View Article Online / Journal Homepage / Table of Contents for this issue

## Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XII.<sup>1</sup> Fluoro-olefin Reactions of Zerovalent Nickel Complexes

By C. S. Cundy, M. Green and F. G. A. Stone,\* Department of Inorganic Chemistry, The University, Bristol **BS8 1TS** 

Bis(cyclo-octa-1,5-diene)nickel reacts with perfluoropropene to give (1,5-C<sub>8</sub>H<sub>12</sub>)Ni(C<sub>3</sub>F<sub>8</sub>) (I), which reacts with triphenyl- or triethyl-phosphine to afford  $(Ph_3P)_2Ni(C_3F_6)$  (IIa) and  $(Et_3P)_2Ni(C_3F_6)$  (IIb), respectively. The zerovalent nickel compounds  $(1,5-C_8H_{12})(Et_3P)_2Ni$ ,  $(1,5-C_8H_{12})[(Bu^n)_3P]_2Ni$ ,  $[(Ph_2PCH_2)_2][(Bu^n)_3P]_2Ni$ , (Et<sub>3</sub>P)<sub>4</sub>Ni, and (Ph<sub>2</sub>PMe)<sub>4</sub>Ni, react with tetrafluoroethylene to give the stable crystalline octafluoronickelacyclopentane complexes  $L_2Ni(CF_2)_4$  (L = Et<sub>3</sub>P, Bu<sup>n</sup><sub>3</sub>P, or Ph<sub>2</sub>PMe; or  $L_2 = Ph_2PCH_2CH_2PPh_2$ ). These complexes readily undergo ligand-exchange reactions, and by treatment with 2,2'-bipyridyl or cyclo-octa-1,5-diene and zinc bromide give, in certain cases, the crystalline derivatives  $C_{10}H_8N_2Ni(CF_2)_4$  (VIII) and  $(1.5-C_8H_{12})Ni(CF_2)_4$  (IX). The diene ligand in the latter can be displaced with triphenylphosphine or  $\gamma$ -picoline to give (Ph<sub>3</sub>P)<sub>2</sub>Ni(CF<sub>2</sub>)<sub>4</sub> and  $(\gamma \text{-picoline})_2 \text{Ni}(\text{CF}_2)_4$ , respectively. Treatment of  $(1,5-C_8H_{12})_2 \text{Ni}$  with  $C_2F_4$  gives an unstable compound, which on addition of Ph<sub>2</sub>PMe or Et<sub>3</sub>P gave L<sub>2</sub>Ni(CF<sub>2</sub>)<sub>4</sub>. The compound  $[(\text{MeO})_3\text{P}]_2 \text{Ni}(\text{CF}_2)_4$  is obtained from tetrafluoroethylene and tetrakis(trimethyl phosphite)nickel, and tetrakis(methyldiphenylphosphine)nickel reacts with trifluoroethylene to give  $(Ph_2PMe)_2Ni(C_2F_3H)_2$ .

THE formation of stable complexes by the reaction of low-valent transition-metal compounds with unsaturated systems carrying electronegative substituents has recently attracted considerable interest.<sup>1-6</sup> The bonding in such complexes,<sup>2,4-6</sup> and the way in which co-ordination modifies the reactivity of the unsaturated system,<sup>5</sup> are both important aspects which are receiving attention. Our detailed study of the reactions between low-valent nickel derivatives and unsaturated fluorinated com-

<sup>1</sup> Part XI, Beverley Clarke, M. Green, and F. G. A. Stone, J. Chem. Soc. (A), 1970, 951.
 <sup>2</sup> W. H. Baddley, J. Amer. Chem. Soc., 1968, 90, 3705.
 <sup>3</sup> J. P. Collman and W. R. Roper, Adv. Organometallic Chem.,

- 1968, 7, 54.
- J. A. McGinnety and J. A. Ibers, Chem. Comm., 1968, 235. <sup>5</sup> M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, J. Chem. Soc. (A), 1968, 2525.

pounds has indicated the existence of an extensive fluorocarbon-nickel chemistry differing in some aspects from that of the other members of the triad, palladium and platinum.7 The reactions of bis(cyclo-octa-1,5diene)nickel with hexafluoroacetone and with 2,2,4,4tetrakis(trifluoromethyl)-1,3-dithietan,8,9 of bis(methylallyl)nickel with tetrafluoroethylene,<sup>8</sup> and of ethylenebis-(triphenylphosphine)nickel with fluoro-olefins and hexafluoroacetone<sup>10</sup> have previously been described. We

<sup>6</sup> M. Cooke and M. Green, J. Chem. Soc. (A), 1969, 651.

7 A. J. Mukhedkar, M. Green, and F. G. A. Stone, J. Chem. Soc. (A), 1969, 3023.

<sup>8</sup> Jane Browning, D. Cook, C. S. Cundy, M. Green, and F. G. A. Stone, *Chem. Comm.*, 1968, 929.

<sup>9</sup> Jane Browning, C. S. Cundy, M. Green, and F. G. A. Stone, J. Chem. Soc. (A), 1969, 20. <sup>10</sup> J. Ashley-Smith, M. Green, and F. G. A. Stone, J. Chem.

Soc. (A), 1969, 3019.

report now an investigation into the fluoro-olefin chemistry of bis(cyclo-octa-1,5-diene)nickel and related tertiary phosphine nickel complexes.

A solution of bis(cyclo-octa-1,5-diene)nickel<sup>11</sup> in

analysis suggested the illustrated structure. In agreement, the <sup>1</sup>H n.m.r. spectrum displayed resonances typical of co-ordinated cyclo-octa-1,5-diene, and the <sup>19</sup>F n.m.r. spectrum showed four resonances with

## TABLE 1

I.r. spectral bands (cm.<sup>-1</sup>) \*

- 1053s, 991w, 964s, 859w, 824m, 770s, 737w, 728vw, 687s, 653m (IIb)  $(Et_{3}P)_{2}Ni(C_{3}F_{6})$ 1417w, 1365m, 1294s, 1255w, 1239vw, 1155s, 1115s, 1088vw, 1068vw, 1048m, 1042m, 1032s, 1024s, 1007m, 985vw, 956s, 890vw, 784m, 765s, 741vw, 717m, 710w, 690s, 632m 2972s, 2941m, 2921m, 2883m, 1456s, 1413m, 1377w, 1329s, 1308w, 1261s, 1253s, 1218m, 1192w, (III)  $(Et_{3}P)_{2}Ni(CF_{2})_{4}$  † 1138vs, 1125s, 1066s, 1038s, 1028s, 1005m, 953vs, 893vs, 829m, 766s, 734w, 715s, 705m, 676w, 646m, 627m (IV)  $(Ph_2PMe)_2Ni(CF_2)_4$ 3082w, 3058w, 3016w, 2995w, 2924w, 1585vw, 1574vw, 1484m, 1435s, 1425w, 1415vw, 1363vw, 1325m, 1312w, 1297vw, 1285w, 1264m, 1247m, 1224m, 1186m, 1157s, 1139vs, 1131vs, 1106w, 1093m, 1079s, 1023w, 996m, 972vs, 963vs, 955vs, 928w, 916w, 906vs, 891vs, 879vs, 845vw, 836w, 833w, 755s, 753s, 735vs, 699vs, 691s, 683w, 645w 2961vs, 2929vs, 2873s, 1466s, 1457s, 1410w, 1378m, 1338m, 1305w, 1249m, 1227m, 1210m, (V)  $[(Bu^n)_3P]_2Ni(CF_2)_4$ 1179w, 1147vs, 1118m, 1088m, 1078s, 1045w, 1006w, 983s, 958vs, 947vs, 912s, 898s, 888vs, 848vs, 825w, 779m, 768m, 716m, 689w
  - 3082vw, 3053w, 3026vw, 3011vw, 2963w, 2928w, 2870vw, 1587vw, 1572vw, 1486w, 1438s, 1414w, [(Ph,PCH,),]Ni(CF,), 1407w, 1330m, 1307w, 1260w, 1247m, 1226w, 1184w, 1159w, 1137s, 1127m, 1099m, 1077s, 1055w, 1020w, 992m, 982s, 968m, 950s, 948vs, 871m, 841vw, 830w, 814m, 741s, 735m, 703m, 694m, 685s, 669m, 640w
- [(MeO)<sub>3</sub>P]<sub>2</sub>Ni(CF<sub>2</sub>)<sub>4</sub>, <sup>1</sup><sub>2</sub>C<sub>6</sub>H<sub>6</sub> 3018w, 2964s, 2910w, 2858m, 1462w, 1445m, 1340m, 1262w, 1250m, 1228w, 1176m, 1146s, (VII) 1133m, 1086s, 1073m, 1042vs, 1027vs, 1018vs, 988s, 958s, 907vs, 845m, 797m, 784s, 753s, 728m, 651m (VIII)  $(C_{10}H_8N_2)Ni(CF_2)_4$ 
  - 3148vw, 3102vw, 3093vw, 1608w, 1602w, 1571vw, 1567vw, 1558vw, 1498vw, 1479m, 1447s, 1418vw, 1351m, 1328vw, 1267m, 1258m, 1226w, 1175vw, 1145s, 1134m, 1108vw, 1083m, 1068w, 1017vw, 1002vw, 987s, 962s, 952s, 921vs, 886m, 849vw, 766s, 740vw, 713s

1485m, 1437m, 1401s, 1367w, 1342w, 1330m, 1304s, 1248vw, 1229w, 1167s, 1121s, 1089s, 1072s,

- 3012w, 2985w, 2956w, 2934w, 2894m, 2838w, 1483w, 1428m, 1341s, 1311w, 1271s, 1261s, 1232m, 1160vs, 1134m, 1094s, 1015s, 994m, 965vs, 911vs, 859m, 834w, 814w, 753m, 642m
  - 3065w, 3011vw, 1589w, 1479m, 1439s, 1434s, 1349w, 1338w, 1311vw, 1268w, 1253m, 1226w, 1180w, 1158m, 1149m, 1138s, 1131s, 1118vw, 1099w, 1089w, 1084m, 1078s, 1022w, 1019w, 991w, 977m, 963s, 959s, 909w, 895vs, 743m, 732m, 686s
- 2931vw, 1622m, 1503w, 1430m, 1335m, 1263m, 1259m, 1232w, 1228w, 1207w, 1142s, 1133s, 1083s, 1062m, 1033w, 984s, 970s, 956s, 919vs, 862vw, 845w, 808m, 802s, 720w, 713w (XI)  $(C_6H_7N)_2Ni(CF_2)_4$  $(Et_{3}P)_{4}(C_{8}H_{12})Ni_{2}(C_{2}F_{4})_{4}$ 
  - 2970m, 2939m, 2010w, 2879m, 1457m, 1425m, 1379w, 1355w, 1325m, 1311m, 1291m, 1271m, 1234w, 1208m, 1196m, 1170m, 1152vs, 1102w, 1072s, 1061s, 1047vs, 1035s, 1002w, 975s, 913s, 898s, 880m, 874w, 851vw, 841vw, 815w, 771s, 756m, 744m, 713w, 700w, 683w, 667w, 652vw, 646vw, 628vw
  - 3082vw, 3063w, 3045vw, 3029vw, 3009vw, 3004w, 2969vw, 1587vw, 1573vw, 1485m, 1479m, 1438s, 1434vs, 1379vw, 1375vw, 1364vw, 1338w, 1323w, 1308w, 1297vw, 1287w, 1261s, 1235w, 1198w, 1179w, 1164w, 1152w, 1146w, 1137w, 1107m, 1096m, 1066m, 1039m, 1030w, 1022w, 1016m, 993vw, 983vw, 964vw, 940s, 934s, 910s, 895vs, 879s, 853m, 847m, 769s, 757w, 745m, 738s, 733s, 717s, 687s

\* Recorded with a Perkin-Elmer 257 grating spectrophotometer using Nujol or hexachlorobutadiene mulls unless otherwise stated. † Nujol and CCl<sub>4</sub>. ‡ CCl<sub>4</sub> and C<sub>6</sub>H<sub>12</sub>. § CCl<sub>4</sub> and CS<sub>2</sub>.

TABLE 2

<sup>19</sup>F chemical shifts (p.p.m.) \* and coupling constants (Hz) for perfluoropropene complexes

| Compound  | F <sup>3</sup> F <sup>4</sup> C <sup>•</sup> C(F <sup>2</sup> )CF <sup>1</sup> |       |               |               | ( $F^2$ and $F^3$ assumed <i>trans</i> ) |        |       |
|---|--|-------|---------------|---------------|--|--------|-------|
|   | $\overline{(1)}$   | (2)   | (3) †         | (4) †         | $\overline{J_{1,2}}$                     | J 2, 3 | J 3.4 |
| C <sub>3</sub> F <sub>6</sub> <sup>a</sup>                            | 72.0   | 192.0 | 107.0         | <b>93</b> .0  | 13.0                                     | 120.0  | 57.0  |
| $(1,5-C_8H_{12})Ni(C_3F_6)^{b}$                                       | 66.2   | 209.0 | 116.8         | $112 \cdot 1$ |  | 79.0   | 168.0 |
| (Et <sub>3</sub> P) <sub>2</sub> Ni(C <sub>3</sub> F <sub>6</sub> ) ° | 65.0   | 214.8 | $122 \cdot 6$ | 111-1         | 14.0                                     | 76.0   | 193.6 |
| $(Ph_3P)_2Pt(C_3F_6)^d$   | 69.6   | 204.3 | 121.7         | 109.5         |  |        | 188.0 |

\* Relative to CCl<sub>3</sub>F (0.00 p.p.m.) increasing to high field. † Calculated values for metal complexes (J.W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Vol. 1, Pergamon Press, Oxford, 1965, p. 310). CCl<sub>3</sub>F solvent (E. Pitcher and F. G. A. Stone, Spectrochim. Acta, 1961, 17, 1244). <sup>b</sup> C<sub>6</sub>H<sub>6</sub> solvent. <sup>c</sup> MeC<sub>6</sub>H<sub>5</sub> solvent at -20°. <sup>d</sup> CDCl<sub>3</sub> solvent (ref. 5).

ether reacts at room temperature with an excess of perfluoropropene to give a volatile, yellow crystalline complex (I). The low thermal stability and high reactivity of the compound towards oxygen precluded elemental carbon and hydrogen analyses, and a mass spectrum could not be obtained. However, a nickel

chemical shifts and coupling constants consistent with co-ordinated perfluoropropene (Table 2). Moreover, pyrolysis of (I) gave as the only volatile products cyclo-octa-1,5-diene and perfluoropropene. Further con-

<sup>11</sup> B. Bogdanovic, M. Kroner, and G. Wilke, Annalen, 1966, 699, 1.

(VI)

(X)

(XII)

(I)  $(1,5-C_8H_{12})Ni(C_3F_6)$ 

(IX)  $(1,5-C_8H_{12})Ni(CF_2)_4$  §

 $(Ph_3P)_2Ni(CF_2)_4$ 

(XIV)  $(Ph_2PMe)_2Ni(C_2F_3H)_2$ 

firmation of the identity of (I) was obtained from a study of the reactions of the complex with triphenyland triethyl-phosphine.

Triphenyl- and triethyl-phosphine both displaced cyclo-octa-1,5-diene from (I) to afford the complexes (IIa) and (IIb) respectively, the former having been previously 10 obtained by treating perfluoropropene with ethylenebis(triphenylphosphine)nickel. The more soluble and more thermally stable triethylphosphine complex (IIb) was also produced by treating cyclo-octa-1,5-dienebis(triethylphosphine)nickel (formed in situ) with perfluoropropene. Perfluoropropene itself is not displaced from (I) by either triphenyl- or triethyl-phosphine, suggesting that (I), (IIa), and (IIb) are probably best regarded as nickel(II) complexes. The absence of bands in the i.r. spectra (Table 1) assignable to classically  $\pi$ -complexed perfluoropropene is in agreement with this suggestion. However, a more useful criterion of bond type is that a change in the internal <sup>19</sup>F-<sup>19</sup>F coupling constants of perfluoropropene on complex formation would indicate a change in the hybridization of the olefinic carbon atoms. The <sup>19</sup>F-<sup>19</sup>F geminal coupling constants  $J_{3,4}$  (Table 2) of the complexes (I) and (IIb) are large compared with that of uncomplexed perfluoropropene, and are of the magnitude observed in substituted cyclopropanes and cyclobutanes.<sup>12</sup> Secondly the *trans*-vicinal coupling constant  $(J_{2,3})$ decreases on complex formation. This suggests 5,13 that the hybridization at the 1,2-carbon atoms of the co-ordinated perfluoropropene approaches  $sp^3$ . Moreover, the increase in  $J_{3,4}$  on replacing cyclo-octa-1,5-diene in (I) by the better  $\sigma$ -donor triethylphosphine suggests that there is a gradation of bond type on going from (I) to (IIb), *i.e.*, the carbons of (IIb) have more  $sp^3$ character than those of (I).



Treatment of the zero-valent platinum complex (Ph<sub>3</sub>P)<sub>4</sub>Pt with an excess of tetrafluoroethylene has been previously shown<sup>5</sup> to result in the displacement of phosphine and the formation of the stable complex  $(Ph_3P)_2Pt(C_2F_4)$ . In contrast, tetrakis(triethylphosphine)nickel and tetrakis(methyldiphenylphosphine)nickel both react rapidly with tetrafluoroethylene to give the very stable crystalline octafluoronickelacyclopentane complexes (III) and (IV). Pyrolysis of (III) in a Pyrex vessel at a temperature sufficient to release volatile products (220°) gave a gaseous mixture containing fluorosilicon derivatives, as indicated by i.r. and mass spectra, thus showing that total degradation of the complex had taken place.

Cyclo-octa-1,5-dienebis(tri-n-butylphosphine)nickel undergoes an analogous reaction with tetrafluoroethylene to that of (Et<sub>3</sub>P)<sub>4</sub>Ni, cyclo-octa-1,5-diene being displaced to form (V). Tetrafluoroethylene selectively displaces tri-n-butylphosphine from 1,2-bis(diphenylphosphino)ethanebis(tri-n-butylphosphine)nickel to give (VI). This latter compound exhibits a remarkable tendency to crystallise with varying amounts of occluded solvent and is difficult to purify. The much less reactive tetrakis(trimethylphosphite)nickel reacts on prolonged heating with tetrafluoroethylene to afford the analogous complex (VII).

Treatment of the complex (V) with 2,2'-bipyridyl results in the immediate displacement of tri-n-butylphosphine, and the formation of the stable compound (VIII). This observation is consistent with the formulation of (III)--(VII) as nickel(II) complexes, which are known<sup>14</sup> to undergo rapid ligand-exchange reactions. Reaction of (V) with cyclo-octa-1,5-diene in the presence of zinc bromide [a scavenger for  $(Bu^n)_3P$ ] gives the yellow, stable crystalline cyclo-octa-1,5-diene complex (IX). Triphenylphosphine and  $\gamma$ -picoline both readily displace cyclo-octa-1,5-diene from (IX) to give (X) and (XI)



respectively. An analogous triphenyl phosphite complex could not be prepared by this method and it may be significant that alone among the nickelacyclopentane derivatives here described only the trimethyl phosphite compound (VII) has not survived storage in a sealed evacuated tube over a period of several months. When carbon monoxide was bubbled through a petroleum solution of (IX) at room temperature, the i.r. spectrum of the liquid showed a new, strong band at 2089 cm.<sup>-1</sup>, suggesting the presence of a species  $(1,5-C_8H_{12})$ Ni- $(CO)(CF_2)_4$ . Addition of methyldiphenylphosphine caused crystallisation of (Ph2MeP)2Ni(CF2)4 (IV), and the disappearance of the 2089 cm.<sup>-1</sup> band from the i.r. spectrum of the mother liquor.

The very stable octafluoronickelacyclopentane complexes (III)-(XI) were characterised by elemental analysis, <sup>1</sup>H and <sup>19</sup>F n.m.r. and mass spectroscopy, and by their i.r. spectra (Table 1).

The <sup>19</sup>F n.m.r. spectra showed two peaks of equal

- <sup>12</sup> W. D. Phillips, *J. Chem. Phys.*, 1956, **25**, 949. <sup>13</sup> R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.
  - <sup>14</sup> D. R. Eaton, J. Amer. Chem. Soc., 1968, 90, 4272.

intensity similar to those previously reported for the analogous heterocyclic compounds  $(CF_2)_4Fe(CO)_4$ <sup>15</sup> and  $(CF_2)_4Co(\pi-C_5H_5)(CO)$ .<sup>16</sup> In the spectra of the nickel complexes (III)-(XI) the low-field signal, assigned to the  $\alpha$ -CF<sub>2</sub> fluorine nuclei adjacent to the nickel atom, occurs at about 103 p.p.m. relative to CCl<sub>3</sub>F. This is some 35 p.p.m. to higher field than the corresponding resonances in the iron and cobalt compounds. However, the signals due to the  $\beta$ -CF<sub>2</sub> groups (~138 p.p.m.) have very similar chemical shifts in the iron, cobalt, and nickel compounds.

In the spectra of (VIII) and (IX) both signals appeared as triplets with splittings of ca. 2 Hz. The apparent chemical-shift equivalence of the fluorine nuclei of a given CF<sub>2</sub> group suggests either a planar octafluoronickelacyclopentane ring or an envelope structure undergoing rapid conformational change. In the spectrum of the 1,2-bis(diphenylphosphino)ethane complex (VI), the low-field signal appeared as a triplet of triplets. Double irradiation of the high-field triplet assigned to the  $\beta$ -CF<sub>2</sub> groups caused the collapse of the low-field signal to an apparent triplet, suggesting that the apparent triplet signal arises because the <sup>31</sup>P nuclei of the ligands and the  $\alpha$ -CF<sub>2</sub> fluorines form an AA'X<sub>2</sub>X<sub>2</sub>' system, where  $|J_{AA'}|$  is large.

At room temperature the spectra of the phosphine complexes (III), (IV), (V), and (X) show an apparent triplet for the  $\alpha$ -CF<sub>2</sub> resonance due to <sup>31</sup>P-<sup>19</sup>F coupling; no  ${}^{19}\text{F}-{}^{19}\text{F}$  coupling was observed. However, at  $-10^{\circ}$ the spectrum of (III) showed fluorine-fluorine coupling between the  $\alpha$ - and  $\beta$ -CF<sub>2</sub> groups. No further changes occurred when the spectra were recorded at  $-50^{\circ}$ . These results suggest that the complexes exist essentially as planar rings which exhibit a small conformational movement at room temperature. Interestingly, a recent X-ray crystallographic study  $^{17}$  of the complex

(Ph<sub>3</sub>P)<sub>2</sub>Pt-O-CMe<sub>2</sub>-O-O has shown that in this compound the five-membered heterocyclic ring is nearly planar.

An attempt to prepare the complex (1,5-C<sub>8</sub>H<sub>12</sub>)Ni- $(C_2F_4)$ , analogous to the perfluoropropene complex (I), was unsuccessful. Bis(cyclo-octa-1,5-diene)nickel reacted in ether or toluene solutions with an excess of tetrafluoroethylene to give a deep orange-red solution, which rapidly deposited nickel at room temperature. Addition of methyldiphenylphosphine to the orange-red solution gave the heterocyclic compound (IV), suggesting the intermediacy of  $(1,5-C_8H_{12})Ni(CF_2)_4$  (IX). However, as mentioned above, (IX) is very stable, and should have been readily isolable from the reaction mixture. It is suggested that  $(1,5-C_8H_{12})Ni(C_2F_4)$  is initially present and that only on treatment with methyldiphenyl-

phosphine in the presence of excess tetrafluoroethylene is the five-membered heterocyclic ring formed. If triethylphosphine is added to the orange-red solution, complex (III) is produced. However, the reaction is clearly extremely complex, because under certain conditions there is no formation of complex (III) upon addition of triethylphosphine. Instead, the reaction takes a different course to give a red crystalline complex (XII) characterised by elemental analysis and i.r., <sup>1</sup>H and <sup>19</sup>F n.m.r.-spectroscopy as possibly, a dinuclear compound containing a C<sub>8</sub>H<sub>12</sub> moiety, four triethylphosphine ligands and four tetrafluoroethylene moieties. Two of the phosphines are extremely labile, and treatment with zinc bromide gave a yellow crystalline complex (XIII) containing two fewer phosphines than the parent compound (XII). The new complex had essentially the same i.r. spectrum and a slightly different <sup>1</sup>H and <sup>19</sup>F n.m.r. spectrum. A number of structures are possible for (XII) and (XIII), and it is hoped that an X-ray crystallographic study will establish their identity.

The reaction between trifluoroethylene and tetrakis-(methyldiphenylphosphine)nickel afforded the pale vellow complex (XIV), characterised by elemental analysis bis(methyldiphenylphosphine)hexafluoronickelaas cyclopentane. The bis-triphenylphosphine analogue has recently <sup>10</sup> been obtained by treating (Ph<sub>3</sub>P)<sub>2</sub>Ni(C<sub>2</sub>H<sub>4</sub>) with trifluoroethylene.

The tendency for zerovalent nickel complexes to form five-membered heterocyclic compounds compared with that of the three-membered ring formation of the platinum(0) complexes so far studied <sup>5,7</sup> is of considerable interest, and may be related to the mechanism of five-membered ring formation. In this connection it is interesting to note that, whereas, tetrafluoroethylene reacts with pentacarbonyliron to give  $(OC)_4Fe(C_2F_4)$ and  $(OC)_4 Fe(CF_2)_4^{15,18-20}$  the corresponding reaction with trans-[(MeO)\_3P]\_2Fe(CO)\_3 and tetrafluoroethylene affords only the three-membered ring compound cis- $(OC)_{2}[(MeO)_{3}P]_{2}Fe(C_{2}F_{4}).^{20}$  Evidently, there is a delicate balance of the various factors concerned with five- and three-membered ring formation, and until these are more fully understood a detailed mechanistic discussion will be reserved for a later paper. Nevertheless, it is suggested that the nickelacyclopentane ring compounds are formed *via* reactive nickelacyclopropane ring compounds.

## EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were recorded on Varian Associates HA 100 and A60 spectrometers. <sup>19</sup>F spectra were measured at 94.1 and 56.4 MHz with Varian Associates HA 100 and Perkin-Elmer R10 spectrometers, respectively. Mass

<sup>&</sup>lt;sup>15</sup> T. A. Manuel, S. L. Stafford, and F. G. A. Stone, J. Amer.

Chem. Soc., 1961, 83, 249. <sup>16</sup> T. D. Coyle, R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, J. Inorg. Nuclear Chem., 1961, 20,

<sup>172.</sup> <sup>17</sup> R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson,

<sup>18</sup> K. F. Watterson and G. Wilkinson, Chem. and Ind., 1959,

<sup>991.
&</sup>lt;sup>19</sup> H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, J. Chem. Soc., 1961, 2738.
<sup>20</sup> R. Fields, M. M. Germain, R. N. Haszeldine, and P. W.

spectra were obtained with an AEI MS902 spectrometer at 70 ev and peaks are quoted for the  ${}^{58}$ Ni isotope.

All operations were carried out in an atmosphere of nitrogen or argon and reactants were sealed into Carius tubes at  $-196^{\circ}$  in vacuo. M.p.s were recorded in sealed, evacuated tubes. Light petroleum refers to the fraction with b.p. 40-60°.

The <sup>19</sup>F n.m.r. coupling constants,  $J_{\rm PF}$ , for the  $\alpha$ -CF<sub>2</sub> apparent triplet signal in the spectra of the octafluoronickelacyclopentane derivatives are given as the distance between the outer lines of the signal, so that  $J_{\rm PF}$  (quoted) =  $|J_{\rm PF} + J_{\rm PF'}|^{.21}$ 

Reaction of Bis(cyclo-octa-1,5-diene)nickel and Perfluoropropene.—A suspension of bis(cyclo-octa-1,5-diene)nickel<sup>11</sup> (0.65 g., 2.36 mmoles) in ether (25 ml.) was introduced into a Carius tube (60 ml.). An excess of hexafluoropropene (4.72 mmoles) was condensed (-196°) into the tube, and the reaction mixture was warmed to 50° and shaken until the solid material had dissolved. After 24 hr. at room temperature, the solvent was removed *in vacuo* and the residue was extracted with light petroleum. Crystallisation (-78°) of the petroleum solution gave yellow crystals of complex (I) (0.26 g., 35%), decomp. >50° (Found: Ni, 19.6.  $C_{11}H_{12}F_6Ni$  requires Ni, 18.6%). The <sup>1</sup>H n.m.r. spectrum ( $C_6H_6$ ) showed bands at  $\tau$  4.60br (4H, CH=C) and 8.31br (8H, CH<sub>2</sub>).

Pyrolysis of Perfluoropropene(cyclo-octa-1,5-diene)nickel (I).—The complex (I) (0.091 g., 0.287 mmole) was pyrolysed at 110°/10 mm.Hg, the volatile products were collected in a trap cooled to  $-196^{\circ}$ . After sublimation compound (I) was returned to the reaction vessel until all the complex was consumed. The volatile products were fractionated *in vacuo* giving cyclo-octa-1,5-diene (0.102 mmole) and perfluoropropene (0.122 mmole) which were identified by i.r. spectroscopy. A black insoluble residue (0.062 g.) remained in the reaction vessel.

Reactions of Complex (I) with Tertiary Phosphines.—(a) Triphenylphosphine. A solution of (I) (0.05 g., 0.16 mmole) and triphenylphosphine (0.083 g., 0.32 mmole) in light petroleum (15 ml.) was stirred for 10 min. at  $-15^{\circ}$ , and for 15 min. at room temperature. The precipitated product was washed with light petroleum (2 × 5 ml.) to afford (IIa) (0.115 g., 99%), identical (i.r. and m.p.) with an authentic sample.<sup>10</sup>

(b) Triethylphosphine. A solution of triethylphosphine (0.074 g., 0.63 mmole) in light petroleum (5 ml.) was added dropwise to a cooled  $(-78^{\circ})$  stirred solution of complex (I) (0.10 g., 0.32 mmole) in light petroleum (10 ml.). After being allowed to reach room temperature (12 hr.), the solution was reduced in volume to 5 ml.; when cooled  $(-78^{\circ})$  pale yellow crystals were deposited. Recrystallisation  $(-78^{\circ})$ , from light petroleum gave (IIb) (0.10 g., 71%), m.p. 59-60° (Found: Ni, 13.0. C<sub>9</sub>H<sub>15</sub>F<sub>6</sub>NiP<sub>2</sub> requires Ni, 13.2%).

Reaction of Cyclo-octa-1,5-dienebis(triethylphosphine)nickel with Perfluoropropene.—Perfluoropropene (11.84 mmoles) was condensed ( $-196^{\circ}$ ) into a Carius tube (50 ml.) containing bis(cyclo-octa-1,5-diene)nickel (0.74 g., 2.96 mmoles) and triethylphosphine (0.63 g., 5.92 mmoles) in light petroleum (20 ml.). After 24 hr. at room temperature the reaction mixture was filtered and cooled ( $-78^{\circ}$ ) to give crystalline (IIb) (0.90 g., 75%).

Reaction of Tetrakis(triethylphosphine)nickel with Tetrafluoroethylene.—An excess of tetrafluoroethylene (6.36 mmoles) was condensed ( $-196^{\circ}$ ) into a Carius tube containing tetrakis(triethylphosphine)nickel (0.85 g., 1.59 mmoles) in light petroleum (16 ml.). After 24 hr. at room temperature the yellow microcrystalline solid was filtered off and washed with light petroleum to afford complex (III) (0.76 g., 96%), m.p. 141—142° (Found: C, 38.3; H, 6.1; Ni, 11.8.  $C_{16}H_{30}F_8NiP_2$  requires C, 38.8; H, 6.1; Ni, 11.9%). The mass spectrum showed peaks at m/e 494 (M, 15%), 313 ( $M - C_4F_7$ , 12%), 294 ( $M - C_4F_8$ , 100%), and 176 ( $M - C_4F_8 - \text{Et}_3P$ , 90%). The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) (-50°) showed peaks at  $\delta$  104.8 (4F, tt,  $\alpha$ -CF<sub>2</sub>,  $J_{FF}$  1.7 Hz,  $J_{PF}$  44.0 Hz,) and 138.9 p.p.m. (4F, t,  $\beta$ -CF<sub>2</sub>,  $J_{FF}$  1.7 Hz). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\tau$  8.64 (12H, m, CH<sub>3</sub>CH<sub>2</sub>P) and 9.05 (18H, m, CH<sub>3</sub>CH<sub>2</sub>P).

Reaction of Tetrakis(methyldiphenylphosphine)nickel with Tetrafluoroethylene.-Similarly, tetrafluoroethylene (4.20 mmoles) and tetrakis(methyldiphenylphosphine)nickel 9 (0.905 g., 1.05 mmoles) in light petroleum (40 ml.) were placed in a Carius tube, which was then heated (80°) and frequently shaken during  $4\frac{1}{2}$  hr. to convert solid (Ph<sub>2</sub>MeP)<sub>4</sub>-Ni into the solid product in high yield. The yellow-brown crystals were collected and washed with light petroleum to give (IV) (0.66 g., 95%), m.p. 182-184° (decomp.) (Found: C, 54.9; H, 4.0; Ni, 9.0. C<sub>28</sub>H<sub>20</sub>F<sub>8</sub>NiP<sub>2</sub> requires C, 54.7; H, 4.0; Ni, 8.9%). The mass spectrum showed peaks at m/e 685 (M, 100%), 477 (M - C<sub>4</sub>F<sub>7</sub>, 1%), 458 (M - C<sub>4</sub>F<sub>8</sub>, 2%), and 258  $(M - C_4F_8 - Ph_2PMe, 55\%)$ . The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed peaks at  $\delta$  101.5 (4F, t,  $\alpha$ -CF<sub>2</sub>,  $J_{PF}$  47.0 Hz) and 138.8 p.p.m. (4F, s,  $\beta$ -CF<sub>2</sub>). The <sup>1</sup>H n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed peaks at  $\tau$  2.72  $(20H, m, C_6H_5P)$  and 8.43br (6H, CH<sub>3</sub>P).

Reaction of Cyclo-octa-1,5-dienebis(tri-n-butylphosphine)nickel with Tetrafluoroethylene.-An excess of tetrafluoroethylene (3.84 mmoles) was condensed  $(-196^{\circ})$  into a Carius tube containing cyclo-octa-1,5-dienebis(tri-n-butylphosphine)nickel 22 (0.61 g., 0.96 mmole) in light petroleum (20 ml.). After 24 hr. at room temperature volatile materials were removed in vacuo, and the residue was recrystallised  $(-78^\circ)$  (twice) from light petroleum (3 ml.) to give yellow crystals of (V) (0.64 g., 90%), m.p. 47-49° (Found: C, 50.9; H, 8.3; F, 23.1; Ni, 8.7. C<sub>28</sub>H<sub>54</sub>F<sub>8</sub>NiP<sub>2</sub> requires C, 50.7; H, 8.2; F, 22.9; Ni, 8.8%). The mass spectrum showed peaks at m/e 662 (M, 100%), 481 (M - $C_4F_7$ , 10%), 462 ( $M - C_4F_8$ , 3%), 260 ( $M - C_4F_8 - Bu_3^nP_7$ 57%). The <sup>19</sup>F n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\delta$  103·3 (4F, t,  $\alpha\text{-}\mathrm{CF}_2,\,J_\mathrm{PF}$  44·8 Hz) and 138·6 p.p.m. (4F, s,  $\beta$ -CF<sub>2</sub>). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at τ 8.39 (36H, m) and 9.03 (18H, m).

Reaction of 1,2-Bis(diphenylphosphine)ethanebis(tri-nbutylphosphine)nickel with Tetrafluoroethylene.—A solution of 1,2-bis(diphenylphosphino)ethane-bis(tri-n-butylphosphine)nickel <sup>22</sup> (0.49 g., 0.57 mmole) in light petroleum (25 ml.) sealed in vacuo in a Carius tube with tetrafluoroethylene (2.28 mmoles), was set aside at room temperature for 10 days. The precipitated solid was collected and washed with light petroleum (2 × 12 ml.) to give yellow microcrystalline (VI) (0.34 g., 91%), m.p. 268—269° (decomp.) (Found: C, 53.7; H, 4.1; Ni, 8.4.  $C_{30}H_{24}F_8NiP_2$ requires C, 54.8; H, 3.7; Ni, 8.9%). The mass spectrum showed peaks at m/e 656.058 (calc. 656.055) (M, 7%) and 477 ( $M - C_4F_7$ , 100%). The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed peaks at  $\delta$  104.0 (4F, tt,  $\alpha$ -CF<sub>2</sub>,  $J_{FF}$  2.3 Hz,  $J_{PF}$ 

<sup>&</sup>lt;sup>21</sup> R. K. Harris, Canad. J. Chem., 1964, 42, 2275.

<sup>&</sup>lt;sup>22</sup> C. S. Cundy, Ph.D. Thesis, Bristol, 1969.

58·1 Hz) and 138·8 p.p.m. (4F, t,  $\beta$ -CF<sub>2</sub>,  $J_{\rm FF}$  2·3 Hz). The <sup>1</sup>H n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed peaks at  $\tau$  2·41 (20H, m, C<sub>6</sub>H<sub>5</sub>P) and 7·96 (4H, d, CH<sub>2</sub>P,  $J_{\rm HP}$  13·3 Hz).

Reaction of Tetrakis(trimethyl phosphite)nickel with Tetrafluoroethylene.—Tetrakis(trimethyl phosphite)nickel <sup>22</sup> (0.60 g., 1.08 mmoles), tetrafluoroethylene (4.32 mmoles), and benzene (10 ml.) were heated in a Carius tube at 100° for 4 days. The volume of the solvent was reduced (2 ml.) in vacuo and light petroleum (15 ml.) was added. The resultant precipitate was washed with light petroleum  $(2 \times 5$  ml.) to give complex (VII) (0.38 g., 64%), m.p.  $89-91^{\circ}$  (Found: C,  $28\cdot2$ ; H,  $3\cdot9$ ; F,  $28\cdot0$ ; Ni, 10·8.  $C_{10}H_{18}F_8P_3Ni,0\cdot5C_6H_6$  requires: C,  $28\cdot6$ ; H,  $3\cdot9$ ; F,  $27\cdot8$ ; Ni,  $10\cdot8\%$ ). The mass spectrum showed peaks at m/e 382  $[M - (MeO)_3P, 1\%]$ ,  $325 (M - C_4F_7, 100\%)$ , 306 (M - $<math>C_4F_8, 3\%)$ ,  $263 [M - C_2F_5 - (MeO)_3P, 2\%]$ , 201 [M - $<math>C_4F_7 - (MeO)_3P, 3\%]$ , and  $188 [M - C_4F_8 - (MeO)_3P,$ <math>3%]. The <sup>19</sup>F n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\delta$  103·6br (4F, s,  $\alpha$ -CF<sub>2</sub>) and 138·9 p.p.m. (4F, s,  $\beta$ -CF<sub>2</sub>). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\tau$  6·21 (9H, d, CH<sub>3</sub>OP,  $J_{HP}$  11·6 Hz) and a benzene resonance.

Reaction of Bis(tri-n-butylphosphine)octafluoronickelacyclopentane (V).—(a) With 2,2'-Bipyridyl. A solution of 2,2'-bipyridyl (0.047 g., 0.302 mmole) in benzene (2 ml.) was added dropwise to a stirred solution of complex (V) (0.20 g., 0.302 mmole) in benzene–light petroleum (6 ml.; 1:2 v/v). The precipitate was washed with benzene–light petroleum (2 × 5 ml.; 1:1 v/v), light petroleum (10 ml.), absolute methanol (5 ml.), and acetone (2 × 5 ml.) to give yellow crystalline complex (VIII) (0.117 g., 94%) decomp. 320—360° (Found: C, 40.7; H, 2.2; F, 36.7; N, 6.9; Ni, 14.2. C<sub>14</sub>H<sub>8</sub>F<sub>8</sub>N<sub>2</sub>Ni requires C, 40.5; H, 2.0; F, 36.6; N, 6.8; Ni, 14.2%). The mass spectrum showed peaks at m/e 414 (M, 5%), and 238 ( $M - C_4F_7$ , 100%). The <sup>19</sup>F n.m.r. spectrum (acetone) showed peaks at  $\delta$  109.0 (4F, t,  $\alpha$ -CF<sub>2</sub>,  $J_{FF}$  1.5 Hz) and 139.4 p.p.m. (4F, t, β-CF<sub>2</sub>,  $J_{FF}$  1.5 Hz).

(b) With Cyclo-octa-1,5-diene. A solution of [(Bu<sup>n</sup>)<sub>3</sub>P]<sub>2</sub>- $Ni(CF_2)_4$  (1.0 g., 1.51 mmoles) in light petroleum (100 ml.) containing cyclo-octa-1,5-diene (0.352 g., 3.26 mmoles) was stirred with zinc bromide (5 g., 22.1 mmoles, water content 1-2%) for 10 hr. The clear, yellow solution was decanted and the volume was reduced (7 ml.) in vacuo to give yellow crystals, which were washed with light petroleum, of complex (IX) (0.20 g., 36%), m.p. 133-135° (decomp.), (Found: C, 39·1; H, 3·2; F, 41·4; Ni, 15·9. C<sub>12</sub>H<sub>12</sub>F<sub>8</sub>Ni requires C, 39.3; H, 3.3; F, 41.4; Ni, 16.0%). The mass spectrum showed peaks at m/e 366 (M, 12.5%), 347 (M - F, 0.3%), 185  $(M - C_4F_7, 59\%)$ , 166  $(M - C_4F_8, 59\%)$ 84%), and 112  $(M - C_4F_8 - C_4H_6, 100\%)$ . The <sup>19</sup>F n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\delta$  103.3 (4F, t,  $\alpha$ -CF<sub>2</sub>,  $J_{\rm FF}$  2.5 Hz) and 138.4 p.p.m. (4F, t,  $\beta$ -CF<sub>2</sub>,  $J_{\rm FF}$  2.5 Hz). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\tau$  4.23 (4H, s) and 7.40 (8H, m).

Reactions of Cyclo-octa-1,5-dieneoctafluoronickelacyclopentane (IX) with Tertiary Phosphines.—(a) Triphenylphosphine. A solution of triphenylphosphine (0.214 g., 0.82 mmole) in ether (5 ml.) was added dropwise to a stirred solution of (IX) (0.15 g., 0.41 mmole) in etherlight petroleum (40 ml.; 1:3 v/v). The crystalline precipitate was washed with light petroleum (20 ml.) to give pale yellow crystalline (X) (0.28 g., 66%), m.p. 182— 183° (Found: C, 61.3; H, 4.0; F, 19.4; Ni, 7.6. C<sub>40</sub>H<sub>30</sub>-F<sub>8</sub>NiP<sub>2</sub> requires C, 61.3; H, 3.9; F, 19.4; Ni, 7.5%). The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed peaks at  $\delta$  99.3 (4F, t,  $\alpha$ -CF<sub>2</sub>, J<sub>PF</sub> 48.0 Hz) and 137.0 p.p.m. (4F, s,  $\beta$ -CF<sub>2</sub>). The  $^1\!H$  n.m.r. spectrum (CH\_2Cl\_2) showed a peak at  $\tau$  2.64 (30H, m, C\_6H\_5P).

(b)  $\gamma$ -Picoline. A similar reaction of complex (IX) (0.08 g., 0.22 mmole) in light petroleum (10 ml.) with  $\gamma$ -picoline (0.18 g., 1.91 mmole) in light petroleum (5 ml.) gave a white crystalline precipitate, which was recrystallised from toluene–light petroleum to give complex (XI) (0.077 g., 79%), m.p. 204—206° (decomp.) (Found: C, 43.1; H, 3.3; F, 34.1; N, 6.2. C<sub>16</sub>H<sub>14</sub>F<sub>8</sub>N<sub>2</sub>Ni requires C, 43.2; H, 3.2; F, 34.2; N, 6.3%). The <sup>19</sup>F n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\delta$  111.7 (4F, s,  $\alpha$ -CF<sub>2</sub>) and 139.8 p.p.m. (4F, s,  $\beta$ -CF<sub>2</sub>). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\tau$  1.42 (4H, d,  $J_{\rm HH}$  6.0 Hz), 2.96 (4H, d,  $J_{\rm HH}$  6.0 Hz) and 7.75 (6H, s,  $\gamma$ -CH<sub>3</sub>).

The Reaction of Tetrakis(methyldiphenylphosphine)nickel with Trifluoroethylene.—Tetrakis(methyldiphenylphosphine)nickel (0.61 g., 0.71 mmole) and trifluoroethylene (2.84 mmoles) in light petroleum (30 ml.) were heated (75°) together in a Carius tube for 24 hr The precipitated solid was separated from the cooled solution and washed with light petroleum (2 × 15 ml.) to yield very pale yellow crystalline (XIV) (0.36 g., 82%), m.p. 133—134° (decomp.), (Found: C, 57.8; H, 4.5; F, 18.3; Ni, 9.4.  $C_{28}H_{22}F_6NiP_2$ requires C, 57.5; H, 4.7; F, 18.1; Ni, 9.4%).

Reaction between Bis(cyclo-octa-1,5-diene)nickel, Tetrafluoroethylene, and Methyldiphenylphosphine or Triethylphosphine.—Bis(cyclo-octa-1,5-diene)nickel (0.58 g., 2.10 mmoles) in toluene (20 ml.) and tetrafluoroethylene (8.40 mmoles) were sealed in vacuo in a Carius tube and shaken at room temperature until the orange-red solution began to decompose. The solution was cooled (-23°) and filtered. Methyldiphenylphosphine (0.844 g., 4.20 mmoles) was added dropwise to the stirred, cooled (-23°) solution, and the reaction mixture was allowed to warm slowly to room temperature. The solvent was removed in vacuo and the residue was triturated with light petroleum to give (IV) (0.800 g., 58%).

A similar reaction with triethylphosphine as the capturing ligand gave (III) (69%) identical with that prepared previously. However, in another reaction bis(cyclo-octa-1,5-diene)nickel (1.0 g., 3.64 mmoles) in ether (30 ml.) and tetrafluoroethylene (14.6 mmoles) were mixed in a Carius tube to give a deep, orange-red solution. When decomposition to nickel became pronounced, the solution was cooled  $(-23^{\circ})$  and filtered. Triethylphosphine (0.861)g., 7.28 mmoles) in ether (5 ml.) was added dropwise to the stirred solution  $(-23^\circ)$ , and the reaction mixture was allowed to reach room temperature during several hours. The volume of the solvent was reduced (5 ml.) in vacuo and the deposited red crystals were collected and washed with light petroleum  $(2 \times 5 \text{ ml.})$  to yield crystalline (XII) (0.97 g., 49%), m.p. 118-120° (decomp.) (Found: C, 43.9; H, 6.6; F, 27.9; Ni, 10.8; P, 11.5. C<sub>40</sub>H<sub>72</sub>F<sub>16</sub>Ni<sub>2</sub>P<sub>4</sub> requires C, 43.7; H, 6.6; F, 27.7; Ni, 10.7; P, 11.3%). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\tau 4.25$  br (4H, s), 7.50 (8H, m), 8.04 (24H, m), and 8.76 (36H, m). The <sup>19</sup>F n.m.r. spectrum (94.1 MHz, CDCl<sub>3</sub>) showed peaks at  $\delta$  97.9 (4F, AB system,  $\delta_{\rm AB}$  1443 Hz,  $J_{\rm AB}$  271 Hz) and 110.8 p.p.m. (4F, m).

Reaction of Complex (XII) with Zinc Bromide.—A solution of complex (XII) (0.15 g., 0.137 mmole in light petroleum) (20 ml.) was stirred with zinc bromide (2.20 g., 9.77 mmoles, 1-2% water content). The orange-red solution rapidly became pale yellow. After 3 hr., the volume of the (decanted) solution was reduced (3 ml.)

in vacuo, and the deposited yellow crystals were collected and washed with light petroleum to give (XIII) (0.09 g., 76%), m.p. 108—109° (Found: C, 39.0; H, 4.8; F, 35.5; Ni, 13.6; P, 7.4.  $C_{28}H_{42}F_{16}Ni_2P_2$  requires C, 39.0; H 4.9; F, 35.3; Ni, 13.6; P, 7.2%). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed peaks at  $\tau$  4.21br (4H, s), 7.44 (8H, q,  $J_{\rm HH}$  14.0 Hz), 8.07 (12H, m) and 8.80 (18H, m). The <sup>19</sup>F n.m.r. spectrum (94.1 MHz, CDCl<sub>3</sub>) showed peaks at  $\delta$  108.5

(4F, AB system,  $\delta_{AB}$  678 Hz,  $J_{AB}$  282 Hz) and 112.4 p.p.m. (4F, m).

We thank the Office of Scientific Research (U.S.A.F.) for support, and the S.R.C. for a Research Studentship. (C. S. C.)

[9/1569 Received, September 15th, 1969]