Reactions of Low Valent Transition Metal Complexes with Fluorocarbons. Part XXIII.[1] Pentafluorophenyl Azide and Hexafluoroazomethane

By **J. Ashley-Smith, M. Green,** and **F. G. A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reaction between pentafluorophenyl azide and $Ni(1,5\text{-}C_8H_{12})_2$ affords green crystals of a tetra-azadiene complex $Ni[(C_6F_5)_2N_4](1,5\text{-}C_8H_{12})$. Cyclo-octa-1,5-diene is displaced by the ligands L = PPh_3, PPh_2Me, $PPhMe_2$, or $P(OMe)_3$ and L_2 = bipyridyl to form $Ni[(C_6F_5)_2N_4]L_2$. ^{1}H N.m.r. measurements on the bisdimethylphenylphosphine and bis(trimethyl phosphite) complexes suggest two different modes of bonding for the tetra-azadiene ligands.

Hexafluoroazomethane reacts with $Ni(1,5\text{-}C_8H_{12})_2$ to give $\overline{Ni{\cdot}N(CF_3)N}(CF_3)(1,5\text{-}C_8H_{12})$ and with *trans*-$[IrCl(CO)(PPh_2Me)_2]$ to form a possible trifluoromethylimido- (nitrene) complex of iridium.

THERE have been several investigations of reactions of organic azides RN_3 (R = alkyl, aryl, or acyl) with transition metal complexes.[2-9] Some of these studies have had as their objective the synthesis of mononuclear nitrene (alkyl- or aryl-imido) complexes; however, binuclear and trinuclear species have been obtained.[2,3] Moreover, in the reaction of methyl azide with $Fe_2(CO)_9$ the complex $Fe(Me_2N_4)(CO)_3$,[2] containing co-ordinated 1,4-dimethyltetra-azadiene,[10] was formed together with a binuclear species. This suggests that not only is there a tendency for species such as $Fe(NR)(CO)_4$ to form complexes in which the ligand (RN) functions as a bridging group, but that the co-ordinated nitrene, or the precursors to such complexes, can readily react with more azide.

A co-ordinated nitrene carrying an electronegative substituent should in principle show less tendency to act as a bridging group. In addition, there should be increased back-bonding from the metal to the empty *p*-orbital of the co-ordinated nitrene thus increasing the stability of a mononuclear complex. With these considerations in mind we have studied some reactions of pentafluorophenyl azide $(C_6F_5N_3)$,[11,12] however, no complexes containing the C_6F_5N ligand were obtained.

Ethylenebis(triphenylphosphine)nickel reacts with pentafluorophenyl azide with evolution of nitrogen and the formation of $Ph_3P{:}NC_6F_5$, there being no evidence for the formation of stable nickel complexes. In contrast, the azide reacted with bis(cyclo-octa-1,5-diene)-nickel at −35° in diethyl ether to form a dark green solution from which dark green crystals of (I) could be obtained. Elemental analyses and a solution molecular weight determination were consistent with the molecular formula $Ni[(C_6F_5)_2N_4](1,5\text{-}C_8H_{12})$. The ^{19}F n.m.r. spectrum showed three multiplets at 147·5, 156·9, and 163·0 p.p.m., indicating that there is only one C_6F_5 environment, and from the shifts that the pentafluorophenyl groups are not directly bonded to the nickel atom.[13] The ^{1}H n.m.r. spectrum showed that the co-ordinated cyclo-octa-1,5-diene was not symmetrically bonded.

Complex (I) readily reacted with triphenylphosphine, methyldiphenylphosphine, dimethylphenylphosphine, trimethyl phosphite, or bipyridyl with displacement of cyclo-octa-1,5-diene and the formation respectively of the crystalline compounds (II)—(VI) characterised by elemental analysis as complexes of general formula $Ni[(C_6F_5)_2N_4]L_2$; molecular weight measurements in solution on (IV) and (V) confirmed the monomeric nature of the complexes. The ^{19}F n.m.r. spectra of (IV) and (V) exhibited sharp resonances with chemical shifts

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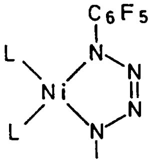
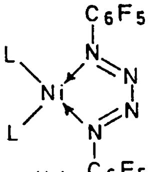
and coupling constants typical of the C_6F_5N group, there being no evidence for more than one pentafluorophenyl group environment. The ^1H n.m.r. spectrum of (IV) showed the CH_3P resonance as an apparent doublet as required [14] by a structure in which the two co-ordinated dimethylphenylphosphine ligands have a relative *cis*-configuration. In contrast, the CH_3OP resonance in the spectrum of (V) appeared as an apparent triplet with a short broad central peak indicative of a moderately large ^{31}P–^{31}P coupling, $|J_{PH} + J_{P'H}| = 11{\cdot}0$ Hz, and more consistent with a structure in which the phosphite ligands have an essentially *trans*-configuration, as might be the case in a tetrahedral complex.

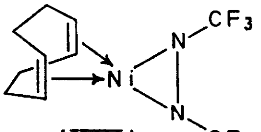


(a)

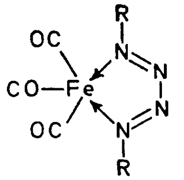


(b)

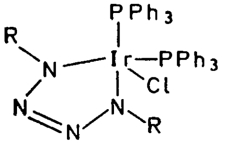
(I) L_2 = 1,5-C_8H_{12}
(II) L = PPh_3
(III) L = $PMePh_2$
(IV) L = PMe_2Ph
(V) L = $P(OMe)_3$
(VI) L_2 = bipyridyl



(VIII)



(XII) R = Me



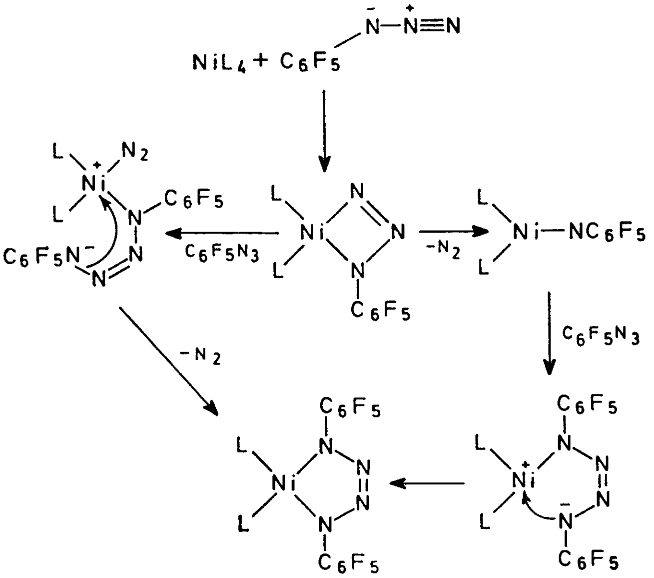
(XIII) R = *p*-F·C_6H_4

It is suggested that these observations are consistent with the presence in compounds (I)—(VI) of co-ordinated 1,4-bis(pentafluorophenyl)tetra-azadiene as shown in the illustrated structures. Previously there have been a number of structures proposed involving co-ordinated tetra-azadienes, although this is the first example of a nickel system.

X-Ray crystallographic studies [10] on $[Fe(Me_4N_4)(CO)_3]$, one of the products of the reaction of methyl azide with $Fe(CO)_5$, and on $[Ir\{(FC_6H_4)_4N_4\}(CO)(PPh_3)_2]^+BF_4^-$ [15] formed in the reaction of $FC_6H_4N_2^+BF_4^-$ with *trans*-$[IrCl(CO)(PPh_3)_2]$, have confirmed the presence in these complexes of a co-ordinated tetra-azadiene ligand. Moreover, comparison of metal-to-nitrogen bond lengths indicate that tetra-azadienes can probably bond to a metal in at least two ways. In the case of the iron complex (structure XII) the azadiene is considered to be bonded to the metal *via* co-ordinate bonds from the 1- and 4-nitrogens; whereas, in (XIII) the iridium atom, which is formally in a Ir^{III} (d^6) oxidation state, is essentially σ-bonded to the 1- and 4-nitrogens, as argued from N–N bond distances.

Clearly the nickel complexes described here can, as illustrated, have either of these two structures, *i.e.* either d^8 (a) or d^{10} (b). Stabilisation of the d^8 complexes involving σ bonds from nickel to the 1- and 4-nitrogen atoms of the 1,4-bis(pentafluorophenyl)tetra-azadiene moieties would be expected to depend on the nature of the ligands L. In particular, a good σ-donor and poor π-acceptor would favour electron release to the azadiene and the formation of the σ-bonded (d^8), structure (a). The ^1H n.m.r. results for compounds (IV) and (V) described above indicate that the balance between these two alternative formulations is quite delicate, and that as might be expected the electron releasing ligand dimethylphenylphosphine favours the d^8 structure (IVa), whereas, the good π-acceptor trimethyl phosphite favours the d^{10} structure (Vb).

The mechanism of formation of a co-ordinated tetra-azadiene ligand on reaction of a low-valent metal complex with an alkyl or aryl azide is clearly of general interest. It is possible that a nitrene complex formed by loss of nitrogen from an initially formed four-membered ring complex, reacts with a further molecule of azide as illustrated; however, such a reaction requires nucleophilic attack by the nitrene nitrogen on the 1,3-dipolarophile RN_3, and in the case of electronegatively substituted systems, *e.g.* C_6F_5N, such a step would be expected to be rather slow. An alternative



SCHEME 1

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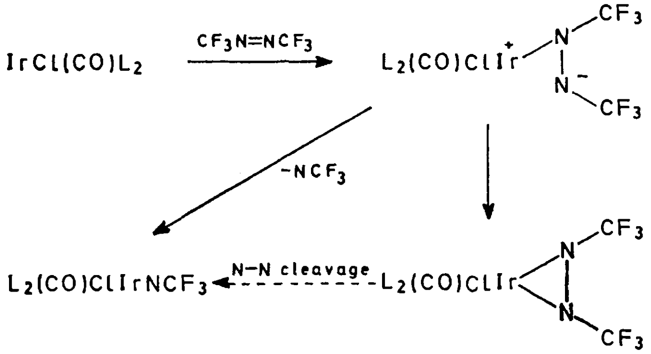
and possibly more feasible reaction path not involving a nitrene intermediate is shown in the scheme, and involves as a driving force the formation of a cationic dinitrogen complex.

In contrast with phosphines, phosphites, or bipyridyl, the poorer σ-donor but very strong π-acceptor hexafluoroacetone forms a 1 : 1 adduct (VII) on reaction with (I). Treatment of this adduct with phosphines or phosphites leads to displacement of both hexafluoroacetone and cyclo-octa-1,5-diene and the formation of (II)—(V). It is possible to formulate (VII) as a Ni^{IV} complex, but clearly further work is required to clarify the nature of this adduct.

As a possible approach to trifluoromethylnitrene complexes, some reactions of hexafluoroazomethane with low-valent metal complexes have been examined.[16] Reaction (−70°) of hexafluoroazomethane $CF_3N{=}NCF_3$, in diethyl ether with bis(cyclo-octa-1,5-diene)nickel produced a low yield (22%) of volatile red-orange crystals of (VIII), which on the basis of elemental analysis and a mass spectrum is formulated as $NiN(CF_3)N(CF_3)(1,5\text{-}C_8H_{12})$, structurally analogous to $NiN(R)N(R)L_2$ [L = PR_3,[17] Bu^tNC [18]] and the platinum complex $PtN(CO_2Et)N(CO_2Et)(PPh_3)_2$.[19] However, complex (VIII) is very unstable and decomposed both *in vacuo* and in solution; the latter property hindering n.m.r. measurements. Variation of the solvent used in the reaction did not result in improved yields or a more stable material, and in benzene no (VIII) was obtained. In view of this result and unsuccessful experiments with phosphine-substituted zerovalent-nickel and -platinum complexes the reaction of hexafluoroazomethane with Ir^I complexes was investigated.

A large excess of $CF_3N{:}NCF_3$ reacted rapidly with *trans*-[$IrCl(CO)(PMePh_2)_2$] in a small volume of benzene to produce very fine white thread-like crystals of (IX). Elemental analyses were in accord with the formula [$IrCl(NCF_3)(CO)(PMePh_2)_2,C_6H_6$], and in agreement the mass spectrum showed a peak at m/e 720, corresponding to a parent ion minus one fluorine atom. The i.r. spectrum showed a single terminal carbonyl band at higher wave number than in *trans*-[$IrCl(CO)(PMePh_2)_2$]. The ^1H n.m.r. spectrum displayed an apparent doublet for the CH_3P resonance suggesting a *cis*-configuration for the methyldiphenylphosphine ligands.[14] The appearance of a peak at τ 2·72 upfield from the phenyl resonances provided support for the suggestion of one benzene molecule of crystallisation. The ^{19}F n.m.r. spectrum showed a single peak at 77·6 p.p.m. to lower field of that observed (79·0 p.p.m.) for hexafluoroazomethane.

After separation of (IX) the benzene was removed *in vacuo* to give an oil, which after repeated precipitations from methylene chloride–hexane afforded white crystals of [$IrCl(NCF_3)(CO)(PMePh_2)_2$] (X). The i.r. spectrum showed a terminal carbonyl band at 2071·5 cm^{-1} ($CHCl_3$) in the same position as for (IX); however, the ^{19}F n.m.r. spectrum showed a singlet at 76·0 p.p.m. and the ^1H n.m.r. spectrum showed the CH_3P resonance as an apparent triplet indicating a relative *trans*-configuration for the phosphine ligands.



SCHEME 2

The available evidence does not allow a distinction to be made between possible trigonal- and tetragonal-bipyramidal structures for (IX) and (X); moreover, our inability to obtain reproducible solution molecular weight measurements for (IX) precludes the firm exclusion of a dimeric structure. Nevertheless it is reasonable to suggest that (X) is a nitrene complex where the bonding between iridium and the CF_3N ligand involves donation of an electron pair from nitrogen to iridium with concomitant back-bonding from filled iridium d-orbitals to an empty p-type orbital of nitrogen, the electronegative trifluoromethyl group serving to enhance π-bonding. Unfortunately, in spite of repeated attempts it has not been possible to grow crystals of (IX) or (X) suitable for an X-ray crystallographic study. The difference in bonding between the system described here and the arylimide and alkylimido-complexes of the type $ReX_3(NR)(PR_3)_2$,[20,21] lies in the relative contribution of π-back bonding to the nitrogen atom. In terms of this nomenclature (X) could be described as a trifluoromethylimido-complex. The related five-co-ordinate complex [$IrCl(CO)_2(PPh_3)_2$] also crystallises with one molecule of benzene and an X-ray structural determination shows a trigonal bipyramidal structure in which the phosphorus ligands are mutually *trans*.[22]

As regards possible ways in which (IX) and (X) could be formed, it is interesting that when the reaction of *trans*-[$IrCl(CO)(PMePh_2)_2$] was carried out in diethyl ether as solvent, an unstable white crystalline solid (XI) was obtained, which showed a single terminal carbonyl

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band in the i.r. at 2069 cm^{-1} ($CHCl_3$). Elemental analyses suggested that (XI) was a 1 : 1 adduct of hexafluoromethane and the iridium(I) complex possibly containing the three-membered ring system $\overline{\text{IrNCF}_3\text{N}}\text{CF}_3$. However, in solution rapid decomposition occurred which did not allow further characterisation by n.m.r. spectroscopy. It is possible that (IX) and (X) are formed from (XI), occupancy of the vacant azomethane π^* antibonding orbitals leading to cleavage of the N–N bond. An alternative path is *via* collapse of an ionic intermediate as illustrated in Scheme 2.

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. external standard). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using, unless otherwise stated, Nujol and hexachlorobutadiene mulls. Mass spectra were recorded using an A.E.I. MS 902 spectrometer at 70 eV. All reactions were performed in an atmosphere of oxygen-free nitrogen or *in vacuo*.

Hexafluoroazomethane was prepared by the published method.[23] Pentafluorophenyl azide was prepared by the method of Haszeldine *et al.*[11] and showed ^{19}F n.m.r. resonances at 152·4 (2F, m, F^2 and F^6, J_{23} 21·0 Hz, J_{25} 6·5 Hz, J_{24} 2·0 Hz), 160·9 (1F, m, F^4, J_{34} 21·5 Hz, J_{24} 2·0 Hz), and 162·5 (2F, m, F^3 and F^5, J_{23} 21·0 Hz, J_{36} 6·5 Hz) p.p.m.

Reaction of Pentafluorophenyl Azide with (a) *Ethylenebis(triphenylphosphine)nickel.*—Addition of pentafluorophenyl azide (0·40 g, 1·9 mmol) in diethyl ether (5 ml) to ethylenebis(triphenylphosphine)nickel (0·50 g, 0·81 mmol) in diethyl ether (10 ml) at room temperature led to immediate effervescence and deposition of nickel metal. Filtration of the reaction mixture and removal of the solvent *in vacuo* gave, after crystallisation of the residue from hexane–methylene chloride, white *crystals* of $C_6F_5NPPh_3$ (0·15 g) (Found: C, 64·8; H, 3·6. $C_{24}H_{15}F_5NP$ requires C, 65·0; H, 3·4%), $\nu_{max.}$ 1504s, 1490s, 1435m, 1321m, 1224m, 1105m, 991w, 981w, 975m, 742w, 716m, and 689m cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 153·8 (m, 2F, F^2, F^6, J_{23} 24 Hz), 168·2 (m, 2F, F^3, F^5, J_{23} 24·0 Hz, J_{34} 21·0 Hz), and 175·5 (m, 1F, F^4, J_{34} 21·0 Hz) p.p.m.

(b) *Bis(cyclo-octa-*1,5-*diene)nickel.*—Pentafluorophenyl azide (1·70 g, 8·1 mmol) in diethyl ether (5 ml) was added dropwise to a stirred suspension of bis(cyclo-octa-1,5-diene)-nickel (1·0 g, 3·6 mmol) in diethyl ether (30 ml) at −35°. After 1 h at −30°, the deep green solution was filtered, and the solvent removed *in vacuo*. The dark green residue was dissolved in methylene chloride (20 ml), hexane was added and the solvent slowly evaporated yielding deep green *crystals* of (I) (1·60 g, 79%), m.p. 95° (decomp.) [Found: C, 42·7; H, 2·4; N, 9·2%; *M*, 513 (C_6H_6). $C_{20}H_{12}F_{10}N_4Ni$ requires C, 43·0; H, 2·2; N, 10·0%; *M*, 557], $\nu_{max.}$ 1511s, 1497s, 1432m, 1337w, 1235w, 1162w, 1062m, 1025m, 1000s, 974s, 865s, 760w, and 717w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 147·5 (m, 4F, F^2 and F^6), 156·9 (m, 2F, F^4), and 163·0 (m, 4F, F^3 and F^5) p.p.m. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·48 (b, s, 1H, CH=CH), 5·3 (b, m, 3H, CH=CH), 7·2 (m, 3H, CH_2), and 7·7 (m, 5H, CH_2). The mass spectrum showed peaks at *m/e* 362 [$(C_6F_5N)_2$], 20%; 209 [$C_6F_5N_3$], 1%; 195 [$C_6F_5N_2$], 20%; 183 [$C_6F_5NH_2$], 10%; 181 [C_6F_5N], 5%; 167 [C_6F_5], 100%; and 108 [C_8H_{12}], 10%.

Reaction of Complex (I) *with* (a) *Triphenylphosphine.*—A solution of triphenylphosphine (0·10 g, 0·38 mmol) in methylene chloride (5 ml) was added dropwise to a stirred (0°) solution of (I) (0·10 g, 0·18 mmol) in methylene chloride (5 ml). The reaction mixture changed colour from green to brown. Addition of hexane (4 ml), followed by slow evaporation of the solvent, afforded deep brown *crystals* of (II) (0·06 g, 33%), m.p. 194° (Found: C, 58·5; H, 3·1; F, 19·7; P, 6·5; N, 5·2. $C_{48}H_{30}F_{10}P_2N_4Ni$ requires C, 59·3; H, 3·1; F, 19·6; P, 6·4; N, 5·8%), $\nu_{max.}$ 1508s, 1503s, 1435s, 1265w, 1190w, 1155w, 1087m, 1049w, 1011w, 975m, 860m, 745m, 736m, 721w, and 690s cm^{-1}.

(b) *Methyldiphenylphosphine.*—Similarly, methyldiphenylphosphine (0·08 g, 0·38 mmol) reacted with (I) (0·10 g, 0·18 mmol) in methylene chloride (10 ml) at 0° to give, from hexane–methylene chloride, deep brown-red *crystals* of (III) (0·06 g, 40%), m.p. 184° (Found: C, 52·6; H, 2·9; N, 6·6. $C_{38}H_{26}F_{10}N_4P_2Ni$ requires C, 53·8; H, 3·0; N, 6·6%), $\nu_{max.}$ 1504s, 1491s, 1432m, 1332w, 1302w, 1189w, 1151w, 1089w, 1015m, 1009m, 969s, 897m, 877m, 853m, 743w, 732m, and 692m cm^{-1}.

(c) *Dimethylphenylphosphine.*—Reaction of (I) (0·10 g, 0·18 mmol) with dimethylphenylphosphine (0·06 g, 0·4 mmol) in methylene chloride (10 ml) at 0° yielded brown-red *crystals* of (IV) (0·07 g, 54%), m.p. 155° (Found: C, 46·8; H, 3·3. $C_{28}H_{22}F_{10}N_4P_2Ni$ requires C, 46·4; H, 3·0%), $\nu_{max.}$ 1513s, 1503s, 1440m, 1293w, 1102w, 1061w, 1029m, 1014s, 975m, 951m, 905m, 860m, 745m, 720m, and 699w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 146·0 (m, 4F, F^2 and F^6, J_{23} 24·0 Hz, J_{25} 7·0 Hz), 162·0 (m, 2F, F^4, J_{34} 22·0 Hz), and 165·2 (m, 4F, F^3 and F^5, J_{23} 24·0 Hz, J_{34} 24·0 Hz, and J_{36} 7·0 Hz) p.p.m. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·3—2·8 (m, 10H, C_6H_5P) and 8·31 (apparent d, 12H, CH_3P, $|J_{PH} + J_{P'H}|$ 12·0 Hz).

(d) *Trimethyl Phosphite.*—Addition of trimethyl phosphite (0·05 g, 0·4 mmol) to (I) (0·10 g, 0·18 mmol) in methylene chloride (10 ml) at 0° yielded, from hexane–methylene chloride, deep green *crystals* of (V) (0·10 g, 80%), m.p. 165° (Found: C, 30·9; H, 2·6; F, 27·4; P, 9·1; N, 8·0%; *M*, 750 in $CHCl_3$. $C_{18}H_{18}F_{10}N_4O_6P_2Ni$ requires C, 31·0; H, 2·6; F, 27·2; P, 8·9; N, 8·1%; *M*, 697), $\nu_{max.}$ 1512s, 1506s, 1190m, 1080m, 1060s, 1040s, 1020s, 995sh, 975s, 865m, 819m, 801m, 769m, and 740m cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 148·0 (m, 4F, F^2 and F^6, J_{23} 17·0 Hz, J_{25} 5·0 Hz), 161·0 (m, 2F, F^4, J_{34} 21·0 Hz, J_{24} 2·5 Hz) and 166·1 (m, 4F, F^3 and F^5, J_{34} 21·0 Hz, J_{36} 5·0 Hz) p.p.m. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed a resonance at τ 6·49 (apparent t, 18H, CH_3OP, $|J_{PH} + J_{P'H}|$ 11·0 Hz).

(e) *Bipyridyl.*—Addition of bipyridyl (0·03 g, 0·19 mmol) to (I) (0·10 g, 0·18 mmol) in methylene chloride (10 ml) at 0° afforded yellow-green *crystals* of (VI) (0·03 g, 27%), m.p. 200—205° (decomp.) (Found: C, 43·7; H, 2·5; N, 13·9. $C_{22}H_8F_{10}N_6Ni$ requires C, 43·7; H, 1·3; N, 13·9%), $\nu_{max.}$ 1602w, 1500s, 1450s, 1310w, 1178w, 1160w, 1052m, 1010s, 996s, 970s, 776m, 741w, and 727w cm^{-1}.

(f) *Hexafluoroacetone.*—An excess of hexafluoroacetone (5 mmol) was condensed (−196°) into a Carius tube containing a solution of (I) (0·10 g, 0·18 mmol) in benzene

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(5 ml). After 24 h at room temperature the solvent was removed *in vacuo* and the crystalline material washed with hexane and dried *in vacuo* to give green *crystals* of (VII) (0·05 g, 39%) (Found: C, 37·5; H, 2·1; N, 7·8. $C_{23}H_{12}F_{16}N_4ONi$ requires C, 38·1; H, 1·7; N, 7·8%), $\nu_{max.}$ 1517s, 1510s, 1320w, 1301w, 1231s, 1220s, 1207s, 1182m, 1150w, 1170w, 1150m, 1030m, 995s, 964m, 880m, 731w, 728w, 710w, and 690m cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 80·4, 152·0, 161·2, 162·2, and 165·0 p.p.m.

Reaction of Hexafluoroazomethane with (a) *Bis(cyclo-octa-1,5-diene)nickel.*—Hexafluoroazomethane (10·0 mmol) was condensed (−196°) into a Carius tube containing bis(cyclo-octa-1,5-diene)nickel (0·5 g, 1·8 mmol) in diethyl ether (10 ml). After 3 days at −20° red crystals were deposited. The crystals were separated by hand and washed with hexane. The orange solution was filtered and the hexane removed *in vacuo* to give red-orange *crystals* of (VIII) (0·13 g, 22%), m.p. 80° (decomp.) (Found: C, 35·3; H, 3·9; F, 34·1; N, 7·8. $C_{10}H_{12}F_6N_2Ni$ requires C, 36·0; H, 3·6; F, 34·3; N, 8·4%), $\nu_{max.}$ 1482w, 1432m, 1308m, 1242—1197vs,br, 1142vs,br, 1102vs,br, 1087s, 981m, 902wm, 882m, 874sh, 861sh, 820w, 772w, 767w, 713w, 682w, and 660m cm^{-1}. The mass spectrum showed peaks at *m/e* 332 [*P*], 185 [1,5-$C_8H_{12}NiF$], 166 [1,5-$C_8H_{12}Ni$], and 128 [CF_2NNCF_2]. The complex was very unstable decomposing in solution and *in vacuo*.

(b) trans-*Chlorocarbonylbis(methyldiphenylphosphine)-iridium.*—(i) *In benzene.* Hexafluoroazomethane (3·0 mmol) was condensed into a Carius tube containing chlorocarbonylbis(methyldiphenylphosphine)iridium (0·15 g, 0·23 mmol) in benzene (10 ml). After 14 h at room temperature, white thread-like *crystals* of (IX) separated; further (24 h) reaction resulted in the solution turning purple. The crystals were separated, washed with benzene (10 ml) and hexane (2 × 10 ml), and dried *in vacuo* to give (IX) (0·03 g, 37%), m.p. 210° (Found: C, 49·8; H, 3·9; F, 7·0. $C_{34}H_{32}ClF_3NOP_2Ir$ requires C, 49·9; H, 3·9; F, 7·0%), $\nu_{max.}$ (CO) 2072 (Nujol), 2071·5 cm^{-1} ($CHCl_3$). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 77·6 (s, 3F, CF_3N) p.p.m. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·62 (m, 20H, C_6H_5P), 2·72 (s, 6H, C_6H_6), and 7·86 (apparent d, 6H, CH_3P, $|J_{PH} + J_{P'H}|$ 11·0 Hz).

The solvent of the decanted solution was removed *in vacuo* and the resultant gum repeatedly reprecipitated from methylene chloride–hexane, and washed with ether to afford white *crystals* of (X) (0·03 g, 34%), m.p. 136—139° (Found: C, 45·6; H, 3·6; F, 7·9; N, 1·9; P, 8·0%; *M*, 745 ($CHCl_3$). $C_{28}H_{26}ClF_3NOP_2Ir$ requires C, 45·4; H, 3·3; F, 7·7; N, 1·9; P, 8·4%; *M*, 739), $\nu_{max.}$ (CO) 2064 (Nujol), 2071·5 cm^{-1} ($CHCl_3$). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a single resonance at 76·0 (s, 3F, CF_3N) p.p.m. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at 2·62 (m, 20H, C_6H_5P) and 7·75 (apparent t, 6H, CH_3P, $|J_{PH} + J_{P'H}|$ 9·0 Hz). The mass spectra of (IX) and (X) exhibited ions at *m/e* 720 [*P* − F] and 692 [*P* − *F* − CO].

(ii) *In diethyl ether.* Hexafluoroazomethane (7·0 mmol) and chlorocarbonylbis(methyldiphenylphosphine)iridium (0·2 g, 0·31 mmol) reacted in diethyl ether (20 ml) at room temperature (16 h) to give a white semi-crystalline precipitate (XI) (0·03 g) (Found: C, 42·7; H, 3·7. $C_{29}H_{26}ClF_6N_2OP_2Ir$ requires C, 42·3; H, 2·3%), $\nu_{max.}$ (CO) 2054 cm^{-1} (Nujol). The complex rapidly decomposed in solution to give purple solutions.

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[2/538 *Received, 7th March*, 1972]

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