Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XVII.[1] Tertiary Arsine–Nickel Complexes

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Treatment of L_4Ni [L = $PhAsMe_2$, L_2 = *o*-$C_6H_4(AsMe_2)_2$] with tetrafluoroethylene or trifluoroethylene gives the stable compounds $L_2\overline{NiCF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2}$ and $L_2\overline{NiCF_2{\cdot}CFH{\cdot}CFH{\cdot}CF_2}$, respectively. Chloro- and bromo-trifluoroethylene react with $(PhMe_2As)_4Ni$ to afford the vinyl compounds $(PhMe_2As)_2Ni(CF{:}CF_2)X$ (X = Cl or Br). Similarly, 1,1-dichloro-2,2-difluoroethylene and 1,2-dichloro-1,2-difluoroethylene gave $(PhMe_2As)_2Ni(CCl{:}CF_2)Cl$ and $(PhMe_2As)_2Ni(CF{:}CFCl)Cl$, respectively, the latter being a mixture of *cis*- and *trans*-vinyl isomers. Hexafluorobuta-1,3-diene reacts with $(PhMe_2As)_4Ni$ to give $(PhMe_2As)_2\overline{NiCF_2{\cdot}CF{:}CF{\cdot}CF_2}$. The complex [*o*-$C_6H_4$-$(AsMe_2)_2$]$\overline{NiC(CF_3)_2{\cdot}O}$, prepared from 1,5-$C_8H_{12}\overline{NiC(CF_3)_2{\cdot}O}$, reacts with $(CF_3)_2CO$ and with $(CF_3)_2CNH$ to form the five-membered ring compounds [*o*-$C_6H_4(AsMe_2)_2$]$\overline{NiC(CF_3)_2{\cdot}O{\cdot}C(CF_3){\cdot}X}$ (X = O or NH). Bis-(π-2-methylallyl)nickel and tetrafluoroethylene react to form a complex containing two C_2F_4 groups per nickel atom.

Previous studies of the reactions of low-valent transition-metal compounds with fluoro-olefins have shown that, depending on the metal, the ligands attached to the metal, and the nature of the fluoro-olefin, either metallocyclopropanes or metallocyclopentanes are formed. For example, the reaction of tetrafluoroethylene with $(Ph_3P)_4Pt$ gives the stable compound $(Ph_3P)_2\overline{PtCF_2{\cdot}CF_2}$,[2] whereas a wide variety of phosphine-substituted L_4Ni complexes react with tetrafluoroethylene to give only octafluoronickelacyclopentane complexes $L_2\overline{NiCF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2}$.[3] In contrast, perfluoropropene reacts with zero-valent platinum[2] and nickel[3] compounds to give in both cases the complexes $L_2\overline{MCF_2{\cdot}CF}{\cdot}CF_3$ (M = Ni or Pt; L = phosphine). The recent observation[4] that a related hexafluoroisopropylideneamine complex $(Ph_3P)_2\overline{PtC(CF_3)_2{\cdot}NH}$, reacts with hexafluoroacetone to give the five-membered ring compound $(Ph_3P)_2\overline{PtC(CF_3)_2{\cdot}NH{\cdot}C(CF_3)_2{\cdot}O}$, suggested a possible general reaction path to five-membered ring compounds *via* three-membered ring complexes. Whether complexes like $(Ph_3P)_2\overline{MC(CF_3)_2{\cdot}O}$ (M = Ni[5,6] or Pt[7]) are stable in the presence of excess of hexafluoroacetone depends both on the identity of the metal and on the co-ordinating ligands. Thus, bis(cyclo-octadiene)nickel reacts with hexafluoroacetone to give $(C_8H_{12})Ni[(CF_3)_2CO]$ which with phosphines affords $L_2Ni[CF_3)_2CO]$.[5] On treatment of some of these complexes with hexafluoroacetone a slow reaction occurs to give $L_2\overline{Ni{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O}$.[8] In contrast, $(Ph_3P)_2Pt[(CF_3)_2CO]$ does not undergo a similar ring expansion reaction. With these observations in mind, the reactions of arsine-substituted nickel compounds and of bis(π-2-methylallyl)nickel[9] have been investigated.

Treatment of tetrakis(dimethylphenylarsine)nickel and bis-[*o*-bis(dimethylarsino)benzene]nickel with tetrafluoroethylene and trifluoroethylene gave the corresponding octafluoronickelacyclopentanes (I) and (II), and hexafluoronickelacyclopentanes (III) and (IV) respectively, in high yield. The air-stable crystalline complexes were characterised by elemental analysis, and by ^1H and ^{19}F n.m.r. and i.r. spectroscopy. The ^{19}F n.m.r. spectra of (I) and (II) showed two peaks of equal intensity with chemical shifts close to those found for the analogous phosphine-substituted compounds,[3] the low field signal being assigned to the α-CF_2 nuclei. At room temperature broad signals were observed, but on cooling (−60 °C) ^{19}F–^{19}F coupling was discernable between the α- and β-CF_2 groups. In agreement with the illustrated structure, the spectrum of (III) showed three resonances of equal intensity, the low field resonances corresponding to α-CF_2 nuclei *trans* to either a hydrogen or a fluorine of a β-CHF, whose ^{19}F resonance occurred at high field split by ^1H and ^{19}F coupling. The low solubility of (IV) precluded measurement of its ^{19}F n.m.r. spectrum.

Bis-[*o*-bis(dimethylarsino)benzene]nickel reacts with halogenofluoro-olefins, but no stable compounds were isolated. However, tetrakis(dimethylphenylarsine)nickel, generated *in situ*, reacted smoothly with chloro- and bromo-trifluoroethylene, 1,1-dichloro-2,2-difluoroethylene and 1,2-dichloro-1,2-difluoro-ethylene to give, respectively the stable crystalline σ-bonded vinylnickel complexes (V), (VI), (VII), and (VIII). The i.r. spectra all showed bands in the region 1710—1630 cm^{-1} in-

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[1] Part XVI, J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, preceding paper.

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

[3] C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 1647.

[4] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3161.

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

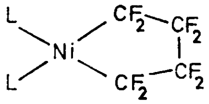
[6] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3019.

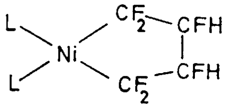
[7] B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.

[8] J. Browning, unpublished observations.

[9] J. Browning, D. J. Cook, C. S. Cundy, M. Green, and F. G. A. Stone, *Chem. Comm.*, 1968, 929.

dicating the presence of a C=C·Ni group,[10] and this was confirmed by the ^{19}F n.m.r. spectra which had chemical shifts and coupling constants characteristic of fluorovinylnickel compounds,[6,10] and fluorovinylmetallic com-


(I; L = $PhMe_2As$)
[II; L_2 = o-$C_6H_4(AsMe_2)_2$]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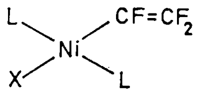
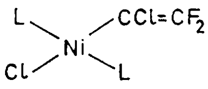
[IV; L_2 = o-$C_6H_4(AsMe_2)_2$]


(V; L = $PhMe_2As$; X = Cl)
(VI; L = $PhMe_2As$; X = Br)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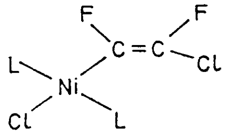
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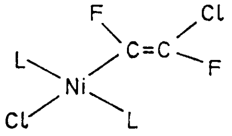
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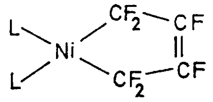
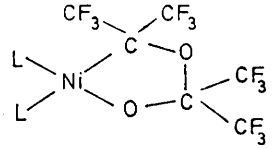
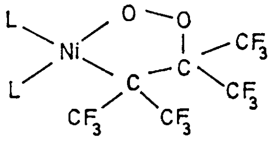

(IX; L = $PhMe_2As$)


[XIa; L_2 = o-$C_6H_4(AsMe_2)_2$]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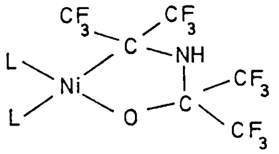
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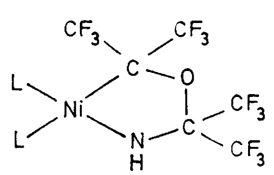
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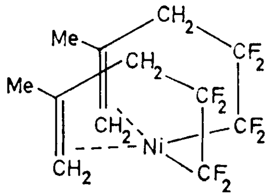
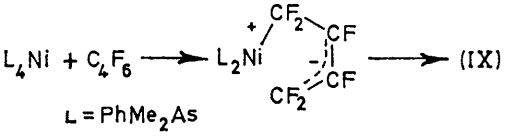

(XIII)

pounds in general.[2] In the reaction involving 1,2-dichloro-1,2-difluoroethylene, a 50 : 50 *cis* : *trans*-mixture of the olefin was used, and the ^{19}F n.m.r. spectrum of the product showed it to be a 50 : 50 mixture of the *cis* and *trans*-vinyl complexes (VIIIa) and (VIIIb). Thus, these reactions parallel those previously described for phosphine-substituted nickel complexes.[6]

The reaction between hexafluorobuta-1,3-diene with tetrakis(triphenylphosphine)platinum has been shown [2] to give the compound $(Ph_3P)_2Pt{\cdot}CF_2{\cdot}CF{\cdot}CF{:}CF_2$. In contrast, tetrakis(dimethylphenylarsine)nickel reacts with hexafluorobuta-1,3-diene to give the yellow crystalline complex (IX), which is formulated as a hexafluoronickelacyclopent-3-ene compound. Its i.r. spectrum showed a band at 1758 cm^{-1}, a frequency similar to that observed for the C=C stretch in fluorocyclopentenes,[11] and, in agreement with the illustrated structure, the ^{19}F n.m.r. spectrum showed only two multiplets at 84·9 and 148·6 p.p.m., with relative intensities of 2 : 1.

It is also interesting that, in contrast with the platinum system, pentacarbonyliron reacts [12] with hexafluorobuta-1,3-diene to give an analogous hexafluorometallocyclopent-3-ene complex $(OC)_4FeCF_2{\cdot}CF{:}CF{\cdot}CF_2$, the structure of which was established by *X*-ray crystallography.[13]

It is difficult to visualise how the five-membered ring compound (IX) could be formed from $(PhMe_2As)_2NiCF_2{\cdot}CF{\cdot}CF{:}CF_2$. Also it seems unlikely that hexafluorobutadiene could react with the nickel compound exclusively in the *cisoid* form to give (IX). There may be an ionic reaction path to five-membered ring compounds, and recent experiments [14] where ionic intermediates have been implicated, suggest that reaction (1) could be the path to (IX).



(1)

Hexafluoroacetone, which has been shown to react with L_4Ni (L = Et_3P, Ph_2PMe; L_2 = 1,5-C_8H_{12}) to give $L_2NiC(CF_3)_2{\cdot}O$, reacts with $(PhMe_2As)_4Ni$ and $[o\text{-}C_6H_4(AsMe_2)_2]_2Ni$ to form mixtures of products, from which crystalline compounds could not be easily isolated. However, the ^{19}F n.m.r. spectrum of the reaction mixture from the latter reaction showed three resonances suggesting the presence of a possible mixture of $[o\text{-}C_6H_4(AsMe_2)_2]NiC(CF_3)_2{\cdot}O$ and $[o\text{-}C_6H_4(AsMe_2)_2]NiC(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O$. In order to test this hypothesis the stable crystalline complex $[o\text{-}C_6H_4(AsMe_2)_2]NiC(CF_3)_2{\cdot}O$ (X) was prepared by displacement of cycloocta-1,5-diene from $(1,5\text{-}C_8H_{12})NiC(CF_3)_2{\cdot}O$.[5] Complex (X) shows a singlet resonance in its ^{19}F n.m.r. spectrum

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

[11] J. K. Brown and K. J. Morgan, *Adv. Fluorine Chem.*, 1965, **4**, 253.

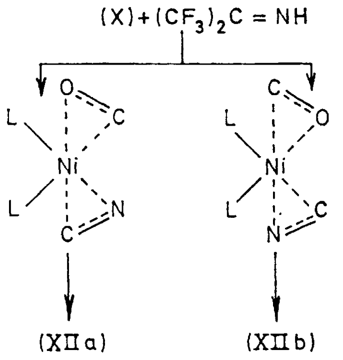
[12] R. L. Hunt, D. M. Roundhill, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 982.

[13] P. B. Hitchcock and R. Mason, *Chem. Comm.*, 1967, 242.

[14] J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc.* (*A*), 1970, 1847.

at 65·3 p.p.m., to low field of that of unco-ordinated hexafluoroacetone (77·2 p.p.m.). Compound (X) reacts with more hexafluoroacetone to give air-stable yellow crystals of a five-membered ring compound (XI). The ^{19}F n.m.r. spectrum showed two complex multiplets at 65·7 and 81·5 p.p.m. corresponding to two $C(CF_3)_2$ groups in different environments. The low field resonance is assigned to an α-$C(CF_3)_2$ group and double irradiation of either peak collapsed the other peak to a singlet. Either (XIa) or (XIb) would accord with the ^{19}F n.m.r. spectrum, but (XIa) seems more likely, since formation of (XIb) would require rupture of a C–O bond during the conversion of the three-membered ring complex into the five-membered ring. It seems improbable that the nickel atom in (X), the oxidation state of which must be approaching +2, would be sufficiently nucleophilic to populate the anti-bonding orbitals of a C=O group to bring about bond cleavage. However, *X*-ray crystallographic studies are expected to establish the nature of (XI).

Hexafluoroisopropylideneamine also reacts with (X) to give orange crystals of (XII), a O,N-heterocyclic compound analogous to the platinum compound formulated as $(Ph_3P)_2PtC(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}NH$.[4] The ^{19}F n.m.r. spectrum showed two peaks at 64·4 and 82·0 p.p.m., and, similarly, double irradiation of either peak collapsed the other peak to a singlet. Two possible isomeric structures for this compound are (XIIa) and (XIIb), and it is not possible to distinguish between them on the present evidence; the formation of either depends on the stereochemistry of the transition state or intermediate leading to their formation.



These experiments show that variation of the ligand (L) in a system of the type $L_2NiC(CF_3)_2{\cdot}O$ can lead to increased reactivity towards molecules like $(CF_3)_2C{=}O$ and $(CF_3)_2C{=}NH$ with a resultant three- to five-membered ring transformation. This suggests that compounds of the type $L_2NiCF_2{\cdot}CF_2$ (L = phosphine or arsine) might be the precursors of the octafluoronickelacyclopentanes.[3] In an attempt to test this idea, an alternative route to nickel–tetrafluoroethylene compounds was examined.

A solution of bis-(π-2-methylallyl)nickel in benzene reacts with an excess of tetrafluoroethylene to give a purple-red crystalline compound which is tentatively assigned the structure (XIII). Elemental analysis and molecular weight measurement showed that the reaction involved the addition of two C_2F_4 molecules to the π-allylic system. The ^{1}H n.m.r. spectrum showed resonances at τ 4·95 and 5·17 corresponding to the co-ordinated methylene protons *cis* and *trans* to a methyl group (τ 8·01), and a triplet resonance at τ 7·22, which is assigned to $CF_2{\cdot}CH_2$ nuclei. In agreement, the ^{19}F n.m.r. spectrum showed two resonances at 100·7 (α-CF_2) and 107·9 (β-CF_2, t, J_{HF} 18 Hz) p.p.m. of equal intensity which were assigned to the two C_2F_4 groups inserted between the nickel atom and the two 2-methylallyl groups.

Complex (XIII) could not be degraded cleanly for identification of the organic ligand, although one reaction with iodine afforded an organic liquid, the ^{1}H and ^{19}F n.m.r. spectra of which were thought to have been in accord with the structure $CH_2{:}CMe{\cdot}CH_2(CF_2)_2{\cdot}CH_2(Me){\cdot}C{:}CH_2$.[9] However, the spectroscopic data would equally well fit a molecule in which a $(CF_2)_4$ unit was present. Moreover, it has since been found that (XIII) reacts with dimethyl(phenyl)arsine to form an insoluble, orange, crystalline complex. A nickel–diene complex of the type previously postulated [9] would be expected to react with displacement of the organic fragment. It is hoped to carry out a crystallographic study on (XIII).

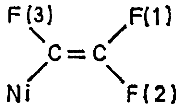
EXPERIMENTAL

^{1}H and ^{19}F n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m.). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer. Molecular weights in solution were measured with a Mechrolab Osmometer. Light petroleum refers to the fraction of b.p. 40—60°. The zero-valent nickel complexes were prepared by addition of either dimethyl(phenyl)arsine or *o*-bis(dimethylarsino)-benzene to a stirred (0°) suspension of bis(cyclo-octa-1,5-diene)nickel in diethyl ether. In the former case the resultant solution was used directly, whereas with the chelating ligand a highly reactive yellow crystalline solid was obtained on removal of the solvent.

Reactions of Tetrakis(dimethylphenylarsine)nickel.—(a) *With tetrafluoroethylene.* An excess of tetrafluoroethylene (4 mmol) was condensed (−196°) into a Carius tube (100 ml) containing tetrakis(dimethylphenylarsine)nickel (1·82 mmol) in diethyl ether (20 ml). When the mixture was warmed to room temperature, crystals separated, which were collected and washed with diethyl ether to give orange *crystals* of (I) (1·1 g, 97%), m.p. 165—166° [Found: C, 38·5; H, 3·5; F, 24·4%; *M*, 565 (in $CHCl_3$). $C_{20}H_{22}As_2F_8Ni$ requires C, 38·6; H, 3·6; F, 24·4%; *M*, 623], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3082w, 3070w, 3032w, 3012w, 2942w, 1588w, 1488m, 1463w, 1440s, 1423m, 1350s, 1310w, 1269m, 1262m, 1255s, 1229m, 1188m, 1165s, 1137m, 1088s, 1081s, 1030w, 1021w, 1005m, 1000m, 985s, 963s, 955s, 912s, 889s, 872s, 857m, 848m, 826w, 749s, 744s, 701s, 680w, and 655w cm^{-1}; ^{19}F n.m.r. spectrum (CH_2Cl_2): 99·0 [4F, t, α-CF_2, $J(F^{\alpha}–F^{\beta})$ <1 Hz] and 139·1 [4F, t, β-CF_2, $J(F^{\alpha}–F^{\beta})$ <1 Hz] p.p.m.; ^{1}H n.m.r. spectrum (CH_2Cl_2): τ 2·64 (10H, m, *Ph*As) and 8·86 (12H, s, *Me*As).

(b) *With trifluoroethylene.* When a solution of trifluoroethylene (4 mmol) and tetrakis(dimethylphenylarsine)nickel (1·82 mmol) in diethyl ether was warmed to room temperature orange crystals of (III) deposited (0·70 g, 65%), m.p. 131° (decomp.) (Found: C, 41·0; H, 4·2; As, 23·6; F, 19·4. $C_{20}H_{24}As_2F_6Ni$ requires C, 41·0; H, 4·1; As, 25·5, F, 19·4%), $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3080w, 3055w, 3030w, 3010w, 2958w, 2935w, 2862w, 1483m, 1440s, 1422m, 1380w, 1339w, 1311w, 1266m, 1242m, 1201w, 1169w, 1155w, 1115s, 1088m, 1072w, 1044m, 1036m, 1026m, 1002w, 991w, 960w, 945s, 927s, 912s, 875s, 853w, 811w, 786s, 770m, 741s, and 699s cm^{-1}; ^{19}F n.m.r. spectrum (CH_2Cl_2): 85·6 (2F, α-CF_2), 95·4 (2F, α-CF_2), and 210·2 (2F, β-CH*F*) p.p.m. (J_{FF} 259 Hz); ^1H n.m.r. spectrum [$(CD_3)_2CO$]: τ 2·64 (10H, m, *Ph*As), 5·02 (2H, d, *CH*F, J_{HF} 54·0 Hz), and 8·98 (12H, s, *Me*As).

(c) *With chlorotrifluoroethylene.* Similarly, reaction of chlorotrifluoroethylene (4 mmol) with tetrakis(dimethylphenylarsine)nickel (1·82 mmol) in diethyl ether (20 ml). After 24 h at room temperature the orange solution was filtered and the volume was reduced *in vacuo*; addition of light petroleum gave orange-brown *crystals* of (V) (0·6 g, 64%), m.p. 87—88° [Found: C, 39·8; H, 4·2; As, 26·7; Cl, 6·7; F, 10·6%; *M*, 476 (in $CHCl_3$). $C_{18}H_{22}As_2ClF_3Ni$ requires C, 40·1; H, 4·1; As, 27·8; Cl, 6·6; F, 10·6%; *M*, 539], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3080w, 3060w, 3039w, 2925w, 1710s, 1584w, 1488m, 1438m, 1422w, 1419w, 1338w, 1310w, 1270w, 1253w, 1231s, 1090w, 1061w, 1055s, 1030w, 1002w, 973s, 909m, 869m, 870s, 845w, 812w, 749s, and 701s cm^{-1}; ^{19}F n.m.r. spectrum (CH_2Cl_2): 87·5 [1F, F(1)], 130·8 [1F, F(2)], and 163·8 [1F, F(3)] p.p.m. [$J_{F(1),F(2)}$ 109·0 Hz, $J_{F(1),F(3)}$, 36·0 Hz, and $J_{F(2),F(3)}$ 109·0 Hz; ^1H n.m.r. spectrum (CH_2Cl_2): τ 2·53 (10H, m, *Ph*As) and 8·43 (12H, s, *Me*As).



(d) *With bromotrifluoroethylene.* In a similar way, bromotrifluoroethylene (4 mmol) was treated with tetrakis(dimethylphenylarsine)nickel (1·82 mmol) in diethyl ether (20 ml). When the solution was warmed to room temperature, it became dark green and deposited nickel. Filtration, followed by addition of light petroleum, gave yellow-brown *crystals* of (VI) (0·69 g, 65%), m.p. 85—85·5° [Found: C, 37·0; H, 3·8; As, 25·4; Br, 13·7; F, 9·8%; *M*, 525 (in $CHCl_3$). $C_{18}H_{22}As_2BrF_3Ni$ requires C, 37·0; H, 3·8; As, 25·7; Br, 13·7; F, 9·8%; *M*, 584], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3080w, 3060w, 3040w, 3020w, 3000w, 2970w, 2930w, 1710m, 1583w, 1489m, 1439m, 1420w, 1410w, 1355w, 1336w, 1310w, 1270w, 1265w, 1252w, 1230s, 1156w, 1089w, 1060w, 1045m, 1030w, 1002w, 971s, 908s, 879s, 846w, 747s, and 700m cm^{-1}; ^{19}F n.m.r. spectrum (CH_2Cl_2): 86·1 [1F, F(1)], 130·8 [1F, F(2)], and 162·9 [1F, F(3)] p.p.m. [$J_{F(1),F(2)}$ 106·0 Hz, $J_{F(1),F(3)}$ 36·0 Hz, and $J_{F(2),F(3)}$ 106·0 Hz; ^1H n.m.r. spectrum (CH_2Cl_2): τ 2·23 (10H, m, *Ph*As) and 7·26 (12H, s, *Me*As).

(e) *With* 1,1-*dichloro*-2,2-*difluoroethylene.* When a solution of 1,1-dichloro-2,2-difluoroethylene (4 mmol) and tetrakis(dimethylphenylarsine)nickel (1·82 mmol) in diethyl ether (20 ml) was warmed to room temperature orange *crystals* deposited of (VII) (0·66 g, 60%), m.p. 72—73·5° [Found: C, 39·1; H, 3·9; As, 27·0; Cl, 12·8; F, 6·6%; *M*, 543 (in $CHCl_3$). $C_{18}H_{22}As_2Cl_2F_2Ni$ requires C, 38·9; H, 4·0; As, 27·0; Cl, 12·8; F, 6·8%; *M*, 556], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3082w, 3062w, 3042w, 3010w, 2932w, 1705m, 1582w, 1488m, 1438m, 1416m, 1338w, 1310w, 1268w, 1255w, 1212s, 1159m, 1122w, 1089m, 1070w, 1030m, 1002w, 983s, 908s, 865s, 830m, 748s, and 700s cm^{-1}; ^{19}F n.m.r. spectrum (CH_2Cl_2): 70·7 [1F, F(1)] and 98·0 [1F, F(2)] [$J_{F(1),F(2)}$ 73·0 Hz] p.p.m.; ^1H n.m.r. spectrum (CH_2Cl_2): τ 2·46 (10H, m, *Ph*As) and 8·45 (12H, s, *Me*As).

(f) *With* 1,2-*dichloro*-1,2-*difluoroethylene* (50 : 50 cis : trans-*mixture*). Similarly, reaction of 1,2-dichloro-1,2-difluoroethylene (4 mmol) with tetrakis(dimethylphenylarsine)nickel (1·82 mmol) in diethyl ether (20 ml) gave yellow *crystals* of (VIIIa) and (VIIIb) (0·91 g, 90%), m.p. 91·5—92° [Found: C, 39·0; H, 3·9; Cl, 12·8; F, 6·8%; *M*, 540 (in $CHCl_3$). $C_{18}H_{22}As_2Cl_2F_2Ni$ requires C, 38·9; H, 4·0; Cl, 12·8; F, 6·8%; *M*, 556], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3080w, 3060w, 3040w, 3005w, 2930w, 1633m, 1585w, 1488m, 1438s, 1416m, 1338w, 1310w, 1226w, 1252w, 1211w, 1190m, 1159w, 1123s, 1100m, 1090m, 1070s, 1049w, 1030s, 1025s, 1003w, 909s, 890s, 870s, 855m, 815w, 779m, 749s, and 700s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances due to (VIIIa) at 88·4 [1F, F(1)] and 106·3 [1F, F(3)] p.p.m. [$J_{F(1),F(3)}$ 14 Hz], and resonances due to (VIIIb) at 123·5 [1F, F(2)] and 131·0 [1F, F(3)] p.p.m. [$J_{F(2),F(3)}$ 122·0 Hz]; ^1H n.m.r. spectrum (CH_2Cl_2): τ 2·50 (10H, m, *Ph*As) and 8·44 (12H, s, *Me*As).

(g) *With hexafluorobuta*-1,3-*diene.* Similarly, an excess of hexafluorobuta-1,3-diene (3 mmol) and tetrakis(dimethylphenylarsine)nickel (1·82 mmol) in diethyl ether (50 ml) gave after 24 h at room temperature yellow crystals of (IX) (0·85 g, 67%), m.p. 125° (decomp.) (Found: C, 41·2; H, 3·8; F, 19·5. $C_{20}H_{22}As_2F_6Ni$ requires C, 41·1; H, 3·8; F, 19·5%), $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3050w, 2990w, 2920w, 1758m, 1581w, 1481m, 1434s, 1415m, 1334s, 1320s, 1303s, 1275w, 1250w, 1186w, 1086s, 1070w, 1021w, 999m, 960s, 929s, 905s, 895s, 869s, 850s, 819m, 740s, 693s, and 672w cm^{-1}; ^{19}F n.m.r. spectrum (Me_2CO): 84·9 (4F, m) and 148·6 (2F, m) p.p.m.; ^1H n.m.r. spectrum (Me_2CO): τ 2·58 (10H, m, *Ph*As) and 8·72 (12H, s, *Me*As).

Reactions of Bis-[o-*bis*(*dimethylarsino*)*benzene*]*nickel.*—(a) *With tetrafluoroethylene.* An excess of tetrafluoroethylene (1·6 mmol) was condensed (−196°) into a Carius tube (100 ml) containing a solution of bis-[*o*-bis(dimethylarsino)benzene]nickel (0·5 g, 0·8 mmol) in diethyl ether (20 ml). After 7 days at room temperature crystals were deposited, which were collected and washed with diethyl ether to give yellow *crystals* of (II) (0·81 g, 71%), m.p. 254—256° (Found: C, 30·7; H, 2·9; As, 27·3; F, 28·0. $C_{14}H_{16}As_2F_8Ni$ requires C, 30·9; H, 3·0; As, 27·5; F, 27·9%), $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3070w, 3030w, 2930w, 1451m, 1435w, 1417m, 1332s, 1275m, 1263m, 1247s, 1227m, 1165m, 1152s, 1134m, 1108s, 1080s, 1022m, 992s, 979m, 951s, 907s, 882s, 843m, 761s, and 653m cm^{-1}; ^{19}F n.m.r. spectrum (CH_2Cl_2): 99·0 p.p.m. [4F, t, α-CF_2, $J(F^{\alpha},F^{\beta}) < 1$ Hz] and 137·5 [4F, t, β-CF_2, $J(F^{\alpha},F^{\beta}) < 1$ Hz]; ^1H n.m.r. spectrum (CH_2Cl_2): τ 2·35 (4H, s, C_6H_4) and 8·31 (12H, s, *Me*As).

(b) *With trifluoroethylene.* Similarly, reaction of trifluoroethylene (1·8 mmol) with bis[*o*-bis(dimethylarsino)benzene]nickel (0·5 g, 0·8 mmol) in diethyl ether (20 ml) gave after 7 days at room temperature a grey-green precipitate. Filtration, reduction of the volume of the solvent *in vacuo*, and addition of light petroleum gave yellow crystals of (IV) (0·75 g, 65%), m.p. 249—250° (Found: C, 33·3;

H, 3·6; As, 29·6; F, 22·5. $C_{14}H_{18}As_2F_6Ni$ requires C, 33·1; H, 3·6; As, 29·5; F, 22·4%), $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3064w, 3018w, 2960w, 2935w, 1451m, 1413m, 1371w, 1338m, 1311w, 1265m, 1239m, 1164m, 1145w, 1112s, 1033m, 1022m, 962w, 940s, 920s, 879s, 863m, 782m, and 766m cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed multiplets at *ca.* 85·0, 95·0, and 210·0 p.p.m., but the complex was too insoluble for accurate measurements; ^{1}H n.m.r. spectrum (CH_2Cl_2): τ 2·20 (4H, s, $C_6\mathit{H}_4$), and 8·78 (12H, s, *Me*As).

Reaction of Cyclo-octa-1,5-*diene*(*hexafluoroacetone*)*nickel with* o-*Bis*(*dimethylarsino*)*benzene*. The arsine (0·9 ml, 4·5 mmol) was added dropwise to a stirred solution of cyclo-octa-1,5-diene(hexafluoroacetone)nickel [5] (1·5 g, 4·56 mmol) in light petroleum–diethyl ether (5 : 1 v/v; 60 ml). The solvent was removed *in vacuo* and the solid was dissolved in methylene chloride (10 ml). Addition of light petroleum gave yellow crystals of (X) o-*bis*(*dimethylarsino*)*benzene*-(*hexafluoroacetone*)*nickel* (1·4 g, 61%), m.p. 189—190° [Found: C, 30·6; H, 3·2; As, 29·0; F, 22·1%; *M*, 547 (in $CHCl_3$). $C_{13}H_{16}As_2F_6ONi$ require C, 30·6; H, 3·2; As, 29·3; F, 22·3%; *M*, 511], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3046w, 3040w, 2920w, 1450m, 1420m, 1308s, 1295s, 1270m, 1267m, 1219m, 1179s, 1163s, 1128s, 1100m, 1091m, 1031w, 955w, 934s, 918m, 906m, 873s, 830s, 755s, 741s, 716w, 695s, and 630w cm^{-1}; ^{19}F n.m.r. spectrum (CH_2Cl_2): 65·3 (6F, s) p.p.m.; ^{1}H n.m.r. spectrum (CH_2Cl_2): τ 2·36 (4H, m, $C_6\mathit{H}_4$) and 8·4 (12H, s, *Me*As).

Reactions of o-*Bis*(*dimethylarsino*)*benzene*(*hexafluoroacetone*)*nickel*.—(a) *With hexafluoroacetone*. An excess of hexafluoroacetone (3 mmol) was condensed (−196°) into a Carius tube containing (X) (0·7 g, 1·38 mmol) in diethyl ether (15 ml). After 4 weeks at room temperature, and 1 week at 60°, the orange-red solution was filtered, the volume of the solvent was reduced *in vacuo*, and light petroleum was added to give yellow *crystals* of (XI) (0·6 g, 65%), m.p. 180—181° [Found: C, 28·7; H, 2·4; As, 22·4; F, 33·7%; *M*, 739 (in C_6H_6). $C_{16}H_{16}As_2F_{12}O_2Ni$ requires C, 28·4; H, 2·4; As, 22·1; F, 33·7%; *M*, 677], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3046vw, 2911vw, 1450w, 1420w, 1285m, 1253m, 1234sh, 1223m, 1199s, 1193w, 1184s, 1165sh, 1150s, 1125w, 1103w, 1061m, 1009w, 964m, 933m, 915w, 882m, 755m, 746w, 725w, 720m, 700w, and 686w cm^{-1}; ^{19}F n.m.r. spectrum (Me_2CO): 65·7 (6F, m) and 81·5 (6F, mm) p.p.m.; ^{1}H n.m.r. spectrum (Me_2CO): τ 2·38 (4H, m, $C_6\mathit{H}_4$) and 8·36 (12H, s, *Me*As).

(b) *With hexafluoroisopropylideneamine*. Similarly, reaction of an excess of hexafluoroisopropylideneamine (3 mmol) with (X) (0·4 g, 0·78 mmol) in diethyl ether (20 ml) gave, after 3 weeks at room temperature, a dark orange solution, which was filtered, the volume of the solvent was reduced *in vacuo*, and light petroleum was added to give orange *crystals* of (XII) (0·48 g, 91%), m.p. 151—153° [Found: C, 28·7; H, 2·6; As, 22·4; F, 31·4; N, 2·3% *M*, 680 (in C_6H_6). $C_{16}H_{17}As_2F_{12}NNiO$ requires C, 28·4; H, 2·5; As, 22·2; F, 33·7; N, 2·1%; *M*, 676], $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3422m, 3045w, 2935w, 1449m, 1435m, 1419m, 1300sh, 1272s, 1259sh, 1246s, 1221s, 1191s, 1174s, 1164s, 1154sh, 1136s, 1124s, 1113s, 1076m, 1066m, 1032sh, 951m, 930m, 910s, 881m, 856sh, 801w, 757m, 745m, 719m, and 699m cm^{-1}; ^{19}F n.m.r. spectrum (Me_2CO): 64·4 (6F, m) and 82·0 (6F, m) p.p.m.; ^{1}H n.m.r. spectrum (Me_2CO): τ 2·29 (4H, m, $C_6\mathit{H}_4$) and 9·38 (12H, s, *Me*As).

Reaction of Bis-(π-2-*methylallyl*)*nickel with Tetrafluoroethylene*.—An excess of tetrafluoroethylene (0·1 mol) was condensed (−196°) into a Carius tube (250 ml) containing a solution in diethyl ether (*ca.* 80 ml) of bis-(π-2-methylallyl)nickel (2·32 g, 13·7 mmol) [prepared from 2-methylallyl bromide (15 g, 72·5 mmol), magnesium (12 g, 0·5 g atom) and anhydrous nickel bromide (6 g, 27·6 mmol) in diethyl ether (150 ml)]. After 2 days at room temperature, the purple-red crystals were collected and washed with benzene (4 × 5 ml) to give *crystals* of (XIII) (2·75 g, 54%), m.p. 110—111° [Found: C, 39·1; H, 3·9; F, 41·1; Ni, 16·0%; *M*, 340 (in acetone). $C_{12}H_{14}F_8Ni$ requires C, 39·1; H, 3·8; F, 41·2; Ni, 15·9%; *M*, 369], $\nu_{max.}$ (Nujol) 3075w, 2719w, 2665w, 1559w, 1323s, 1295m, 1219m, 1150s, 1140sh, 1096m, 1080s, 1074sh, 1060m, 1035w, 1002m, 979m, 940w, 929w, 919w, 907m, 889w, 863s, 829w, 779vw, 723w, and 690m cm^{-1}; ^{19}F n.m.r. spectrum ($CDCl_3$): 100·7 (4F, s) and 107·9 (4F, t, J_{HF} 18·0 Hz) p.p.m.; ^{1}H n.m.r. spectrum (Me_2CO): τ 4·95 (2H, d, $C\mathit{H}_2$=C, J_{HH} <0·5 Hz), 5·17 (2H, d, $C\mathit{H}_2$=C, J_{HH} <0·5 Hz), 7·22 (4H, t, $CF_2{\cdot}C\mathit{H}_2$, J_{HF} 18·0 Hz), and 8·01 (6H, s, *Me*C).

Reaction of (XIII) *with Dimethyl*(*phenyl*)*arsine*.—Tetrafluoroethylene (1 mmol) was condensed (−196°) into a tube containing a suspension of (XIII) (0·5 g, 1·4 mmol) and dimethyl(phenyl)arsine (0·25 g, 1·4 mmol) in benzene (30 ml). The tube and contents was shaken at room temperature for 13 days; the colour slowly changed and orange crystals separated. The crystals were collected, washed with benzene (3 × 3 ml) and light petroleum (3 × 3 ml) to give orange *crystals* of (XIV) (0·59 g, 80%), m.p. 154—156° (decomp.) (Found: C, 43·3; H, 4·6; As, 13·3; F, 27·8. $C_{20}H_{25}AsF_8Ni$ requires C, 43·6; H, 4·6; As, 13·6; F, 27·6%), $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3111w, 3058m, 3052m, 2980m, 2955m, 2942m, 2920m, 1970w, 1919w, 1899w, 1830w, 1820w, 1795w, 1769w, 1649w, 1595w, 1585w, 1575w, 1487w, 1443s, 1423m, 1411m, 1375m, 1341s, 1236s, 1197s, 1170s, 1160s, 1141s, 1089m, 1071s, 1051s, 1031s, 1002sh, 990s, 975s, 966s, 929m, 913s, 901s, 891sh, 845m, 823s, 784s, 745s, 716m, 695s, 682s, and 640w cm^{-1}.

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