been reported previously in syntheses employing

[5] (*a*) Bellamy, " The Infrared Spectra of Complex Molecules," Wiley, New York, 2nd edn., 1958, p. 42; (*b*) Stafford and Stone, *Spectrochim. Acta*, 1961, **17**, 412.

[6] Roberts, " An Introduction to Spin–Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," Benjamin, New York, 1961.

[7] (*a*) McConnel, Reilly, and McClean, *J. Chem. Phys.*, 1956, **24**, 479; (*b*) Coyle, Stafford, and Stone, *Spectrochim. Acta*, 1961, **17**, 968; (*c*) Pitcher and Stone, *Spectrochim. Acta*, 1961, **17**, 1244.

[8] (*a*) Seyforth and Wada, *Inorg. Chem.*, 1962, **1**, 78; (*b*) Seyferth, Wada, and Maciel, *Inorg. Chem.*, 1962, **1**, 232.

perfluorovinylmagnesium bromide, similar additions of alkyl-Grignard reagents to fluoro-olefins are known.[9] Moreover, vinyl-lithium reacts with triethylperfluorovinylsilane to yield a compound, Et_3SiCF:CF·CH:CH$_2$.[8a]

Treatment of the anions [π-C$_5$H$_5$·Fe(CO)$_2$]$^-$ and [Mn(CO)$_5$]$^-$ with perfluoroallyl chloride affords dicarbonyl-π-cyclopentadienyl-σ-perfluoropropenyliron [10] and pentacarbonyl-σ-perfluoropropenylmanganese,[11] respectively. These results prompted an investigation of the reaction between perfluoroallyl chloride and the anion [π-C$_5$H$_5$·Ni(CO)]$^-$ to determine whether rearrangement of the perfluoroallyl group to the perfluoropropenyl group would also occur. A small amount of dark red liquid was obtained. The fluorine-19 n.m.r. spectrum showed that it was a mixture of π-C$_5$H$_5$·Ni(CO)·CF$_2$·CF:CF$_2$ and π-C$_5$H$_5$·Ni(CO)CF:CF·CF$_3$. Intensity measurements indicated that the major component was the perfluoroallylnickel complex, which is interesting in view of related reactions where perfluoropropenyl derivatives of manganese and iron were obtained, predominantly, if not exclusively, as *trans*-isomers.[7c]

In an attempt to prepare an alkyl derivative of nickel, methyl iodide was added to a solution of the anion [π-C$_5$H$_5$·Ni(CO)]$^-$ in tetrahydrofuran. A low yield of a volatile compound, too unstable to be analysed, was obtained. The infrared spectrum of this compound (Table 2) is in agreement with the structure π-C$_5$H$_5$·Ni(CO)Me. Decomposition of π-C$_5$H$_5$·Ni(CO)Me appears to be greatly accelerated by impurities, but the complex could be stored indefinitely at −78° in a clean vessel.

TABLE 2.

Infrared spectral bands of some organonickel compounds.

Compound	Carbonyl stretching frequencies (cm.$^{-1}$) *	Other bands (cm.$^{-1}$) †
π-C$_5$H$_5$·Ni(CO)Me	2036vs, 1991w ‡	3105vw, 2985w, 2980w, 1833w, 1402w, 1365w, 1348w, 1143m, 1111vw, 1047w, 1015m, 938w, 837w, 823s, b, 762m.
π-C$_5$H$_5$·Ni(CO)CF$_3$	2078vs, 2032w ‡	3125vw, 1400m, 1351w, b, 1069 vs, 1024s, 976w, 903w, 868w, 835w, 799s, 704w.
π-C$_5$H$_5$·Ni(CO)C$_2$F$_5$	2081vs, 2034w ‡	3125vw, 1600w, 1517m, 1449w, 1401m, 1353w, 1295s, 1272m, 1178vs, b, 1047s, b, 1026s, b, 976w, 910s, b, 834w, 801s, 729m, b.
π-C$_5$H$_5$·Ni(Ph$_3$P)C$_2$F$_5$	—	2985w, 1481w, 1437m, 1385w, 1282m, 1259sh, 1176s, b, 1163s, b, 1092m, 1026s, 974m, b, 910m, 833w, 787s, 738m, b, 690m, b.
π-C$_5$H$_5$·Ni(CO)C$_3$F$_7$	2080vs, 2034w ‡	3125vw, 1449w, b, 1381m, 1342sh, 1323s, 1216vs, 1188vs, 1163s, 1155s, 1086s, 1040s, 1024s, b, 1000sh, 870w, 829w, 801s, 726w, 724s, 657m.

* Cyclohexane solution, CaF$_2$ prism. † Measured in carbon disulphide and tetrachloroethylene solutions, NaCl prism. ‡ ^{13}C–O stretching frequency.

The stability of the perfluoroalkyls, π-C$_5$H$_5$·Ni(CO)R$_f$, as compared with that of the methyl compound π-C$_5$H$_5$·Ni(CO)Me, provides yet another example of the stabilization of a transition-metal–carbon σ-bond by the presence of fluorine atoms on carbon.[12] Details of the infrared and n.m.r. spectra of the perfluoroalkylnickel compounds are summarized in Tables 2 and 3. The carbonyl stretching frequencies of the perfluoroalkylnickel compounds occur at higher frequencies than those in the alkyl derivative π-C$_5$H$_5$·Ni(CO)Me. Similar changes in frequency have been observed with other fluoroalkyl- and alkyl-transition

[9] Tarrant and Warner, *J. Amer. Chem. Soc.*, 1954, **76**, 1624.

[10] King, Stafford, Treichel, and Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3604.

[11] (*a*) Kaesz, King, and Stone, *Z. Naturforsch.*, 1960, **15*b***, 763; (*b*) McClellan, *J. Amer. Chem. Soc.*, 1961, **83**, 1598.

[12] (*a*) Treichel and Stone, *Adv. Organometallic Chem.*, 1964, **1**, 143; (*b*) King, Pitcher, Stafford, Treichel, and Stone, " Advances in the Chemistry of the Coordination Compounds " (ed. Kirschner), Macmillan, New York, 1961, p. 619.

TABLE 3.

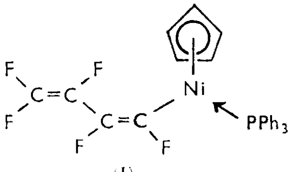
Fluorine-19 and proton chemical shifts and spin coupling constants (c./sec.) of some perfluoroalkylnickel compounds.*

Compound	$\delta_{(C_5H_5)}$ †	$\delta_{(CF_3)}$ ‡	$\delta_{(\beta\text{-}CF_2)}$ ‡	$\delta_{(\alpha\text{-}CF_2)}$ ‡	$J_{(F_\alpha\text{-}F_\beta)}$	$J_{(F_\beta\text{-}F_\gamma)}$	$J_{(F_\alpha\text{-}F_\gamma)}$
π-C_5H_5·Ni(CO)CF_3	4·64	−5·6					
π-C_5H_5·Ni(CO)C_2F_5	4·53	83·5		73·0	2·2		
π-C_5H_5·Ni(CO)C_3F_7	4·50	79·2	118·8	70·2	1·0	1·4	9·8
π-C_5H_5·Ni(Ph_3P)C_2F_5 ¶ ...	4·08	82·1		81·1 **	2·3		

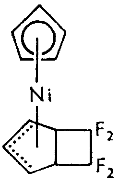
* Studied with CCl_3F as solvent, solution concentration about 10%. † Chemical shifts expressed in τ units. Hexamethyldisiloxane internal standard. ‡ Chemical shifts (p.p.m.) are relative to CCl_3F, increasing to high field. ¶ Measured in dichloromethane solution, CCl_3F internal standard. ** This resonance is split by the ^{31}P nucleus (J = 38·0 c/s.).

metal carbonyl compounds,[7c 13] and have been interpreted in terms of the higher electronegativity of the fluorocarbon groups and the current view of the nature of metal-carbon bonds in metal–carbonyl linkages.[14]

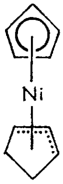
In the nickel complexes, resonances of fluorine atoms bonded to carbon atoms linked directly to the metal show the same large shift to low field as do similar fluorine atoms in other perfluoroalkyl-transition metal complexes.[15]



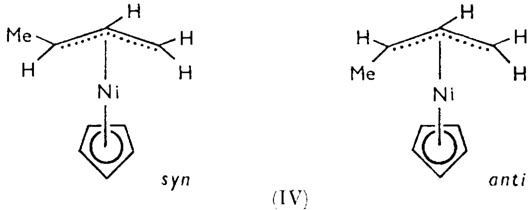
(I)



(II)



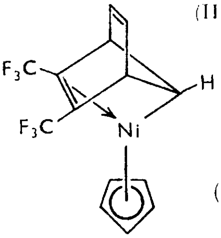
(III)



syn

anti

(IV)



(V)

If one considers ferrocene as a *pseudo*aromatic hydrocarbon, then cobaltocene in many respects behaves as if it were a delocalized radical, such as the triphenylmethyl radical. If the analogy is carried one step further, nickelocene, with two unpaired electrons, can be considered to have a free double bond. There will thus be a tendency for nickelocene to react in such a way as to " saturate " this double bond. The saturated state may be taken as a structure in which nickel obeys the effective atomic-number rule. We have previously reported[16] that tetrafluoroethylene reacts with nickelocene to give a π-cyclopentenyl-type nickel complex having such a structure (II). Moreover, other workers[17] had earlier obtained by reduction of nickelocene, π-cyclopentadienyl-π-cyclopentenylnickel. This compound also has a structure (III) in which nickel has an electronic configuration similar to krypton. These results prompted a study of reactions between nickelocene and ethylene, butadiene, and hexafluorobut-2-yne.

Interestingly, ethylene reacted with nickelocene under milder conditions than tetrafluoroethylene. However, the product was not an adduct similar to (II), but rather (III).

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[13] Pitcher and Stone, *Spectrochim. Acta*, 1962, **18**, 585.
[14] Nyholm, *Proc. Chem. Soc.*, 1961, 273.
[15] Pitcher, Buckingham, and Stone, *J. Chem. Phys.*, 1962, **36**, 124.
[16] McBride, Pruett, Pitcher, and Stone, *J. Amer. Chem. Soc.*, 1962, **84**, 497.
[17] Dubeck and Filbey, *J. Amer. Chem. Soc.*, 1961, **83**, 1257.

Although (III) was obtained in low yield, the reaction was reproducible in either tetrahydrofuran or light petroleum at temperatures from 75 to 95°. Trifluoroethylene and 1,1-difluoroethylene, on the other hand, were less reactive towards nickelocene than tetrafluoroethylene. Moreover, no cyclopentenyl derivative was isolated from these reactions but there were indications that traces of (III) were produced.

Reaction between nickelocene and butadiene produced a red air-sensitive liquid. From this liquid, a mixture of *syn*- and *anti*-π-cyclopentadienyl-π-1-methylallylnickel was obtained. The nature of the product (IV) was suggested by a study of the proton n.m.r. spectrum, and confirmed by independent synthesis. The reaction of crotyl chloride with the potassium salt of carbonyl-π-cyclopentadienylnickel gave a material identical to the volatile complex obtained from nickelocene and butadiene:

$$\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CH_2Cl + [C_5H_5{\cdot}NiCO]^- \longrightarrow C_5H_5{\cdot}Ni{\cdot}C_4H_7 + CO + Cl^-}$$

This synthesis has the advantage that little or no nickelocene is produced, unlike other methods [17–19] that have been employed in the preparation of mixed nickel complexes. In this reaction, carbon monoxide is evolved at room temperature.

Hexafluorobut-2-yne and nickelocene react at room temperature to give approximately equal amounts of the previously known $[\pi\text{-}C_5H_5{\cdot}Ni]_2C_4F_6$,[20] and a new compound of composition $C_{14}H_{10}F_6Ni$. On the basis of its proton n.m.r. spectrum this complex is assigned structure (V), which is very similar to that of a compound obtained earlier by treating nickelocene with dimethyl acetylenedicarboxylate.[21]

EXPERIMENTAL

Apparatus and Instruments.—Experiments were conducted in a vacuum system of conventional design. Infrared spectra were obtained by using a Perkin-Elmer model 21 double-beam spectrophotometer. Fluorene-19 nuclear magnetic resonance spectra were recorded at 56·4 Mc./sec., with a Varian V4300B spectrometer equipped with a superstabilizer. Proton measurements were made on a Varian A-60 spectrometer. Mass spectra were recorded by using a Consolidated Electrodynamics Corporation model 21-103C spectrometer at an ionizing voltage of 70 ev.

Perfluoroalkylnickel Derivatives.—(a) *Carbonyl-π-cyclopentadienyl-σ-perfluoropropylnickel.* Perfluoropropyl iodide (2·0 g.; 6·8 mmoles) was added to a sample [4] of $[\pi\text{-}C_5H_5{\cdot}Ni(CO)]_2$ (0·9 g.; 3 mmoles) in benzene (8 ml.) under nitrogen, and the mixture was kept at room temperature for 20 min. The solution was then filtered and solvent removed (20 mm.; 25°). The residual oil was then fractionated in the vacuum line with a trap held at 0°. Material passing this trap was discarded. The fractionation was repeated several times to give a red-purple liquid *complex* (150 mg.; 16%) (Found: C, 33·9; H, 1·7; F, 41·2. $C_9H_5F_7NiO$ requires C, 33·7; H, 1·6; F, 41·5%).

(b) *Carbonyl-π-cyclopentadienyl-σ-perfluoroethylnickel.* Perfluoroethyl iodide (6·6 g.; 27 mmoles) was distilled into an evacuated bulb containing $[C_5H_5{\cdot}Ni(CO)]_2$ (5·0 g.; 16 mmoles) and benzene (15 ml.) at −196°. The bulb was removed from the vacuum line, warmed to room temperature, and rotated frequently during 1 hr. and then the benzene slowly removed under reduced pressure through a trap held at −45°. The material, retained in this trap, was refractionated by use of a trap cooled with an ice–salt bath. A red-purple liquid *compound* (800 mg.; 18%) [Found: C, 35·7; H, 2·0; F, 35·2; Ni, 21·5%; *M* (mass spectrum), 270. $C_8H_5F_5NiO$ requires C, 35·5; H, 1·9; F, 35·1; Ni 21·7%; *M*, 270] collected.

(c) *Carbonyl-π-cyclopentadienyl-σ-perfluoromethylnickel.* From a similar experiment to that in (b) above, $[C_5H_5{\cdot}Ni(CO)]_2$ (3·0 g.; 10 mmoles) and perfluoromethyl iodide (3·5 g.; 18 mmoles) yielded the red *liquid* $\pi\text{-}C_5H_5{\cdot}Ni(CO)CF_3$ (400 mg.; 18%) (Found: C, 38·2; H, 2·4; F, 25·6. $C_7H_5F_3NiO$ requires C, 38·1; H, 2·3; F, 25·8%).

[18] Fischer and Werner, *Ber.*, 1959, **92**, 1423.
[19] McClellan, Hoehn, Cripps, Muetterties, and Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.
[20] Boston, Sharp, and Wilkinson, *J.*, 1962, 3488.
[21] Dubeck, *J. Amer. Chem. Soc.*, 1960, **82**, 502.

(d) *π-Cyclopentadienyl-σ-perfluoroethyl(triphenylphosphine)nickel.* A solution of $\pi\text{-}C_5H_5\cdot Ni(CO)C_2F_5$ (600 mg.; 2·2 mmoles) and triphenylphosphine (600 mg.; 2·3 mmoles) in dichloromethane (15 ml.) was left at room temperature for 3 hr. The solvent was evaporated (20 mm., 25°) to give a dark green residue. This material was crystallized twice (cyclohexane) to give a dark green crystalline *complex* (850 mg.; 76%) (Found: C, 59·2; H, 3·7; F, 18·8. $C_{25}H_{20}F_5NiP$ requires C, 59·4; H, 4·0; F, 18·8%), m. p. 164—165°.

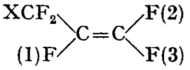
π-Cyclopentadienyl(triphenylphosphine)nickel Iodide.—To $[C_5H_5\cdot Ni(CO)]_2$ (2·0 g.; 6·7 mmoles) and dichloromethane (30 ml.), under nitrogen and cooled (ice–salt bath), was added iodine (1·6 g., 6·3 mmoles) dissolved in dichloromethane (15 ml.) during 1 hr. 15 min. later, triphenylphosphine (3·5 g.; 13 mmoles) in dichloromethane (15 ml.) was added. Solvent was removed (20 mm., 25°) and the residue was crystallized (cyclohexane) to give a few large red crystals and much amorphous powder. The crystals were recrystallized (cyclohexane) to give air-stable red *prisms* (2·3 g.; 36%), m. p. 140—141° (Found: C, 54·1; H, 3·0; I, 24·9. $C_{23}H_{20}NiIP$ requires C, 53·9; H, 2·9; I, 24·7%).

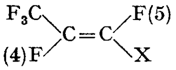
π-Cyclopentadienyl-σ-perfluorobutadienyl(triphenylphosphine)nickel.—A solution of $\pi\text{-}C_5H_5\cdot Ni(CO)I$ in tetrahydrofuran (30 ml.) was prepared from $[C_5H_5\cdot Ni(CO)]_2$ (3·0 g.; 10 mmoles) and iodine (2·5 g.; 10 mmoles) at −20° under nitrogen. A solution of perfluorovinylmagnesium bromide in tetrahydrofuran (30 ml.) was prepared from perfluorovinyl bromide (6·6 g.; 41 mmoles) and magnesium (1·0 g.; 42 g.-atoms) at −20°.[22] This second solution was added to the nickel complex and the resulting mixture stirred for 1 hr. at −20°, and for a further hour at room temperature, then filtered, and the solvent removed (20 mm., 25°). The residue, part solid and part liquid, was extracted with pentane, and the solution filtered. Solvent was removed (20 mm., 25°) and the volatile material taken into the vacuum line. The liquid product was then fractionated to remove material passing a trap held at −20°. Each transfer left a non-volatile residue. The infrared spectrum of the product (600 mg.) showed three bands in the C=C stretching region at 1775, 1710, and 1680 cm.$^{-1}$. The liquid (300 mg.) was then dissolved in hexane (3 ml.) and a saturated solution of triphenylphosphine (300 mg., 1·1 mmoles) in hexane was added. Carbon monoxide was evolved. After 2 hr. the green precipitate was crystallized (hexane) to give a dark green air-stable crystalline *compound* (350 mg.), m. p. 114—115° (Found: C, 61·6; H, 3·8; F, 17·6; P, 6·0. $C_{27}H_{20}F_5NiP$ requires C, 61·3; H, 3·8; F, 17·9; P, 5·8%).

Carbonyl-π-cyclopentadienyl-σ-perfluoroallyl- and -perfluoropropenylnickel.—A solution of $K[C_5H_5\cdot Ni(CO)]$ was prepared from $[C_5H_5\cdot Ni(CO)]_2$ (3·0 g.; 10 mmoles) and potassium (0·85 g.; 21 g.-atoms) in tetrahydrofuran (15 ml.) under nitrogen.

TABLE 4.

Fluorine-19 chemical shifts and spin coupling constants of perfluoroallyl- and perfluoropropenylnickel and related compounds.

	Chemical shifts (p.p.m.) *				Spin coupling constants (c./sec.)					
	δ_{CF_2}	$\delta_{F(1)}$	$\delta_{F(2)}$	$\delta_{F(3)}$	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	J_{1,CF_2}	J_{2,CF_2}	J_{3,CF_2}
X = $\pi\text{-}C_5H_5\cdot Ni(CO)$ † ...	57	175	112	104	113	32	72	19	32	6
X = Cl ‡	58	185	106	95	118	39	56	19	31	6

	δ_{CF_3}	$\delta_{F(4)}$	$\delta_{F(5)}$	$J_{4,5}$	J_{4,CF_3}	J_{5,CF_3}
X = $\pi\text{-}C_5H_5\cdot Ni(CO)$ † ...	67	166	106	130	12	20
X = $Mn(CO)_5$ ‡	67	165	95	127	12	23
X = $\pi\text{-}C_5H_5\cdot Fe(CO)_2$ ‡	66	166	86	131	13	22

* Relative to CCl_3F increasing to high field. † Studied in CCl_3F solution concentration ~15%.
‡ Data taken from ref. 7*c*.

Perfluoroallyl chloride (3·8 g.; 23 mmoles) was condensed into tetrahydrofuran (15 ml.), cooled to −78° and evacuated, and the mixture then allowed to warm to −20°. The solution of the nickel salt was added during 20 min. The mixture was stirred at −20° for 15 min. and

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[22] (*a*) Knunyants, Sterlin, Yatsenko, and Pinkina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 1345; (*b*) Kaesz, Stafford, and Stone, *J. Amer. Chem. Soc.*, 1959, **81**, 6336.

then for an additional hour at room temperature. Solvent was removed (20 mm., 25°), the residue extracted with pentane, and the extract filtered. Pentane was removed (20 mm., 25°) and the volatile residue taken into the vacuum line. The material was fractionated through a trap held at 0° to remove the last traces of solvent. A deep red liquid (250 mg.; 5%) (Found: C, 38·3; H, 2·0; F, 33·4. Calc. for $C_9H_5F_5NiO$: C, 38·2; H, 1·8; F, 33·6%) was obtained.

The pattern of the observed resonances in the fluorine-19 n.m.r. spectrum of this liquid was similar to that of a spectrum of a mixture of perfluoroallyl chloride and pentacarbonyl-*trans*-perfluoropropenylmanganese.[7c] Results are summarized in Table 4.

On the basis of the coupling constants, the perfluoropropenylnickel complex is considered to have the *trans*-configuration.

Reaction Between Ethylene and Nickelocene.—Ethylene (3·7 g.; 132 mmoles), nickelocene (12·0 g.; 83 mmoles), and pentane (30 ml.) were heated at 70° for 36 hr. The products were washed with pentane and the solution filtered under nitrogen. Solvent was evaporated (20 mm., 25°) and the residue chromatographed on alumina. A red fraction, eluted with pentane, was collected under nitrogen and solvent was evaporated (20 mm., 25°) to give red air-sensitive crystals (300 mg.; 2·5%), whose infrared spectrum was identical with that of an authentic sample of (III), prepared from nickelocene and sodium amalgam in ethanol.[17]

Other weak bands were present on the chromatographic column but disappeared before they could be eluted.

Reaction Between Butadiene and Nickelocene.—Nickelocene (12 g.; 64 mmoles), butadiene (6·9 g.; 123 mmoles), and tetrahydrofuran (30 ml.) were heated at 95° for 24 hr. The products were filtered under nitrogen. Solvent was evaporated (20 mm., 25°) and the residue was extracted with pentane. The filtered pentane extract was chromatographed on alumina, pentane being used as eluant. Three closely spaced red bands appeared on the column. The first fraction was collected under nitrogen. Solvent was evaporated leaving a pyrophoric red oil (1·0 g., 9·5% yield), which was taken into the vacuum system and purified by trap-to-trap distillation. The complex (IV) slowly passes a trap held at 0°.

The second material was also a red, air-sensitive liquid (2 g.), distillable at 60° *in vacuo*. Despite poor resolution of the n.m.r. spectrum, an intense, sharp peak was observed at τ 4·92. This resonance is almost certainly due to a π-cyclopentadienyl ring. A third red material (4 g.) was also obtained; non-volatile, and apparently polymeric, it was not further investigated.

The mass spectrum of (IV) indicated a molecular formula, $C_9H_{12}Ni$. The major nickel-containing ions and their relative abundances were: $C_9H_{12}Ni^+$(100), $C_5H_6Ni^+$(163), $C_5H_5Ni^+$(44), $C_4H_6Ni^+$(44), and Ni^+(126). The large amount of the $C_5H_6Ni^+$ ion, which must be formed by re-arrangement of a hydrogen atom, serves as a warning that detailed structural assignments from the mass spectra of these complexes should be made only with extreme caution.

The proton n.m.r. spectrum of (IV) was complicated by the presence of the two *syn*- and *anti*-isomers and a large number of spin coupling interactions. Similar difficulties were encountered with the complexes *syn*- and *anti*-tricarbonyl-π-1-methylallylcobalt.[23] However, the availability of a nearly pure sample of one isomer greatly facilitated the interpretation of the spectra of these cobalt complexes. The most intense peak in the spectrum of (IV) occurs at τ 4·91, and is assignable to the protons of a π-cyclopentadienyl ring.[18] A resonance of low intensity which appears as a multiplet at τ 5·1 is probably due to the central proton of the allylic system present in both isomers. The prominent doublets at τ 7·56 and 8·8 which both show a splitting of 6·0 c./sec. are due to the methyl groups. Additional resonances occurring in the region τ 7·1—9·4 were poorly resolved.

In view of the less-than-ideal nature of the n.m.r. spectrum, independent synthesis of the complex was undertaken. A solution of $K[C_5H_5{\cdot}Ni(CO)]$ was prepared by stirring a mixture of $[C_5H_5{\cdot}Ni(CO)]_2$ (2·0 g.; 6·7 mmoles) and potassium (0·3 g.; 7·5 g.-atoms) in dry tetrahydrofuran (25 ml.) for 30 min. under nitrogen. The solution was removed from excess of potassium, then cooled in an ice-bath, and crotyl chloride (1·0 g.; 11 mmoles) added during 10 min. The solution was stirred overnight. Solvent was evaporated (20 mm., 25°) and the volatile material was taken into the vacuum system. This was purified by trap-to-trap distillation. The fraction passing a trap held at −20° was discarded, leaving the red liquid π-cyclopentadienyl-π-1-methylallylnickel (700 mg.; 29%) [Found: C, 60·7; H, 7·0%; *M* (mass spectrum), 178. $C_9H_{12}Ni$

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[23] (*a*) Moore, Jonassen, Joyner, and Bertrand, *Chem. and Ind.*, 1960, 1304; (*b*) Bertrand, Jonassen, and Moore, *Inorg. Chem.*, 1963, **2**, 601.

requires C, 60·4; H, 6·8%; *M*, 178]. The i.r. and n.m.r. spectrum was identical with that of (IV).

Reaction Between Hexafluorobut-2-yne and Nickelocene.—Nickelocene (8·0 g.; 42 mmoles), hexafluorobut-2-yne (7·4 g.; 46 mmoles), and tetrahydrofuran (30 ml.) were kept at room temperature for 3 days. Hexafluorobut-2-yne (1·0 g.; 6 mmoles) was recovered under vacuum. The remainder of the material was then extracted with dichloromethane, the extract filtered, and the solvent evaporated (20 mm., 25°). The residue was extracted with pentane and the extract chromatographed on alumina. A yellow band was eluted with pentane to give an oily yellow solid. Repeated sublimation (30°/0·1 mm.) gave orange crystals (300 mg.; 2%) of (V), m. p. 74—75° (Found: C, 48·2; H, 3·1; F, 32·8. $C_{14}H_{10}F_6Ni$ requires C, 47·9; H, 2·9; F, 32·5%).

A dark green band was eluted with pentane–dichloromethane (9 : 1) to give a green-black solid. Sublimation of this solid (40°/0·1 mm.) gave $[\pi\text{-}C_5H_5\cdot Ni]_2C_4F_6$ (150 mg.), m. p. 89—90° (lit.,[20] 92°), having infrared spectrum identical with that of an authentic sample, prepared as described elsewhere.[20]

A sample of (V) (50 mg.; 0·14 mmole), hexafluorobut-2-yne (70 mg.; 0·44 mmole), and tetrahydrofuran (1 ml.) were sealed in a glass ampoule. After several months at room temperture, the solution was still yellow. Since dilute solutions of $(\pi\text{-}C_5H_5\cdot Ni)_2C_4F_6$ are intensely coloured, this indicates that the latter is not formed from (V).

The proton n.m.r. spectrum of (V) was recorded as a 10% solution in trichlorofluoromethane. Chemical shifts of the absorptions and relative intensities were as follows τ 3·30(2), 4·72(5), 6·17(2), 7·67(1). These shifts are very similar to those [τ 3·38(2), 4·70(5), 6·3(8), 7·82(1)] observed in the spectrum of a sample prepared by us of the compound obtained from nickelocene and dimethyl acetylenedicarboxylate.[21] The spectrum of (V) can be assigned as follows: τ 4·72, single sharp signal due to $\pi\text{-}C_5H_5$ ring; τ 3·30 multiplet, uncomplexed olefinic protons; τ 6·17 multiplet, two protons at bridgehead; τ 7·67 multiplet, proton on carbon atom σ-bonded to nickel in (V).[21,24] The fluorine-19 spectrum of (V) contains a single absorption at 59·7 p.p.m. (relative to CCl_3F) in the chemical shift range characteristic of CF_3 groups adjacent to carbon–carbon double bonds.[7c]

We are indebted to Dr. Warren Steele for recording the mass spectra of some of the complexes.

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[24] Pitcher, Ph.D. Thesis, Harvard University, 1962.