Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XXVI.[1] 1,1,1-Tris(diphenylphosphinomethyl)- and 1,1,1-Tris(diphenylarsinomethyl)-ethane

By **P. K. Maples, M. Green, and F. G. A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

A series of nickel complexes $Ni{\cdot}CF_2{\cdot}CF(X)[Me{\cdot}C(CH_2EPh_2)_3]$ (X = F, H, or CF_3; E = P or As) containing tripodal ligands has been prepared. Treatment of $Pt{\cdot}CF_2{\cdot}CF_2(AsPh_3)_2$ with 1,1,1-tris(diphenylphosphinomethyl)ethane affords the related platinum compound $Pt{\cdot}CF_2{\cdot}CF_2[Me{\cdot}C(CH_2PPh_2)_3]$. The complex $Ni{\cdot}CF_2{\cdot}CF_2[Me{\cdot}C(CH_2PPh_2)_3]$ does not react with tetrafluoroethylene whereas the arsine analogue readily yields $Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2[Me{\cdot}C(CH_2AsPh_2)_3]$ by a ring-expansion reaction. The latter exchanges the arsine ligand with $Me{\cdot}C(CH_2PPh_2)_3$ or PPh_3 to give $Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2[Me{\cdot}C(CH_2PPh_2)_3]$ and $Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2(PPh_3)_2$, respectively.

REACTIONS of a variety of d^{10} nickel compounds containing uni- or bi-dentate ligands with tetrafluoroethylene afford octafluoronickelacyclopentane complexes $Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2L_2$ (L = PEt_3, $PMePh_2$, PBu_3, $P(OMe)_3$, diphos,[2] $AsMe_2Ph$, diars,[3] Bu^tNC[4]). In contrast, all-*trans*-cyclododeca-1,5,9-trienenickel reacts with tetrafluoroethylene to give the three-membered ring complex $Ni{\cdot}CF_2{\cdot}CF_2$(cdt) which appeared unreactive towards an excess of the fluoro-olefin.[5] Moreover, treatment of the cyclododecatriene complex with triphenylphosphine afforded $Ni{\cdot}CF_2{\cdot}CF_2(PPh_3)_2$ which readily yielded $Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2(PPh_3)_2$ with C_2F_4. These results[5] implicated three-membered ring complexes as intermediates in the formation of the octafluoronickelacyclopentane compounds, and also suggested that a vacant co-ordination site is critical in the conversion of three- into five-membered ring complexes. It was assumed that with $Ni{\cdot}CF_2{\cdot}CF_2$(cdt) the triene ligand blocks access to nickel of a second molecule of tetrafluoroethylene. In an attempt to elucidate further the effect of co-ordination number in these processes we have examined reactions of fluoro-olefins with zero-valent nickel complexes containing the potentially tridentate ligands 1,1,1-tris(diphenylphosphinomethyl)ethane [$MeC(CH_2PPh_2)_3$; tdpme] and 1,1,1-tris(diphenylarsinomethyl)ethane [$MeC(CH_2AsPh_2)_3$; tdame]. The new compounds obtained were characterised by elemental analysis (Table), i.r., and ^1H and ^{19}F n.m.r. spectroscopy.

Reaction of an excess of tetrafluoroethylene with a toluene solution equimolar in tdpme and Ni(cdt)[6] at −78° rapidly afforded the complex $Ni{\cdot}CF_2{\cdot}CF_2$[tdpme] (I). The latter is also readily formed by displacement of cyclododeca-1,5,9-triene from $Ni{\cdot}CF_2{\cdot}CF_2$(cdt) by tdpme. In contrast, reaction of Ni(tdpme) with tetrafluoroethylene proceeds only slowly (60°) to give complex (I), indicating that addition of tetrafluoroethylene before complete co-ordination of the tridentate phosphine is the kinetically favoured process in the reaction between C_2F_4, tdpme, and Ni(cdt).

The ^{19}F n.m.r. spectrum of (I) showed a quartet, relative intensity 1 : 3 : 3 : 1, centred at 111·4 p.p.m. (rel. CCl_3F) due to coupling with three equivalent phosphorus nuclei (J_{PF} 46·4 Hz). The presence of three phosphorus atoms in apparent equivalent chemical environments was confirmed by the ^1H spectrum of the ligand methylene protons which appeared as a single doublet (J_{PH} 7·5 Hz) at τ 7·65, and a quartet (J_{PH} 2·3 Hz) for the $CH_3{\cdot}C$ protons at τ 8·40. Although tdpme is known to function as both a bi- and as a tri-dentate ligand,[7] the above n.m.r. evidence indicates participation of all three potential co-ordination centres in (I).

Since stereochemical non-rigidity is a very common property of five-co-ordinate systems,[8] variable-temperature ^1H and ^{19}F n.m.r. studies were carried out on complex (I) (Figure). A broadening of both the fluorine and methylene signals was observed as the temperature was lowered (−100°), but unfortunately the coelescence temperature was not reached.

The character of the ^{19}F n.m.r. spectra of the analogous tetrafluoroethylene complexes $Pt{\cdot}CF_2{\cdot}CF_2(PPh_3)_2$[9] and $Rh{\cdot}CF_2{\cdot}CF_2(\pi\text{-}C_2H_4)(\pi\text{-}C_5H_5)$[10] suggests essentially rigid $M{\cdot}CF_2{\cdot}CF_2$ (M = Pt or Rh) systems with a relatively high barrier to rotation for the fluoro-olefin. This could follow from extensive back-bonding from the metal to the π^* orbital of tetrafluoroethylene. The variation with temperature of the n.m.r. spectra of (I) is indicative of a

---

[1] Part XXV, J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, preceding paper.

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

[3] Jane Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 453.

[4] M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2828.

[5] A. Greco, M. Green, S. K. Shakshooki, and F. G. A. Stone, *Chem. Comm.*, 1970, 1374.

[6] B. Bogdanovic, M. Krone, and G. Wilke, *Annalen*, 1966, **699**, 1.

[7] W. O. Seigl, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, 1971, **10**, 2158; and references cited therein.

[8] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266.

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

[10] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

less-rigid structure. The dynamic mechanism which leads to the apparent magnetic equivalence of the phosphorus nuclei with respect to the fluorine could be due either to an intramolecular polytopal isomerisation or an intramolecular dissociative process.

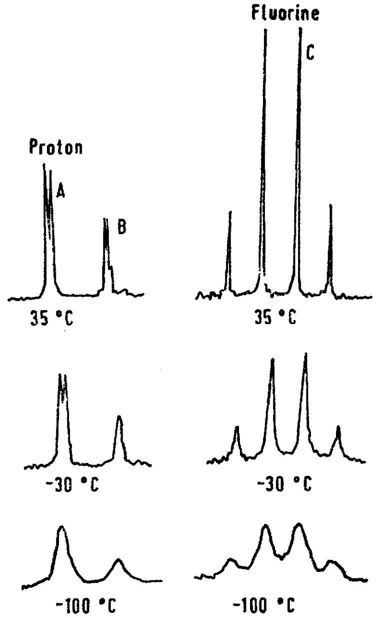
TABLE

Analytical [a] and physical data for the fluorocarbon complexes

	Compound	M.p. [b]	Colour	Yield (%)	C	H	F	P or As
(I)	$\mathrm{NiCF_2CF_2(tdpme)}$ [c]	240—243°	Yellow	72	66·2 (65·9)	5·2 (5·0)	9·4 (9·7)	11·4 (11·9)
(II)	$\mathrm{PtCF_2CF_2(tdpme)}$	201—202	White	66	56·3 (56·3)	4·4 (4·3)	8·7 (8·3)	10·1 (10·1)
(III)	$\mathrm{NiCF_2CFH(tdpme)}$	120—135 [d]	Yellow	34	67·1 (67·5)	5·0 (5·3)		
(IV)	$\mathrm{NiCF_2CF(CF_3)(tdpme)}$	180—195 [d]	Yellow	62	63·7 (63·4)	4·8 (4·7)	13·6 (13·7)	
(V)	$\mathrm{NiCF_2CF_2(tdame)}$ [e]	199—212 [d]	Yellow	68	56·1 (56·4)	4·0 (4·3)	8·3 (8·3)	25·1 (24·6)
(VI)	$\mathrm{NiCF_2CFH(tdame)}$	110—118 [d]	Yellow	21	58·4 (58·2)	4·1 (4·4)		
(VII)	$\mathrm{NiCF_2CF(CF_3)(tdame),\tfrac{1}{2}C_6H_6}$	140—150 [d]	Yellow	55	56·1 (56·4)	4·3 (3·9)	11·2 (11·4)	22·1 (22·4)
(VIII)	$\mathrm{NiCF_2CF_2CF_2CF_2(tdpme)}$ [g]	227—228	Yellow	93	61·5 (61·2)	4·7 (4·5)	17·2 (17·2)	10·2 (10·5)
(IX)	$\mathrm{NiCF_2CF_2CF_2CF_2(tdame),C_6H_6}$ [h]	138—139	Red	86	56·3 (56·0)	4·2 (4·1)	13·6 (13·9)	20·2 (20·6)

[a] Calculated values given in parentheses. [b] Sealed-tube under N_2. [c] tdpme = $\mathrm{CH_3C[CH_2PPh_3]_3}$, tdame = $\mathrm{CH_3C[CH_2AsPh_3)_3}$. [d] With decomposition. [e] Found: Ni, 6·6. Reqd.: 6·4%. [f] Found: Ni, 6·0. Reqd.: 5·9%. [g] Found: Ni, 6·8. Reqd.: 6·6%. [h] Found: Ni, 5·5. Reqd.: 5·4%.

If ready but reversible dissociation of the phosphine groups is occurring addition of a suitable reagent would be expected to lead to complex formation with one of the phosphorus atoms in (I). However, no reaction was observed with either methyl iodide or cumene hydroperoxide to form either a methyl phosphonium iodide or a phosphine oxide derivative, respectively. It would seem more likely that positional exchange of the phosphorus atoms occurs through a turnstile-rotation mechanism, or a Berry pseudo-rotation coupled with a turnstile-rotation process, as suggested [11] to account for the observed rapid positional exchange in the stereochemically closely related compound $\mathrm{MeC(CH_2O)_3\text{-}P{\cdot}O{\cdot}C(CF_3)_2{\cdot}C(CF_3)_2O}$.



^1H (100 MHz) and ^{19}F (94·1 MHz) n.m.r. spectra of $\mathrm{Ni{\cdot}CF_2{\cdot}CF_2(tdpme)}$ in CH_2Cl_2 as a function of temperature. A, ligand methylene protons; B, ligand methyl protons; C, tetrafluoroethylene fluorine nuclei

Confirmation of the stereochemical non-rigidity of the five-co-ordinate tetrafluoroethylene complexes of the kind reported herein was shown by studying the n.m.r. spectra of $\mathrm{Pt{\cdot}CF_2{\cdot}CF_2(tdpme)}$ (II), prepared by treating $\mathrm{Pt{\cdot}CF_2{\cdot}CF_2(AsPh_3)_2}$ [12] with 1,1,1-tris(diphenylphosphinomethyl)ethane. Both the ^1H and ^{19}F resonance patterns and behaviour of these spectra at low temperatures were similar to the corresponding spectra of (I). The simplicity of the ^{19}F spectrum of (II), a quartet at 127·0 p.p.m. (J_{PF} 27·0 Hz) with platinum satellites (J_{PtF} 293·0 Hz), is in striking contrast to the more complicated ^{19}F spectrum of the stereochemically rigid complex $\mathrm{Pt{\cdot}CF_2{\cdot}CF_2(PPh_3)_2}$, where the fluorine nuclei form part of an $X_2AA'X_2'$ system.[9]

Trifluoroethylene and perfluoropropene react with Ni(tdpme) to give complexes (III) and (IV) respectively. These compounds are formed more rapidly by treating Ni(cdt) with tdpme in benzene in the presence of trifluoroethylene or perfluoropropene. Complex (III) is unstable in the solid state and also in solution in the absence of excess of trifluoroethylene. It is interesting to compare the formation of $\mathrm{Ni{\cdot}CF_2{\cdot}CFH(tdpme)}$ with the reaction of trifluoroethylene with $\mathrm{Ni(PMePh_2)_4}$ which affords the five-membered ring complex $\mathrm{Ni(CF_2CFH)_2\text{-}(PMePh_2)_2}$.[2]

The ^{19}F n.m.r. spectrum of (III) shows two complex

---

[11] I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, 1971, **4**, 288.

[12] R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc.* (*A*), 1971, 2472.

multiplets centred at 96·7 (2F) and 195 (1F) p.p.m. The spectrum of $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)(tdpme)}$ (IV) showed multiplets at 64·1 (3F), 93·1 (2F) (centre of AB pattern) and 182·8 (1F) p.p.m., and was thus similar to those previously obtained[2] for $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)}$ [$\mathrm{L = PPh_3, PEt_3}$; $\mathrm{L_2 = 1,5\text{-}C_8H_{12}}$]. The ligand $\mathrm{CH_2}$ protons of both (III) and (IV) appeared as single doublets in the ^{1}H spectra.

Several attempts to obtain nickelacyclopentane ring compounds from (I), (III), and (IV) by further reaction with fluoro-olefin were unsuccessful. Both thermal and photochemical methods led to recovery of unchanged starting materials.

In an attempt to obtain an octafluoronickelacyclopentane complex containing a tridentate ligand the reaction between 1,1,1-tris(diphenylarsinomethyl)ethane-nickel and tetrafluoroethylene was investigated and shown to give $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}C}}\mathrm{F_2(tdame)}$ (IX). In contrast, on excess of tetrafluoroethylene and an equimolar toluene solution of Ni(cdt) and tdame at −78° afforded the three-membered ring complex $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}C}}\mathrm{F_2}$-(tdame) (V). Direct evidence for the intermediacy of (V) in the formation of (IX) was achieved by quantitatively converting (V) in the presence of tetrafluoroethylene at 60° into the five-membered ring complex. The formation of (IX) is in direct contrast to the analogous phosphine systems described above.

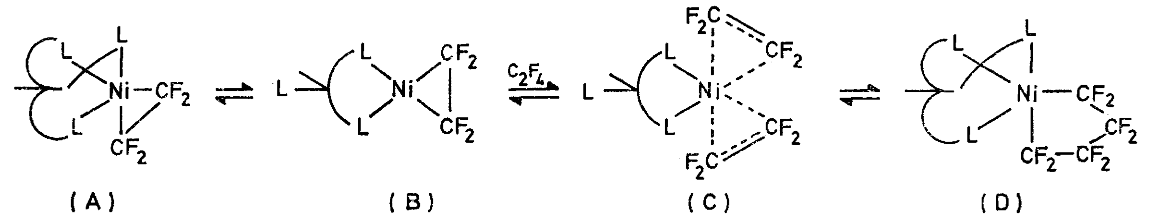
The ^{19}F n.m.r. spectrum of (V) showed a single peak at 107·5 p.p.m. while the ^{1}H spectrum showed the methylene-ligand protons as a single sharp peak at τ 7·78. Both observations suggest complete co-ordination of the arsine ligand. At low temperatures (−100°) both spectra showed line broadening which suggests stereochemical non-rigidity; unfortunately, however, temperatures were not reached at which fluxional behaviour had ceased.

The ^{19}F n.m.r. spectrum of (IX) with signals of equal intensity at 94·5 and 137·6 p.p.m. (α- and β-$\mathrm{CF_2}$ groups respectively) is characteristic of complexes containing the $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}C}}\mathrm{F_2}$ group.[2,13] The ^{1}H n.m.r. showed a sharp singlet at τ 7·67, indicating that maximum ligand co-ordination is retained even in the ring-expanded product.

Trifluoroethylene and perfluoropropene both reacted with equimolar solutions of Ni(cdt) and tdame to give adducts (VI) and (VII), respectively. Reaction of (VI) with trifluoroethylene yielded an inseparable mixture of isomeric five-membered ring complexes, as indicated[14] by the very complex ^{19}F n.m.r. spectra observed. Low solubility prevented analysis of these spectra. Treatment of (VII) under a variety of conditions with an excess of perfluoropropene did not lead to a ring-expansion reaction.

The tripodal ligand in $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}C}}\mathrm{F_2(tdame)}$ (IX) is readily displaced by triphenylphosphine to give $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}C}}\mathrm{F_2(PPh_3)_2}$ [2] and by 1,1,1-tris(diphenylphosphinomethyl)ethane to give $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}C}}\mathrm{F_2}$-(tdpme) (VIII); the latter, as mentioned above, is unobtainable by ring expansion of complex (I) with tetrafluoroethylene. Although tdpme might have behaved as a bidentate ligand in (VIII), the n.m.r. spectra showed that all three phosphorus atoms were equivalently bonded. The ^{19}F spectrum showed peaks of equal intensity at 104 and 138·5 p.p.m., the former due to the α-$\mathrm{CF_2}$ groups appeared as a quartet (J_{PF} 18·8 Hz). The ^{1}H spectrum showed the methylene groups as a single sharp doublet (J_{PH} 6·1 Hz) at τ 7·93. From the n.m.r. data it appears that an intramolecular polytopal rearrangement also occurs in complexes (VIII) and (IX).

Three principles emerge from this work concerning the conversion of three-membered ring fluoro-olefin complexes into five-membered ring compounds; the marked effect of metal co-ordination number; the intermediacy of the group $\mathrm{Ni(C_2F_4)}$ in the formation of $\mathrm{Ni(CF_2)_4}$; and the sensitivity of the ring expansion reaction towards the nature of the fluoro-olefin. These facts can be explained on the basis that the formation of fluoronickelacyclopentane rings involves a transition state (C) containing two co-ordinated fluoro-olefin molecules (Scheme).



Scheme

The inertness of (I) towards an excess of tetrafluoroethylene could be due to the absence of any intramolecular phosphine dissociation so that a co-ordinatively unsaturated species (B) is not formed. Co-ordination of a second molecule of fluoro-olefin to (A) could be blocked by the tridentate ligand. The synthesis of (VIII) by ligand exchange proves the lack of any thermodynamic instability in the five-membered ring complex. In contrast to the inertness of (I) towards $\mathrm{C_2F_4}$, intramolecular dissociation of an arsenic–nickel bond in (V) may be sufficient to allow formation of an intermediate (B) and subsequent co-ordination of a second fluoro-

---

[13] F. G. A. Stone, *Pure and Appl. Chem.*, 1972, **30**, 551.

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

olefin molecule (C). The latter step may require a change in bonding between the nickel atom and the originally co-ordinated tetrafluoroethylene molecule so that there is less π-bonding and consequently more electron density at the nickel atom.

The sensitivity of five-membered ring formation towards the nature of the fluoro-olefin is evidenced by the total lack of reactivity of $\mathrm{Ni{\cdot}CF_2{\cdot}CF(CF_3)(tdame)}$ (VII) compared with $\mathrm{Ni{\cdot}CF_2{\cdot}CF_2(tdame)}$ (V) towards $\mathrm{CF_2{:}CFCF_3}$ and $\mathrm{C_2F_4}$, respectively. Moreover, when (V) was treated with perfluoropropene, thus limiting the role of $\mathrm{CF_2{:}CFCF_3}$ to only that of the attacking fluoro-olefin, exchange rather than ring expansion occurred to give (VII). Reaction of the latter with excess tetrafluoroethylene afforded (IX) with displacement of perfluoropropene. These results suggest that the increased bulkiness of both co-ordinated or attacking $\mathrm{CF_2{:}CFCF_3}$ renders a transition state similar to (C) impossible in these particular complexes on steric grounds.

The i.r. spectra of the new compounds described herein served as a rough structural guide. The spectra of complexes containing five-membered fluorocarbon rings showed strong absorbances in the region 1100—1350 and 900—950 cm^{-1} which were absent in the analogous three-membered ring compounds.

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 and 94·1 MHz, respectively. Chemical shifts measured in dichloromethane, are relative to $\mathrm{Me_4Si}$ (τ 10·00) and $\mathrm{CCl_3F}$ (0·00 p.p.m. internal standard). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using Nujol and hexachlorobutadiene mulls. All operations were conducted in an atmosphere of dry oxygen-free nitrogen. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane was prepared as described previously.[15] The arsine analogue tdame was prepared using the same method, substituting triphenylarsine for triphenylphosphine. Similar procedures were used to prepare compounds (I)—(VI) and so a detailed method is given only for (I).

Synthesis of $\mathrm{Ni{\cdot}CF_2{\cdot}CF_2(tdame)}$.—(*a*) A solution of tdpme (1·25 g, 2 mmol) in toluene (10 ml) was added dropwise to a stirred suspension of Ni(cdt) (0·44 g, 2 mmol) in diethyl ether (20 ml) at −78°. The solution changed from dark red to green during the course of the addition. After 1 h the solution was cooled to −196°, and an excess of tetrafluoroethylene (5 mmol) was condensed into the vessel. Warming to −78° produced a light yellow solution from which yellow crystals slowly deposited. Solvent was decanted and the solid washed with hexane. Recrystallization from methylene chloride–n-hexane afforded yellow *needles* (I) (1·12 g, 72%). ^{19}F N.m.r.: 111·4 p.p.m. (q, 4F, J_{PF} 46·4 Hz). ^{1}H N.m.r.: τ 8·40 (q, 3H, $\mathrm{CH_3{\cdot}C}$, J_{PH} 2·3 Hz), 7·65 (d, 6H, $\mathrm{CH_2{\cdot}P}$, J_{PH} 7·5 Hz), 2·84 (m, 30H, $\mathrm{C_6H_5}$).

(*b*) An excess of tetrafluoroethylene (4 mmol) was condensed into a flask containing a suspension of Ni(cdt) (0·36 g, 1·64 mmol) in ether (20 ml) at −196°. Upon warming to −78° yellow crystals of $\mathrm{Ni{\cdot}CF_2{\cdot}CF_2(cdt)}$ were precipitated. Dropwise addition of tdpme (1·02 g, 1·64 mmol) in toluene (10 ml) and warming to room temperature gave (I) (0·64 g, 50%).

(*c*) A suspension of Ni(tdpme)[16] (0·68 g, 1 mmol) in benzene (25 ml) was introduced into a Carius tube (60 ml). An excess of tetrafluoroethylene (5 mmol) was condensed (−196°) into the tube, and the mixture was heated at 60° for 48 h. The Ni(tdpme) slowly dissolved giving a light yellow solution. Solvent was removed *in vacuo* and the oily residue was crystallized from methylene chloride–n-hexane to give complex (I) (0·55 g, 70%).

Synthesis of $\mathrm{Ni{\cdot}CF_2{\cdot}CFH(tdpme)}$.—As in (*a*) above, Ni(cdt) (0·30 g, 1·36 mmol) and tdpme (0·85 g, 1·36 mmol) in the presence of an excess of trifluoroethylene (4 mmol) afforded yellow crystals of complex (III) (0·35 g), from benzene–n-hexane. In the absence of an excess of $\mathrm{CF_2{\cdot}CFH}$, the complex decomposed rapidly in solution. ^{19}F N.m.r.: 96·7 p.p.m. (m, 2F, $\mathrm{CF_2}$) and 195·0 (m, 1F, CFH). ^{1}H N.m.r.: τ 8·42 (q, 3H, $\mathrm{CH_3{\cdot}C}$, $J_{\mathrm{PH}} < 2$ Hz), 7·64 (d, 6H, $\mathrm{CH_2{\cdot}P}$, J_{PH} 6·0 Hz), 2·80 (m, 30H, $\mathrm{C_6H_5}$).

Synthesis of $\mathrm{Ni{\cdot}CF_2{\cdot}CF(CF_3)(tdpme)}$. As in (*a*) above, treatment of Ni(cdt) (0·28 g, 1·27 mmol) and tdpme (0·80 g, 1·27 mmol) with $\mathrm{CF_2{:}CF(CF_3)}$ (6 mmol) gave crystals of complex (IV) (0·66 g), from benzene–n-hexane. ^{19}F N.m.r. 64·1 p.p.m. (m, 3F, $\mathrm{CF_3}$), 93·1 (m, 2F, $\mathrm{CF_2}$), 182·8 (m, 1F, CF). ^{1}H N.m.r.: τ 8·44 (q, 3H, $\mathrm{CH_3{\cdot}C}$, J_{PH} 2·6 Hz), 7·62 (d, 6H, $\mathrm{CH_2{\cdot}P}$, J_{PH} 7·0 Hz), and 2·85 (m, 30H, $\mathrm{C_6H_5}$).

Synthesis of $\mathrm{Ni{\cdot}CF_2{\cdot}CF_2(tdpme)}$.—As in (*a*) above, Ni(cdt) (0·53 g, 2·4 mmol) and tdame (1·82 g, 2·4 mmol) in the presence of tetrafluoroethylene (6 mmol) gave *needles* of complex (V) (1·50 g), from methylene chloride–n-hexane. ^{19}F N.m.r.: 107·5 p.p.m. (s, 4F, $\mathrm{CF_2}$). ^{1}H N.m.r.: τ 8·46 (s, 3H, $\mathrm{CH_3{\cdot}C}$), 7·78 (s, 6H, $\mathrm{CH_2{\cdot}As}$), and 2·73 (m, 30H, $\mathrm{C_6H_5}$).

Synthesis of $\mathrm{Ni{\cdot}CF_2{\cdot}CFH(tdame)}$.—Similarly, Ni(cdt) (0·21 g, 0·95 mmol) and tdame (0·87 g, 0·95 mmol) with trifluoroethylene (4 mmol) gave a yellow-brown solid. Recrystallization from benzene–n-hexane gave *crystals* of complex (VI) (0·18 g).

Synthesis of $\mathrm{Ni{\cdot}CF_2{\cdot}CF(CF_3)(tdame),\frac{1}{2}C_6H_6}$.—As in (*a*) above, Ni(cdt) (0·22 g, 1 mmol) and tdame (0·76 g, 1 mmol) with perfluoropropene (3 mmol) gave complex (VII) as yellow *crystals* (0·53 g), from benzene–n-hexane. The presence of 0·5 mol of benzene of crystallization was confirmed by n.m.r. spectroscopy. ^{19}F N.m.r.: 64·7 p.p.m. (m, 3F, $\mathrm{CF_3}$), 90·8 (m, 2F, $\mathrm{CF_2}$), and 181·0 (m, 1F, CF). ^{1}H N.m.r.: τ 8·46 (s, 3H, $\mathrm{CH_3{\cdot}C}$), 7·69 (s, 6H, $\mathrm{CH_2{\cdot}As}$), and 2·69 (m, 33H, $\mathrm{C_6H_5As}$ and $\mathrm{C_6H_6}$).

Preparation of $\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2(tdame),C_6H_6}$.—A suspension of Ni(tdame) (0·41 g, 0·5 mmol) in benzene (30 ml) was introduced into a Carius tube (100 ml). An excess of tetrafluoroethylene (3·5 mmol) was condensed into the tube (−196°) and the mixture was heated at 60° for 48 h. The suspended yellow complex Ni(tdame) slowly dissolved yielding a clear red solution. Addition of n-hexane (30 ml) precipitated a red solid which when recrystallized from benzene–n-hexane gave red prisms of complex (IX) (0·43 g). The presence of 1 mol of benzene of crystallization was

---

[15] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1962, 1490.

[16] P. J. Maples, M. Green, and F. G. A. Stone, to be submitted.

confirmed from the ^{1}H n.m.r. spectrum: τ 8·82 (s, 3H, $CH_3{\cdot}C$), 7·67 (s, 6H, $CH_2{\cdot}As$), and 2·62 (m, 36H, C_6H_5As and C_6H_6). ^{19}F N.m.r. 9·45 p.p.m. (t, 2F, α-CF_2, $J_{F_\alpha F_\beta}$ 3·0 Hz), and 137·6 (t, 2F, β-CF_2).

Reaction Between $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}C}}\mathrm{F_2}$(tdame) *and Tetrafluoroethylene*.—An excess of C_2F_4 (3 mmol) was condensed into a Carius tube containing a benzene (30 ml) solution of complex (V) (0·42 g, 0·47 mmol). After 16 h at 60° solvent was removed to give red *crystals* of (IX) (0·38 g), from benzene–n-hexane.

Synthesis of $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}C}}\mathrm{F_2}$(tdpme).—A mixture of complex (IX) (0·51 g, 0·5 mmol) and tdpme (0·32 g, 0·5 mmol) was refluxed in benzene (*ca.* 20 ml) for 24 h. The clear yellow solution was filtered and the solvent was removed *in vacuo*. Recrystallisation of the residue from methylene chloride–n-hexane gave yellow *crystals* of (VIII) (0·38 g). ^{19}F N.m.r.: 103·9 p.p.m. (q, 2F, α-CF_2, J_{PF} 18·8 Hz) and 138·5 (s, 2F, β-CF_2). ^{1}H N.m.r.: τ 9·25 (q, 3H, $CH_3{\cdot}C$, J_{PH} <2 Hz), 7·93 (d, 6H, $CH_2{\cdot}P$, J_{PH} 6·1 Hz), and 2·83 (m, 30H, C_6H_5).

Synthesis of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F_2}$(tdpme).—A mixture of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F_2(AsPh_3)_2}$ (0·51 g, 0·56 mmol) and tdpme in ether (30 ml) was refluxed for 18 h. Solvent was removed *in vacuo* to give colourless *needles* of complex (II) (0·35 g), from methylene chloride–n-hexane. ^{19}F N.m.r.: 127·0 p.p.m. (q, 4F, J_{PF} 27·0, J_{PtF} 293·0 Hz). ^{1}H N.m.r.: τ 9·10 (q, 3H, $CH_3{\cdot}C$, J_{PH} <2 Hz), 7·45 (d, 6H, $CH_2{\cdot}P$, J_{PH} 4·1 Hz), and 2·79 (m, 30H, C_6H_5).

We thank the U.S.A.F. Office of Scientific Research through its European Office for support.

[2/1597 *Received, 6th July,* 1972]