Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part VII.[1] Bis(triphenylphosphine)(π-ethylene)nickel and Tetrakis(methyldiphenylphosphine)nickel

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Bis(triphenylphosphine)(π-ethylene)nickel reacts with hexafluoroacetone to form $(Ph_3P)_2Ni[(CF_3)_2CO]$, and with chloro- and bromo-trifluoroethylene to give the vinyl complexes *trans*-$(Ph_3P)_2Ni(CF{:}CF_2)X$ [X = Cl or Br]. A *cis–trans* mixture of 1,2-dichloro-1,2-difluoroethylene reacts similarly forming a mixture of *trans*-$(Ph_3P)_2Ni$(*cis*-CF:CFCl)Cl and *trans*-$(Ph_3P)_2Ni$-(*trans*-CF:CFCl)Cl. Analogous reactions take place with tetrakis(methyldiphenylphosphine)nickel. Hexafluoropropene, hexafluorocyclobutene, 1,1-difluoroethylene, and monofluoroethylene displace ethylene from $(Ph_3P)_2Ni(C_2H_4)$ to afford $(Ph_3P)_2Ni$(fluoro-olefin) complexes; whereas trifluoroethylene gives the compound $(Ph_3P)_2Ni(CF_2CFH)_2$, postulated to contain a five-membered C_4Ni ring. The nickel(II) complexes $(Ph_3P)_2Ni(R_F)I_2$ (R_F = CF_3 or C_3F_7) are formed when R_FI is reacted with $(Ph_3P)_2Ni(C_2H_4)$. Pentafluorobenzoyl chloride reacts with $(Ph_3P)_2Ni(C_2H_4)$ to form $(Ph_3P)_2Ni(C_6F_5)Cl$.

RECENTLY we described[2] the synthesis of complexes $1,5\text{-}C_8H_{12}Ni[(CF_3)_2CX]$ (X = O or S), which form the compounds $(R_3P)_2Ni[(CF_3)_2CX]$ by reaction with tertiary phosphines. Bis(triphenylphosphine)(π-ethylene)nickel is reported[3] to undergo an unusual reaction with tetrafluoroethylene to form $(Ph_3P)_3Ni(C_2F_4)$. Here we report studies on reactions of other fluorocarbon compounds with $(Ph_3P)_2Ni(C_2H_4)$ and with $(Ph_2MeP)_4Ni$. The idendity of the crystalline complexes obtained (Table 1) was established by analysis and i.r. (Table 2) and ^1H and ^{19}F n.m.r. spectroscopy (Table 3).

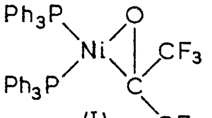
TABLE 1

Fluorocarbon-nickel complexes

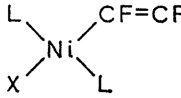
			Found (%)							Required (%)						
		M.p.	C	H	Br/Cl/I	F	P	Ni	M	C	H	Br/Cl/I	F	P	Ni	M
(I)	$(Ph_3P)_2Ni[(CF_3)_2CO]$	234—235°	62·3	4·1		15·3	8·1	8·0		62·5	4·1		15·3	8·3	7·9	
(II)	*trans*-$(Ph_3P)_2Ni(CF{:}CF_2)Cl$	169	65·6	4·2	5·2	8·3	9·2	8·7		65·5	4·3	5·1	8·2	8·8	8·4	
(III)	*trans*-$(Ph_3P)_2Ni(CF{:}CF_2)Br$	159—161	61·0	4·2	10·1	8·0	8·1	8·0	730	61·3	4·2	10·8	7·7	8·3	7·9	744
(IV)	*trans*-$(Ph_3P)_2Ni(CCl{:}CF_2)Cl$	184	64·1	4·3	9·5					63·7	4·2	9·9				
(V)	*trans*-$(Ph_2MeP)_2Ni(CF{:}CF_2)Cl$	125	58·0	4·8	6·3				590	58·4	4·5	6·2				575
(VI)	*trans*-$(Ph_3P)_2Ni(CF{:}CFCl)Cl$	179	64·1	4·5	9·5		8·7		688	63·7	4·2	9·9		8·7		716
(VII)	*trans*-$(Ph_2PMe)_2Ni(CF{:}CFCl)Cl$	134—135	56·5	4·5	12·1				600	56·7	4·5	12·0				591
(VIII)	$(Ph_3P)_2Ni(CF_3CFCF_2)$	142—143	63·5	4·4			8·5			63·8	4·1			8·5		
(IX)	$(Ph_3P)_2Ni(cyclo\text{-}C_4F_6)$	148	64·1	4·1		15·2				64·5	4·1		15·1			
(X)	$(Ph_3P)_2Ni(CF_2CFH)_2$	125—130	64·1	4·5		14·9			710	64·3	4·3		15·3			747
(XI)	$(Ph_3P)_2Ni(CF_2CH_2)$	110 dec.	70·2	5·2		5·1				70·5	5·0		5·8			
(XII)	$(Ph_3P)_2Ni(CFHCH_2)$	90 dec.	72·5	5·3						72·5	5·3					
XIII)	$(Ph_3P)_2Ni(CF_3)I_2$	207—209	49·5	3·5	28·3	6·4			925	49·1	3·4	27·9	6·3			906
(XIV)	$(Ph_3P)_2Ni(C_3F_7)I_2$	220—222	46·2	3·2	24·7				990	46·5	3·0	25·2				1006
(XV)	$(Ph_3P)_2Ni(C_6F_5)Cl$	210	63·7	3·7	4·7					64·0	3·8	4·5				

Hexafluoroacetone rapidly reacts with an ether solution of $(Ph_3P)_2Ni(C_2H_4)$ to form (I), a compound previously obtained by treating $(\pi\text{-}C_8H_{12})Ni[(CF_3)_2CO]$ with triphenylphosphine.[2] The ^{19}F n.m.r. spectrum of (I) shows a doublet; this splitting arises from $^{31}P-^{19}F$ coupling with the phosphorus nucleus *trans* to the CF_3 groups, assuming that J_{PF} *trans* > J_{PF} *cis*. As previously discussed,[2,4] these observations suggest a square-planar structure as depicted, in which the nickel atom is formally in a 2+ oxidation state.

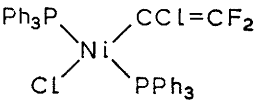
Chlorotrifluoroethylene, bromotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene react with $(Ph_3P)_2Ni(C_2H_4)$ in ether to form the air-stable crystalline complexes (II), (III), and (IV) respectively. The complexes are σ-bonded nickel–fluorovinyl complexes as illustrated, and not the nickel analogues of the recently described[5] $(Ph_3P)_2Pt$(fluoro-olefin) complexes. The i.r. spectra of (II), (III), and (IV) show, in each case, a medium to strong band in the region 1700—1720 cm^{-1} indicating the presence of a fluorovinyl group σ-bonded to a



(I)



(II) L = Ph_3P, X = Cl
(III) L = Ph_3P, X = Br
(V) L = Ph_2PMe, X = Cl



(IV)

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[2] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 20.

[3] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356.

[4] B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.

[5] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

TABLE 2

I.r. spectra (cm.$^{-1}$) *

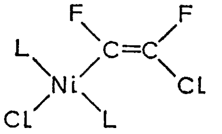
(I)	1585w, 1570w, 1475m, 1432s, 1305s, 1215m, 1172s, 1162w, 1136sh, 1130s, 1097sh, 1093m, 1027w, 998w, 932s, 822m, 754w, 742m, 738m, 696sh, 690s
(II)	1718s, 1585w, 1570w, 1435s, 1431s, 1308w, 1229s, 1183m, 1158w, 1118w, 1098s, 1067m, 1053s, 1027w, 999w, 972s, 751s, 741s, 702s, 690s
(III)	1725w, 1715m, 1478m, 1436s, 1431s, 1308w, 1230m, 1185w, 1156w, 1118w, 1095sh, 1090m, 1065w, 1052m, 1025w, 998w, 969s, 750m, 740s, 700m. 690s
(IV)	1710s, 1700sh, 1769w, 1585w, 1570w, 1479m, 1435sh, 1432s, 1303w, 1282w, 1262w, 1205s, 1185w, 1155w, 1118w, 1099sh, 1095s, 1065w, 1026m, 999m, 958s, 845w, 827m, 756m, 750m, 742s, 715w, 699s, 690s
(V)	1705m, 1482m, 1436s, 1302w, 1281w, 1253w, 1240w, 1166s, 1096s, 1075w, 1063w, 1048w, 1030w, 1023w, 995w, 964s, 881s, 774m, 730s, 690s
(VI)	1632w, 1585w, 1570w, 1479m, 1436sh, 1433s, 1338w, 1305w, 1203w, 1185w, 1155w, 1122w, 1094s, 1083m, 1079w, 1040w, 1025m, 999w, 970w, 955w, 882m, 767m, 742s, 698s, 690s
(VII)	1625w, 1590w, 1573w, 1485m, 1458s, 1436s, 1335w, 1310w, 1264w, 1185m, 1170m, 1123m, 1103s, 1053w, 1035w, 1026w, 1000w, 964w, 855s, 768w, 745m, 735s, 693s
(VIII)	1583w, 1475m, 1431s, 1291s, 1165m, 1151m, 1110s, 1094m, 1085w, 1065w, 1038w, 1026m, 993w, 960s, 771s, 739s, 720w, 690w, 680m
(IX)	1580w, 1482m, 1438s, 1432s, 1400s, 1290w, 1256s, 1227s, 1160w, 1139w, 1093m, 1061s. 1051m, 1020s, 1009m, 950w, 915s, 909s, 876s, 738m, 722s, 718s, 709w, 695sh, 690s
(X)	1585w, 1571w, 1481m, 1479m, 1439s, 1432s. 1364m, 1347w, 1332w, 1314m, 1260s, 1236w, 1196w, 1170w, 1160m, 1150m, 1119s, 1102m, 1094m, 1070w, 1050w, 1029w, 1015m, 961w, 945m, 924s, 875s, 778m, 765w, 750m, 741s, 722w, 703m, 695s
(XI)	1583w, 1475m, 1431s, 1366w, 1305w, 1260w, 1186sh, 1180m, 1155w, 1120m, 1094m, 1087m, 1069w, 1024m, 995w, 872w, 846m, 840m, 752m, 745s, 740s, 720w, 692s
(XII)	1585w, 1475m, 1430s, 1304w, 1180s, 1118m, 1092s, 1086s, 1067w, 1022m, 995w, 820w, 738s, 720w, 690s
(XIII)	1583w, 1570w, 1478m, 1431s, 1183m, 1158m, 1125m, 1095m, 1073w, 1030w, 1000w, 745s, 727s, 695s
(XIV)	1585w, 1570w, 1481m, 1435s, 1433s, 1325m, 1260w, 1210m, 1180m, 1160w, 1146w, 1110s, 1096s, 1073w, 1030w, 998w, 960w, 795w, 742m, 736w, 723m, 715w, 702w, 690s
(XV)	1489s, 1468m, 1440s, 1420s, 1340w, 1300w, 1265w, 1170w, 1145w, 1110w, 1085m, 1040w, 1030w, 1015w, 987w, 939s, 778m, 740m, 730m, 710w, 693m, 680s, 652w

* Recorded with a Perkin–Elmer 257 grating spectrophotometer, using Nujol mulls.

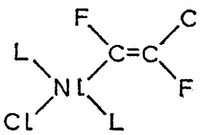
metal.[5-7] Examination of the ^{19}F n.m.r. spectra confirmed this assumption, in that the spectra of (II) and (III) showed three multiplets with coupling constants and chemical shifts (Table 3) characteristic[7] of the group $Ni{\cdot}CF{:}CF_2$. The spectrum of (IV) showed two typical vinylic resonances with geminal ^{19}F–^{19}F coupling as expected for $Ni{\cdot}CCl{:}CF_2$.[7] The magnitude of the ^{31}P–^{19}F coupling constants suggests, by comparison[5,7] with *cis*- and *trans*-$(Et_3P)_2M(CF{:}CF_2)X$ (M = Ni, Pd, or Pt), that the phosphine ligands in (II), (III), and (IV) have a relative *trans*-configuration.

Support for this stereochemical assignment was obtained from a study of the reaction of tetrakis(methyldiphenylphosphine)nickel with chlorotrifluoroethylene. The crystalline product (V) was characterised as a perfluorovinyl complex by the presence of a strong $C{:}C$ band at 1705 cm^{-1}. The ^{19}F n.m.r. spectrum (Table 3) confirmed the presence of the $Ni{\cdot}CF{:}CF_2$ systems, and comparison of the ^{31}P–^{19}F coupling constants observed for (V) with those of (II) and (III) indicated that they had an identical stereochemistry, *i.e.* a relative *trans*-configuration for the phosphine ligands. Moreover, the ^1H n.m.r. spectrum of (V) confirmed[8,9] the *trans*-assignment, because the CH_3P signal appeared as an apparent triplet, *i.e.* an $X_3AA'X_3'$ system with substantial AA′ coupling.

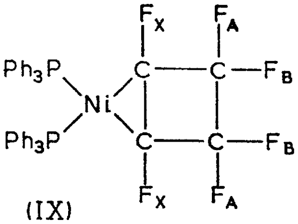
A mixture (1 : 1) of *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene reacted with $(Ph_3P)_2Ni(C_2H_4)$ to form an inseparable mixture of the crystalline complexes (VIa) and (VIb). The corresponding reaction with tetrakis(methyldiphenylphosphine)nickel gave a mixture of (VIIa) and (VIIb). The identity and stereochemistry of these compounds as σ-bonded nickel–fluorovinyl complexes was clearly defined by the i.r. (Table 2), ^{19}F n.m.r., and ^1H n.m.r. (Table 3) spectra. The presence of a mixture of isomers in (VI) and (VII) was demonstrated by the appearance of four multiplets in the ^{19}F n.m.r. spectra.



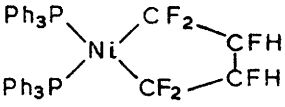
(VIa) L = Ph_3P
(VIIa) L = Ph_2PMe



(VIb) L = Ph_3P
(VIIb) L = Ph_2PMe

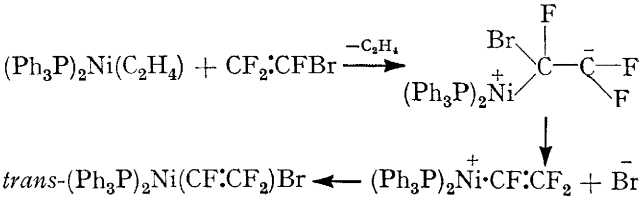


(IX)



(X)

The possible mechanism of formation of (II)—(VII) merits comment. A plausible reaction path could proceed *via* an intermediate carbanion formed by direct nucleophilic attack of the nickel complex on the fluoro-olefin, followed by migration of halide anion, *e.g.*,



$$(Ph_3P)_2Ni(C_2H_4) + CF_2{:}CFBr \xrightarrow{-C_2H_4} (Ph_3P)_2\overset{+}{Ni}-CFBr-\overset{-}{C}F_2$$

$$\downarrow$$

$$trans\text{-}(Ph_3P)_2Ni(CF{:}CF_2)Br \longleftarrow (Ph_3P)_2\overset{+}{Ni}{\cdot}CF{:}CF_2 + \overset{-}{Br}$$

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[6] S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, 1961, **17**, 412.

[7] A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 66.

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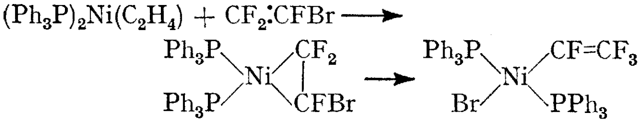
[9] R. K. Harris, *Inorg. Chem.*, 1966, **5**, 701.

Such a mechanism has been proposed for the formation of fluorovinyl–metal carbonyl complexes in the reaction of fluoro-olefins with carbonylmetal anions.[10] However, by analogy with the related platinum system,[5] a more likely reaction path is initial formation of a fluoro-olefin complex, which rapidly undergoes a 'vinyl-rearrangement':



These results, and similar observations with the related palladium system,[11] indicate a reactivity sequence Pt < Pd < Ni for the rearrangement of chloro- or bromo-fluoroethylenes on these metals.

TABLE 3

Fluorine-19 chemical shifts (p.p.m.) * and coupling constants (c./sec.) for complexes $F^1F^2C{:}C(F^3)NiL_2X$ (F^2 and F^3 *trans*), $F^1F^2C{:}C(Cl)NiL_2X$ (F^1 and F^2 geminal), $(Cl)F^2C{:}C(F^3)NiL_2X$ (F^2 and F^3 *trans*), and $(Cl)F^1C{:}C(F^3)NiL_2X$ (F^1 and F^3 *cis*)

	δ(1)	δ(2)	δ(3)	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J(P,F^1)$	$J(P,F^2)$	$J(P,F^3)$
(II) *trans*-$(Ph_3P)_2Ni(CF{:}CF_2)Cl$	88·2	130·3	158·0	105	40·0	110	7·0	7·0	5·5
(III) *trans*-$(Ph_3P)_2Ni(CF{:}CF_2)Br$	88·6	130·3	157·0	114	36·0	110	7·0	7·0	5·5
(IV) *trans*-$(Ph_3P)_2Ni(CCl{:}CF_2)Cl$	98·2	72·9		72			2·0		
(V) *trans*-$(Ph_2PMe)_2Ni(CF{:}CF_2)Cl$ [a]	89·2	130·4	159	105	40	110	7·0	7·0	5·5
† (VIa) *trans*-$((Ph_3P)_2Ni(CF\overset{c}{:}CFCl)Cl$	90·1		100·1		13·0		7·5		
(VIb) *trans*-$(Ph_3P)_2Ni(CF\overset{t}{:}CFCl)Cl$		118·9	130·1			122		5·5	7·5
† (VIIa) *trans*-$(Ph_2PMe)_2Ni(CF\overset{c}{:}CFCl)Cl$ [b]	91·7		103·9		12·0		7·0		
(VIIb) *trans*-$(Ph_2PMe)_2Ni(CF\overset{t}{:}CFCl)Cl$ [b]		122	130·1			121·5		7·0	7·0

* ^{19}F chemical shifts are rel. to CCl_3F (0·0 p.p.m.) increasing to high field. † Complexes (VI) and (VII) studied as mixtures, see text.

[a] ^1H n.m.r. resonances (studied at −60° in CH_2Cl_2) at τ 2·40—2·69 [20H, m, C_6H_5P] and τ 8·23 [6H, t, CH_3P, J_{PH} 6·5 c./sec.]. [b] ^1H n.m.r. resonances (studied at −60° in CH_2Cl_2) at τ 2·39—2·70 [20H, m, C_6H_5P] and τ 8·14 [6H, t, CH_3P, J_{PH} 6·5 c./sec.].

Treatment of $(Ph_3P)_2Ni(C_2H_4)$ with hexafluoropropene, hexafluorocyclobutene, 1,1-difluoroethylene, and monofluoroethylene displaced the ethylene and gave, respectively, the crystalline complexes (VIII), (IX), (XI), and (XII) with molecular formula $(Ph_3P)_2Ni$(fluoro-olefin). These complexes show no band in their i.r. spectra (Table 2) corresponding to a fluorovinyl–nickel group, also there are no bands which can obviously be attributed [5,12] to co-ordinated double-bonds. Thus, the compounds are probably best regarded as nickel(II) complexes, analogous to the platinum compounds.[5] Unfortunately, except for (IX), ^{19}F n.m.r. spectra could not be obtained due to decomposition of the complexes in solution. The ^{19}F n.m.r. spectrum of the hexafluorocyclobutene complex (IX) showed three multiplets with equal intensities at 87·6 (F_A), 116·0 (F_B) and 180·0 p.p.m. (F_X). The two multiplets at lowest field arise from the two fluorine nuclei of the CF_2 groups being non-equivalent, so that one fluorine nucleus of each pair is nearer to the nickel atom.[5] Although the 'AB' patterns were too complex for detailed analysis, the value (198·0 c./sec.) of $J(F_AF_B)$ is similar to that observed for substituted fluorocyclobutanes.[13]

Trifluoroethylene also reacts with $(Ph_3P)_2Ni(C_2H_4)$, but in contrast the stable crystalline complex (X) was obtained, which probably contains a nickel(II) five-membered heterocyclic-ring system. However, only broad complex multiplets were observed in the ^{19}F and ^1H n.m.r. spectra, suggesting that the reaction affords a mixture of isomers. We have recently characterised several nickel complexes of the type $L_2Ni(CF_2)_4$.[14a]

Treatment of the zero-valent platinum or palladium complexes $(Ph_3P)_4M$ or $(Ph_2PCH_2{\cdot}CH_2PPh_2)_2M$ with perfluoroalkyl iodides has been shown [15] to give the perfluoroalkyl(iodo) compounds $(Ph_3P)_2M(R_F)I$ or (diphos)$M(R_F)I$ ($R_F = CF_3$, C_2F_5, or C_3F_7). These reactions are clearly related to those which occur between (diphos)$Ni(CO)_2$ and C_2F_5I or C_3F_7I, affording (diphos)$Ni(R_F)I$ ($R_F = C_2F_5$ or C_3F_7).[16] However, the reaction of ethylenebis(triphenylphosphine)nickel with CF_3I or C_3F_7I takes a different course, forming respectively the crystalline maroon complexes (XIII) and (XIV), characterised as monomeric five-co-ordinate nickel(III) complexes (Table 1). In agreement with their formulation as nickel(III) complexes, broad ^{19}F n.m.r. resonances were observed, and both complexes were found to have magnetic moments of 1·9 B.M. by means of Evans' n.m.r. method.[17] In contrast with the reaction between $(Ph_3P)_2Ni(C_2H_4)$ and CF_3I or C_3F_7I, the zerovalent nickel complex $(Bu^n{}_3P)_2Ni(C_8H_{12})$ reacts with CF_3I to give the expected product $(Bu^n{}_3P)_2Ni(CF_3)I$, albeit together with $(Bu^n{}_3P)_2NiI_2$.[14b]

Pentafluorobenzoyl chloride also reacts with bis(triphenylphosphine)(π-ethylene)nickel to give a yellow

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[14a] C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), in the press.

[14b] C. S. Cundy, Ph.D. Thesis, Bristol University, 1969.

[15] D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 164.

[16] D. W. McBride, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 1963, 723.

[17] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

crystalline complex (XV). The absence of an aryl band in the i.r. spectrum (Table 2) suggested that the compound might be similar in nature to (I). However, the ^{19}F *n.m.r.* signal of the *ortho*-fluorine nuclei were at low field (see below) indicating [18] that (XV) has the molecular formula $(Ph_3P)_2Ni(C_6F_5)Cl$. The latter is probably formed by decarbonylation of an intermediate C_6F_5CONi complex.

EXPERIMENTAL

Fluorine-19 and ^1H n.m.r. spectra were measured at 94·1 and 100 MHz respectively on a Varian HA 100 spectrometer. Molecular weight measurements were determined in chloroform with a Mechrolab Osmometer. All reactions were carried out under nitrogen. ^{19}F N.m.r. studies showed that the commercial sample (Penninsular Chemical Co.) of $CFCl{:}CFCl$ used contained approximately equal amounts of the *cis*- and *trans*-isomer. Two peaks were observed at 105·1 (*cis*) and 119·6 (*trans*) p.p.m.[19]

Preparation of Bis(triphenylphosphine)(π-ethylene)nickel.—Details of the synthesis of $(Ph_3P)_2Ni(C_2H_4)$ have not been given.[20] In this work the compound was prepared as follows. Diethoxyethylaluminium, made by adding ethanol (5·7 g., 12·4 mmoles) to triethylaluminium (7·1 g., 6·2 mmoles) at 0°, was added dropwise with stirring to anhydrous nickel acetylacetonate (5·0 g., 18·2 mmoles) and triphenylphosphine (10·24 g., 39 mmoles) in diethyl ether (100 ml.) saturated with ethylene at 0°. Ethylene was bubbled through the reaction mixture during the addition. After 24 hr. at 0°, the yellow crystalline precipitate was filtered off, washed with ether (0°, 2 × 30 ml.), and hexane (30 ml.), and dried *in vacuo* to afford bis(triphenylphosphine)(π-ethylene)nickel (9·5 g., 92%) (Found: C, 74·5; H, 5·4%. Calc. for $C_{38}H_{34}P_2Ni$: C, 74·4; H, 5·6%), $\nu_{max.}$ (Nujol) 1479m, 1433s, 1260w, 1188w, 1152w, 1118w, 1090m, 1085m, 1069w, 1036w, 995w, 752w, 742m, 731m, and 690s cm.$^{-1}$.

Reactions of $(Ph_3P)_2Ni(C_2H_4)$.—(a) *With hexafluoroacetone.* A sample (0·5 g., 0·81 mmole) of $(Ph_3P)_2Ni(C_2H_4)$ in diethyl ether (20 ml.) was introduced into a Carius tube (100 ml.). Hexafluoroacetone (5 mmoles) was condensed (−196°) into the tube, and the reaction mixture was warmed to room temperature. After 12 hr. the solvent was removed under reduced pressure, and the benzene-soluble material was recrystallised from benzene to give golden-brown *crystals* (I) (0·34 g., 61·5%). The ^{19}F n.m.r. spectrum (in CH_2Cl_2) showed a single resonance at 65·2 p.p.m. (CF_3C, J_{PF} *trans* 12·2 c./sec., J_{PF} *cis* $<1·0$ c./sec.).

(b) *With chlorotrifluoroethylene.* To $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) in diethyl ether (20 ml.) was added chlorotrifluoroethylene (5 mmoles). After 12 hr. at room temperature, solvent was removed under reduced pressure and the residue was recrystallised from benzene, and washed with hexane to give golden-brown *crystals* (II) (0·36 g., 64%).

(c) *With bromotrifluoroethylene.* The product from the reaction of $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) with bromotrifluoroethylene (5 mmoles) was recrystallised from benzene to afford golden-brown *crystals* (III) (0·53 g., 87%).

(d) *With* 1,1-*dichloro*-2,2-*difluoroethylene.* Complex (IV) (0·36 g., 63%) was obtained as yellow *crystals* by treating $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) with 1,1-dichloro-2,2-difluoroethylene (5 mmoles) in diethyl ether (20 ml.); it was recrystallised from methylene chloride–hexane.

(e) *With a* cis–trans *mixture of* 1,2-*dichloro*-1,2-*difluoro*, *ethylene.* Bis(triphenylphosphine)(π-ethylene)nickel (0·5 g., 0·81 mmole) and 1,2-dichloro-1,2-difluoroethylene (5 mmoles) afforded, as revealed by ^{19}F n.m.r. studies, a *cis–trans* mixture of (VIa) and (VIb) (0·51 g., 87%). The yellow *crystals* were recrystallised from methylene chloride–hexane.

(f) *With hexafluoropropene.* By reaction of $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) with hexafluoropropene (5 mmoles) the complex (VIII) (0·53 g., 89%) was obtained as lemon-yellow *crystals*, which rapidly decomposed in solution.

(g) *With hexafluorocyclobutene.* Similarly, $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) and hexafluorocyclobutene (5 mmoles) reacted to form opaque yellow *crystals*, which were washed with ether (10 ml.) and hexane (10 ml.) to give (IX) (0·45 g., 75%). The complex decomposed slowly in benzene solution.

(h) *With trifluoroethylene.* Treatment of $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) with trifluoroethylene (5 mmoles) in diethyl ether (15 ml.) gave yellow *crystals* (X) (0·35 g., 58%); these were washed with ether (10 ml.) and hexane (10 ml.).

(i) *With* 1,1-*difluoroethylene.* The complex (XI) (0·48 g., 92%) was obtained similarly as yellow *crystals* by treating $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) with 1,1-difluoroethylene (5 mmoles).

(j) *With monofluoroethylene.* Similarly (XII) (0·28 g., 56%) was obtained from $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) and $CFH{:}CH_2$ (5 mmoles).

(k) *With trifluoroiodomethane.* $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) and trifluoroiodomethane (5 mmole) in diethyl ether (15 ml.) were sealed in a Carius tube. After 24 hr. at room temperature a maroon *crystalline* solid was filtered off to give (XIII) (0·53 g., 72%), from methylene chloride–hexane.

(l) *With heptafluoroiodopropane.* A similar reaction of $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·81 mmole) with heptafluoroiodopropane (5 mmoles) gave maroon *crystalline* (XIV) (0·6 g., 75%).

(m) *With pentafluorobenzoyl chloride.* A solution of pentafluorobenzoyl chloride (0·5 g., 2·2 mmoles) in ether (5 ml.) was added dropwise with stirring to a solution of $(Ph_3P)_2Ni(C_2H_4)$ (0·5 g., 0·8 mmole) in ether (15 ml.). After 2 days at room temperature, solvent was removed under reduced pressure and the residue was dissolved in methylene chloride (10 ml.). Addition of hexane (5 ml.) precipitated a blue powder, and slow evaporation of the solvent gave yellow *crystals* (XV) (0·4 g., 63%), from methylene chloride–hexane. The ^{19}F n.m.r. spectrum (in CH_2Cl_2) showed resonances at 120·5 [2F, d, F^1, F^5, $J(F^{1,2}) = J(F^{4,5})$ 25·0 c./sec.], 162·6 [1F, t, F^3, $J(F^{2,3}) = J(F^{3,4})$ 18·5 c./sec.] and 163·7 p.p.m. [2F, m, F^2, F^4, $J(F^{2,3})$ 18·5 c./sec., $J(F^{1,2})$ 25·0 c./sec.]. This spectrum is very similar to that of *trans*-$(Et_3P)_2Ni(C_6F_5)Cl$ [18] further confirming the nature of (XV).

Reactions of Tetrakis(methyldiphenylphosphine)nickel.—(a) *With chlorotrifluoroethylene.* Tetrakis(methyldiphenylphosphine)nickel (0·5 g., 0·58 mmole) in diethyl ether (15 ml.) in a sealed tube was treated with chlorotrifluoro-

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ethylene (5·0 mmoles). After 12 hr. at room temperature, solvent was removed under reduced pressure. The yellow gum was heated under reflux in hexane (30 ml.) to give (V) (0·30 g., 89%) as an orange powder from methylene chloride–hexane.

(b) *With a* cis–trans *mixture of* 1,2-*dichloro*-1,2-*difluoroethylene*. A similar reaction of tetrakis(methyldiphenylphosphine)nickel (0·5 g., 0·58 mmole) with 1,2-dichloro-1,2-difluoroethylene (5 mmoles) gave an inseparable isomeric orange crystalline mixture (VIIa) and (VIIb) (0·51 g., 87%); purified by recrystallisation from methylene chloride–hexane.

We thank the U.S. Air Force Office of Scientific Research through its European Office of Aerospace Research for support of the work described, and the S.R.C. for a research studentship (J. A.-S.).

[9/1042 *Received, June* 19*th*, 1969]