## Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XIV.<sup>1</sup> Hexafluoroisopropylideneamine-nickel and -platinum Complexes

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Ethylenebis(triphenylphosphine)nickel reacts with the imine hexafluoroisopropylideneamine or the N-methylamine to form stable crystalline complexes  $[Ni(Ph_3P)_2((CF_3)_2CNR)]$  (R = H or Me). Reaction of bis(cycloocta-1,5-diene)nickel with N-methylhexafluoroisopropylideneamine affords  $[Ni(1,5-C_8H_{12}){(CF_3)_2CNMe}]$ . which on treatment with triphenylphosphine, methyldiphenylphosphine, bipyridyl, or 1,2-bis(dimethylphosphinó)ethane, gives stable imine complexes, cyclo-octa-1,5-diene being displaced. In contrast, trimethyl phosphite displaces both the diene and the imine from  $[Ni(1.5-C_8H_{12}){(CF_3)_2CNMe}]$ .

The analogous platinum complexes  $[Pt(Ph_3P)_2\{(CF_3)_2CNR\}]$  (R = H or Me) are obtained by reaction of transstilbenebis (triphenylphosphine) platinum with the corresponding imine. Trifluoroacetic acid reacts with  $[Pt(Ph_3P)_2 - V_2 - V_2$  ${(CF_3)_2CNH}$  to form the platinum(IV) complex  $[Pt(Ph_3P)_2{(CF_3)_2CNH}(CF_3CO_2)_2]$ , whereas a similar reaction with the *N*-methyl analogue gives  $[Pt(Ph_3P)_2(H){(CF_3)_2CNMe}(CF_3CO_2)]$ . Treatment of  $[Pt(Ph_3P)_2{(CF_3)_2CNH}$ with hexafluoroacetone leads to a ring-expansion reaction and the formation of a five-membered heterocyclic ring compound. Hexafluoroacetone displaces N-methylhexafluoroisopropylideneamine from  $[Pt(Ph_3P)_2\{(CF_3)_2-$ CNMe}] to give the known complex  $[Pt(Ph_3P)_2\{(CF_3)_2CO\}]$ .

THE electrophilic ketone, hexafluoroacetone, oxidatively adds to low-valent transition-metal complexes, such as those of nickel(0),<sup>2,3</sup> palladium(0)  $^4$  and platinum(0)  $^4$ with  $d^{10}$  configuration and those of iridium(I)<sup>4</sup> and ruthenium(0) <sup>5</sup> with  $d^8$  configuration, affording stable complexes which are thought to have a rigid threemembered ring structure  $\dot{M}C(CF_3)_2\dot{O}$  (M = metal). Here we report the synthesis and some reactions of the related hexafluoroisopropylideneamine-nickel and -plati-

num complexes. Ethylenebis(triphenylphosphine)nickel, which reacts with hexafluoroactone to form [Ni(Ph<sub>3</sub>P)<sub>2</sub>{(CF<sub>3</sub>)<sub>2</sub>CO}],<sup>3</sup> reacts in ether solution at room temperature with both hexafluoroisopropylideneamine,<sup>6</sup> and N-methylhexafluoroisopropylideneamine<sup>6</sup> to afford respectively the orange, crystalline complexes (I) and (II). N-Methylhexafluoroisopropylideneamine also reacts with an ether solution of bis(cyclo-octa-1,5-diene)nickel to give orange crystals of (III). The imine complexes have good thermal stability, are stable in air for short periods in the solid state, but are rather air sensitive in solution.

Treatment of (III) with triphenylphosphine afforded (II), identical with that prepared directly from ethylenebis(triphenylphosphine)nickel. Similarly, reaction of

<sup>1</sup> Part XIII, A. J. Mukhedkar, V. A. Mukhedkar, M. Green, and F. G. A. Stone, preceding paper. <sup>2</sup> J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone,

J. Chem. Soc. (A), 1969, 20.

(III) with methyldiphenylphosphine, bipyridyl or 1,2bis(dimethylphosphino)ethane led to the displacement of cyclo-octa-1,5-diene  $(1,5-C_8H_{12})$  and the formation of the stable crystalline complexes (IV), (V), and (VI) from which the bonded N-methylhexafluoroisopropylideneamine could not be released by the addition of excess of ligand. In contrast, reaction of (III) with the good  $\pi$ -acceptor, trimethyl phosphite, led to displacement of both the diene and the imine ligands and the formof tetrakis(trimethyl phosphite)nickel. This ation observation parallels the previously reported <sup>2</sup> reaction of  $[Ni(1,5-C_8H_{12}){(CF_3)_2CO}]$  with carbon monoxide, which affords cyclo-octa-1,5-diene, hexafluoroacetone, and tetracarbonylnickel. Thus, the stability of the imine and related hexafluoroacetone complexes is dependent on a balance of the  $\sigma$ -donor and  $\pi$ -acceptor properties of the co-ordinating ligands.

Treatment at room temperature of an ether solution of *trans*-stilbenebis(triphenylphosphine)platinum with hexafluoroisopropylideneamine, or the N-methyl analogue, resulted in the displacement of trans-stilbene and the formation of the stable crystalline platinum complexes (VII) and (VIII).

The spectroscopic properties of the nickel- and platinum-imine complexes (I)---(VIII) support their

<sup>4</sup> B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, J. Chem. Soc. (A), 1968, 167.

 <sup>6</sup> M. Cooke and M. Green, J. Chem. Soc. (A), 1969, 651.
<sup>6</sup> W. J. Middleton and C. G. Krespan, J. Org. Chem., 1965, 30, 1398.

<sup>&</sup>lt;sup>3</sup> J. Ashley-Smith, M. Green, and F. G. A. Stone, J. Chem. Soc. (A), 1969, 3019.

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formulation as being isostructural with the nickel(II) and platinum(II) hexafluoroacetone complexes.<sup>2,4</sup> In agreement with the proposed  $\sigma$ -bonded three-membered ring structures, the i.r. spectra of (I)—(VIII) showed no bands readily assignable to a  $\pi$ -complexed imine. The free ligands have bands due to C=N at 1670 [(CF<sub>3</sub>)<sub>2</sub>-CNH] and 1705 [(CF<sub>3</sub>)<sub>2</sub>CNMe] cm<sup>-1</sup>, which disappear upon co-ordination.

The <sup>19</sup>F n.m.r. spectrum of hexafluoroisopropylideneamine shows bands at 73.1 and 74.9 p.p.m. ( $J_{FF}$  6;  $J_{\text{HF}} 2.5 \text{ Hz}$ ) due to CF<sub>3</sub> groups in syn- and anti- environments relative to the hydrogen atom. Similarly, the spectrum of the N-methyl analogue,  $(CF_3)_2$ CNMe, has bands at 66.9 and 73.4 p.p.m. ( $J_{\rm FF}$  8;  $J_{\rm HF}$  2.5 and 1.9 Hz). In contrast, the corresponding spectra of the nickel- and platinum-imine complexes showed only a single resonance shifted some 10.0 p.p.m. downfield from that of the parent imine. In the case of the cycloocta-1,5-diene complex (III) a single sharp resonance was observed with no evidence of spin-spin coupling. However, the spectra of the phosphine complexes (I), (II), (IV), (VII), and (VIII) showed a single doublet. which probably arises through <sup>31</sup>P-<sup>19</sup>F coupling with the phosphine trans to the  $(CF_3)_2C$  group.<sup>4</sup> The spectrum of the nickel 1,2-bis(dimethylphosphino)ethane complex (VI) at room temperature shows no evidence of <sup>31</sup>P-<sup>19</sup>F coupling, but when the solution is cooled  $(-95 \,^{\circ}\text{C})$ such coupling appears. A similar effect has been previously observed 2,7 with nickel-hexafluoroacetone complexes and may be due to phosphine dissociation or to a weakening of the bonding to the ligand.

The apparent equivalence of the geminal  $CF_3$  chemical shifts in the metal complexes (I)—(VIII) is surprising since one  $CF_3$  group is ostensibly syn to a hydrogen or methyl group and the other syn to a lone pair. A possible explanation is that rapid inversion is occurring at the nitrogen atom, the inversion proceeding via a symmetrical intermediate formed by  $\pi$ -bonding from a filled nitrogen  $2p_{\pi}$  orbital to a vacant platinum  $6p_{\pi}$  orbital:



A similar mechanism for inversion at a nitrogen atom was proposed<sup>8</sup> to account for the racemisation and proton exchange of the low-spin  $d^8$  complexes [Pt(Meen)-(phen)]<sup>2+</sup> and [Pt(Meen)(NH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>.

An attempt to confirm this hypothesis by examining the low temperature <sup>19</sup>F n.m.r. spectra of the imine complexes was inconclusive; only line broadening occurred when the solutions were cooled (-95 °C). Other explanations for the apparent n.m.r. equivalence of the CF<sub>3</sub> groups are possible. The nitrogen atoms may be  $sp^2$  hybridised so that the N-bonded methyl group or proton is coplanar with the PtCN ring, as might occur on population of the  $\pi^*$  anti-bonding orbitals of the imine. It seems unlikely that the C-N bond of the imines breaks on complex formation and that the compounds are nickel(0) or platinum(0) derivatives to which a nitrene (NH or NMe) and a carbene [(CF<sub>3</sub>)<sub>2</sub>C] are co-ordinated. The displacement of N-methylhexafluoroisopropylideneamine from (III) on treatment with tri-

methyl phosphite, mentioned before, makes this ex-

planation improbable. It is hoped that an X-ray

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<sup>&</sup>lt;sup>7</sup> C. S. Cundy, Ph.D. Thesis, University of Bristol, 1969.

<sup>&</sup>lt;sup>8</sup> J. B. Goddard and F. Basolo, Inorg. Chem., 1969, 8, 2223.

crystallographic study <sup>9</sup> of the platinum complex (VIII) will clarify the stereochemistry of the complexes.

Treatment of hexafluoroisopropylideneaminebis(triphenylphosphine)platinum (VII) with an excess of trifluoroacetic acid in methylene chloride at room temperature affords a white crystalline complex (IX), which, on the basis of elemental analysis and molecular weight measurements, is formulated as a platinum(IV) complex. The i.r. spectrum of (IX) showed a band at 1785 cm<sup>-1</sup> assignable to the carbonyl group of the CF<sub>3</sub>CO<sub>2</sub>Pt moiety. In agreement with the illustrated structure, the <sup>19</sup>F n.m.r. spectrum showed a resonance at 63·0 p.p.m. (d, with <sup>195</sup>Pt satellites) assignable to apparently equivalent geminal CF<sub>3</sub> groups of an intact

Pt·C(CF<sub>3</sub>)<sub>2</sub>·NH ring, the chemical shift being similar to that observed in the spectrum of (VII), and a broad signal at 76·1 p.p.m., which at  $-95^{\circ}$  sharpened up to a singlet corresponding to two equivalent CF<sub>3</sub>CO<sub>2</sub>Pt groups. The presence of <sup>31</sup>P<sup>-19</sup>F coupling suggests that the illustrated stereochemistry with the phosphine ligands *cis* to each other is correct, since in related octahedral hexafluoroacetone complexes with *trans*phosphines both *cis* to a (CF<sub>3</sub>)<sub>2</sub>C group there was no evidence of <sup>31</sup>P<sup>-19</sup>F coupling.<sup>4</sup> The presence of only one CF<sub>3</sub>CO<sub>2</sub>Pt resonance in the <sup>19</sup>F n.m.r. spectrum is, of course, also in agreement with the illustrated stereochemistry.

The mechanism suggested above involving rapid inversion at the nitrogen centre of the  $d^8$  imine complexes clearly cannot be extended to explain the apparent equivalence of the geminal CF<sub>3</sub> groups in the  $d^6$  platinum(IV) complex (IX), where platinum uses all p orbitals in forming  $\sigma$  bonds. Therefore, until structural studies <sup>9</sup> are completed any suggestion must necessarily be tentative. It is possible that co-ordination of an imine simply lowers the barrier to inversion of the nitrogen atom, as occurs in the racemisation of certain cobalt(III) complexes of N-methylethylenediamine.<sup>10</sup>

The analogous reaction between trifluoroacetic acid and (VIII) afforded the crystalline complex (XI), characterised by elemental analysis, and by i.r. and n.m.r. spectroscopy. The <sup>19</sup>F n.m.r. spectrum showed multiplets at 57.5 and 64.0 p.p.m. which on double irradiation collapsed to doublets with <sup>195</sup>Pt satellites, and are assigned to inequivalent geminal CF<sub>3</sub> groups. An additional resonance at 75.0 p.p.m. is assigned to CF<sub>3</sub>CO<sub>2</sub>Pt. A careful search in the high-field part of the <sup>1</sup>H n.m.r. spectrum provided no evidence for a Pt-H resonance. This may be attributed to the presence of spin-spin coupling with <sup>31</sup>P and <sup>195</sup>Pt nuclei, and to the relatively low solubility of the complex.

It is suggested that (IX) and (XI) are formed by the oxidative addition of trifluoroacetic acid to form a Pt-H species, which in the case of (IX) undergoes protolysis with more trifluoroacetic acid to form the bistrifluoroacetate compound. It is interesting that tetrafluoroacetate compound. It is interesting that tetrafluoroethylenebis(triphenylphosphine)platinum has recently been reported <sup>11</sup> to react with trifluoroacetic acid to give a ring-opened product,  $(Ph_3P)_2Pt(O_2CCF_3)-CF_2CF_2H$ , possibly *via* a platinum(IV) hydride.

An ether solution of (VII) reacts slowly with an excess of hexafluoroacetone to form the five-membered heterocyclic ring compound (X). The <sup>19</sup>F n.m.r. spectrum was in agreement with the structure proposed. Two resonances of equal intensity occurred at 64.1 and 81.0 p.p.m. Double irradiation of the high-field band collapsed the low-field band to a doublet with <sup>195</sup>Pt satellites, which is therefore assigned to a  $(CF_3)_2C$ group directly attached to platinum, the doublet arising owing to spin-spin coupling with the <sup>31</sup>P nucleus of the phosphine trans to the  $(CF_3)_2C$  group. Double irradiation of the low-field band collapsed the highfield band to a singlet, there being no evidence of <sup>195</sup>Pt-<sup>19</sup>F spin-spin coupling. Thus, the high field band is assigned to a  $(CF_3)_2C$  group not directly attached to platinum. These observations are consistent with either structure (Xa) or (Xb) for the product of the reaction of hexafluoroacetone with (VII). An X-ray crystallographic study,9 which is in progress, should allow a decision between these alternative structures. The <sup>19</sup>F n.m.r. spectrum of the compound (1,5-C<sub>8</sub>H<sub>12</sub>)-

 $\Pr^{1} \cdot O \cdot C(CF_3)_2 \cdot O \cdot C(CF_3)_2$  shows bands at  $68 \cdot 1$  and  $81 \cdot 4$  p.p.m.^{12}

An attempt to expand the ring in (VIII) and in (I) by treating these complexes with hexafluoroacetone led to ligand displacement reactions however, the products being respectively the known complexes  $[Pt(Ph_3P)_2(CF_3)_2CO]^4$  and  $[Ni(Ph_3P)_2\{(CF_3)_2CO\}].^3$ 

Clearly, a variety of different reaction paths may be proposed to explain the formation of (X). However, it is almost certainly necessary to accommodate the observed displacement reactions as well as the ring expansion reactions within any reaction scheme. A mechanism which can explain both sets of observations involves the reversible formation of an intermediate platinum(IV) complex which can either rearrange



within the co-ordination sphere to form the ringexpanded product or lead to exchange of imine for hexafluoroacetone. A similar mechanism might account

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<sup>&</sup>lt;sup>9</sup> X-Ray crystallographic study in progress.

<sup>&</sup>lt;sup>10</sup> D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, J. Amer. Chem. Soc., 1967, 89, 3428.

<sup>&</sup>lt;sup>11</sup> D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, Chem. Comm., 1969, 613.

<sup>&</sup>lt;sup>12</sup> D. J. Cook, unpublished observation.

for the formation of the complexes  $[Ni(R_3P)_2(CF_2)_4]$ .<sup>13</sup> The six-co-ordinate platinum and nickel complexes, postulated as intermediates, do not necessarily require



that these metals be in as high an oxidation state as +4. The actual oxidation state may be less depending on the degree of back bonding with the fluorocarbon ligand.

It is tempting to relate the above observations to the recently reported reaction of the oxygen complex [Pt(Ph<sub>3</sub>P)<sub>2</sub>O<sub>2</sub>] with acetone<sup>14</sup> or carbon dioxide<sup>15</sup> to form five-membered heterocyclic ring complexes.

## EXPERIMENTAL

<sup>1</sup>H and <sup>19</sup>F N.m.r. spectra were recorded on a Varian HA 100 spectrometer at 100 and 94-1 MHz, respectively. Chemical shifts are relative to tetramethylsilane ( $\tau$  10-00) and trichlorofluoromethane (0-00 p.p.m.). I.r. spectra were recorded for samples in Nujol with a Perkin-Elmer 257 spectrophotometer. All reactions were conducted under nitrogen.

Reactions of Ethylenebis(triphenylphosphine)nickel.<sup>3</sup>—(a) With hexafluoroisopropylideneamine. Hexafluoroisopropylideneamine (3 mmol) was condensed ( $-196^{\circ}$ ) into a Carius tube (25 ml) containing ethylenebis(triphenylphosphine) nickel (0.5 g, 0.81 mmol) in diethyl ether (10 ml). After 18 h at room temperature orange crystals separated, which were recrystallised from benzene to give orange crystals of (I) (0.46 g, 75%), m.p. 201° (Found: C, 62.8; H, 4.0; F, 15.4; N, 1.7. C<sub>39</sub>H<sub>31</sub>F<sub>6</sub>NNiP<sub>2</sub> requires C, 62.6; H, 4.2; F, 15.3; N, 1.9%);  $v_{max}$  3025w, 1573w, 1465m, 1423m, 1345m, 1291m, 1195m, 1180m, 1170m, 1151w, 1130s, 1114s, 1085m, 1015w, 998w, 901m, 780w, 745w, 732m, 725m, and 683s cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (benzene): single resonance at 61.9 p.p.m. (6F, d,  $J_{PF}$ 8.0 Hz).

(b) With N-methylhexafluoroisopropylideneamine. Similarly, treatment of ethylenebis(triphenylphosphine)nickel (0.5 g, 0.81 mmol) in diethyl ether (10 ml) with N-methylhexafluoroisopropylideneamine (3 mmol) gave orange crystals of (II) (0.5 g, 81%), m.p. 183° [Found: C, 62.8; H, 4.5; F, 15.0; N, 1.5%; M (in C<sub>6</sub>H<sub>6</sub>), 750. C<sub>40</sub>H<sub>33</sub>F<sub>6</sub>-NNiP<sub>2</sub> requires C, 63.0; H, 4.4; F, 15.0; N, 1.8%; M, 762];  $\nu_{max}$  3040w, 2800w, 1585w, 1480m, 1430m, 1372m,

<sup>13</sup> C. S. Cundy, M. Green, and F. G. A. Stone, J. Chem. Soc. (A), 1970, 1647. 1327s, 1297s, 1223vs, 1186m, 1165w, 1155w, 1140w, 1105s, 1100s, 1090s, 1028w, 987m, 930m, 790m, 750m, 739s, 700s, and 691s cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (benzene): single resonance at 58.2 p.p.m. (6F, d,  $J_{\rm PF}$  8.0 Hz); <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>):  $\tau$  2.8—2.9 (30H, m, C<sub>8</sub>H<sub>5</sub>P) and 7.42 (3H, apparent t,  $J_{\rm HP}$  6.5 Hz).

Reaction Between Bis(cyclo-octa-1,5-diene)nickel and N-N-Methylhexa-Methylhexafluoroisopropylideneamine. fluoroisopropylideneamine (10 mmol) was condensed (-196°) into a Carius tube (25 ml) containing bis(cycloocta-1,5-diene)nickel (1.0 g, 3.65 mmol) in diethyl ether (10 ml). After 18 h at 0 °C the resultant orange solution was filtered and the solvent was removed in vacuo. The residue was recrystallised  $(-78^\circ)$  from hexane to give orange crystals of (III) (0.3 g, 24%), m.p. 80-85° (decomp.) [Found: C, 41.5; H, 3.9; N, 3.9%; M (mass spectrum) 345. C<sub>12</sub>H<sub>15</sub>F<sub>6</sub>NNi requires C, 41.8; H, 4.3; N, 4.1%; M, 345];  $\nu_{max}$  1583w, 1475m, 1432m, 1420w, 1347s, 1306s, 1274w, 1240m, 1226vs, 1193s, 1182m, 1140s, 1120s, 1081m, 1020w, 995m, 956m, 936s, 860w, 812w, 779m, 749w, 732m, 701s, and 689w cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (benzene): single sharp resonance at 60.8 p.p.m. (6F, s); <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>): 7 4.9 (4H, m, CH=CH) and 7.4-7.8br (11H, m).

Reactions of (III).—(a) With methyldiphenylphosphine. A solution of methyldiphenylphosphine (0·15 g, 0·75 mmol) in diethyl ether (5 ml) was added dropwise to a stirred solution of (III) (0·10 g, 0·29 mmol) in diethyl ether (10 ml). The solvent was removed *in vacuo*, and the residue was washed with ether (0·5 ml) and recrystallised (-78°) from ether to afford yellow *crystals* of (IV) (0·11 g, 59%), m.p. 110° (Found: C, 56·5; H, 4·6. C<sub>28</sub>H<sub>29</sub>F<sub>6</sub>NNiP<sub>2</sub> requires C, 56·3; H, 4·6%);  $v_{max}$  3065w, 2770w, 1583w, 1483m, 1436s, 1326m, 1301m, 1220m, 1175s, 1140s, 1080w, 999w, 890s, 836w, 785w, 759m, 744s, 719w, and 699s cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (benzene): single resonance at 57·8 p.p.m. (6F, d,  $J_{\rm PF}$  8·0 Hz).

(b) With bipyridyl.—Similarly, treatment of (III) (0.10 g, 0.29 mmol) in diethyl ether (10 ml) with a solution of bipyridyl (0.10 g, 0.39 mmol) in diethyl ether (5 ml) gave ether-insoluble, dark purple crystals of (V) (0.11 g, 93%), m.p. 230—232° (decomp.) (Found: C, 43.0; H, 2.8; N, 11.0.  $C_{14}H_{11}F_6N_3Ni$  requires C, 42.7; H, 2.8; N, 10.7%);  $v_{max}$ . 1690m, 1460m, 1435s, 1363w, 1300s, 1285s, 1263w, 1236w, 1210m, 1170vs, 1149w, 1123w, 1110w, 1099s, 1045w, 981m, 920m, 785m, 755m, 749m, 730m, 718w, and 690m cm<sup>-1</sup>. The <sup>19</sup>F n.m.r. spectrum of this complex could not be obtained owing to decomposition in solution.

(c) With bis-1,2-(dimethylphosphino)ethane. Similarly, reaction of (III) (0·10 g, 0·29 mmol) with bis-1,2-(dimethylphosphino)ethane (0·05 g, 0·33 mmol) in diethyl ether (10 ml) gave a red powder, which gave red crystals of (VI) (0·08 g, 69%), (from diethyl ether-hexane), m.p. 120—122° (decomp.) (Found: C, 31·5; H, 5·3.  $C_{10}H_{17}F_6NNiP_2$  requires C, 31·0; H, 5·0%);  $\nu_{max}$  1445s, 1425m, 1329s, 1290s, 1222s, 1187vs, 1160s, 1132s, 1110s, 1099s, 999m, 939s, 890m, 872m, 845w, 832w, 798w, 777w, 736m, 710s, and 696w cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (benzene): single sharp resonance at 58·0 p.p.m. (6F, s).

Reaction Between Stilbenebis(triphenylphosphine)platinum and Hexafluoroisopropylideneamine.—Hexafluoroisopropyl-

<sup>15</sup> P. J. Hayward, D. M. Blake, C. J. Nyman, and G. Wilkinson, Chem. Comm., 1969, 987.

<sup>&</sup>lt;sup>14</sup> R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Comm.*, 1968, 1498.

ideneamine (3 mmol) was condensed (--196°) into a Carius tube (50 ml) containing a suspension of stilbenebis(triphenylphosphine)platinum (0.80 g, 0.88 mmol) in diethyl ether (10 ml). After 3 h the crystalline precipitate was recrystallised from methylene chloride, to give white crystals of (VII) (0.45 g, 57%), m.p. 196° [Found: C, 52·9; H, 3·5; F, 12·6; N, 1·7%; M (in CHCl<sub>3</sub>), 885. C<sub>39</sub>H<sub>31</sub>F<sub>6</sub>-NP<sub>2</sub>Pt requires C, 53·0; H, 3·5; F, 12·9; N, 1·6%; M, 884];  $\nu_{\rm max}$  3280w, 3060w, 1580w, 1475m, 1432m, 1345m, 1284s, 1190m, 1181, 1165w, 1145vs, 1124vs, 1100s, 1030w, 1001w, 914m, 830w, 816w, 736m, and 698s cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>): single resonance at 62·3 p.p.m. (6F, d with <sup>195</sup>Pt satellites,  $J_{\rm PF}$  12·0,  $J_{\rm PtF}$  84·0 Hz).

Reaction Between Stilbenebis(triphenylphosphine)platinum and N-Methylhexafluoroisopropylideneamine.-Similarly, N-methylhexafluoroisopropylideneamine (3 mmol) with stilbenebis(triphenylphosphine)platinum (0.8 g, 0.88 mmol) in diethyl ether (10 ml) gave an ether-insoluble material which afforded white crystals of (VIII) (0.55 g, 70%)(from methylene chloride), m.p. 220° [Found: C, 53.2; H, 3.5; N, 1.5%; M (in CHCl<sub>3</sub>), 940.  $C_{40}H_{33}F_6NP_2Pt$ requires C, 53.5; H, 3.8; N, 1.6%; M, 898]; v<sub>max</sub> 3065w, 2800w, 1585w, 1480m, 1437s, 1315s, 1293s, 1275w, 1225vs, 1190s, 1173w, 1149w, 1127vs, 1105s, 1036w, 1005m, 943m, 854w, 815m, 760m, 755m, 715m, and 706s cm<sup>-1</sup>; the <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>): single resonance at 59.7 p.p.m. (6F, d with <sup>195</sup>Pt satellites,  $J_{PF}$  13.0,  $J_{PtF}$  81.0 Hz); <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>):  $\tau$  2.95 (30H, m, C<sub>6</sub>H<sub>5</sub>P) and 7.46 (3H, apparent t with <sup>195</sup>Pt satellites,  $J_{\rm HP}$  6.5, J<sub>IIPt</sub> 34.0 Hz).

Reactions of (VII).—(a) With trifluoroacetic acid. To a solution of (VII) (0·10 g, 0·11 mmol) in methylene chloride (5 ml) was added an excess of trifluoroacetic acid (0·2 ml). After 10 min at room temperature the solvent was removed in vacuo and the residue was triturated with diethyl ether. The resultant white powder gave white crystals of (IX) (0·08 g, 64%) (from methylene chloride-hexane) m.p. 258° [Found: C, 46·3; H, 2·9; P, 5·9%; M (in CHCl<sub>3</sub>) 1200. C<sub>43</sub>H<sub>33</sub>F<sub>12</sub>NO<sub>4</sub>P<sub>2</sub>Pt requires C, 46·5; H, 2·8; P, 5·6%; M, 1110];  $\nu_{max}$  3300w, 3070w, 1785m, 1585m, 1480m, 1435s, 1347m, 1300s, 1201vs, 1180s, 1156s, 1127s, 1100s, 1031w, 1003w, 915w, 844w, 793m, 755m, 750m, 712s, and 699s cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>): at 63·0 p.p.m. (6F, d with <sup>195</sup>Pt satellites,  $J_{PF}$  9·0,  $J_{PtF}$  67·0 Hz) and 76·1br (6F, s).

(b) With hexafluoroacetone. An excess of hexafluoro-

acetone (10 mmol) was condensed (-196°) into a tube containing a solution of (VII) (0·10 g, 0·11 mmol) in diethyl ether (10 ml). After 2 days at room temperature, the white precipitate was recrystallised from methylene chloride-hexane to give white crystals of (X) (0·09 g, 78%), m.p. 252° [Found: C, 47·6; H, 3·1; F, 21·8; N, 1·4; P, 6·1%; M (in CHCl<sub>3</sub>), 1060. C<sub>42</sub>H<sub>31</sub>F<sub>12</sub>NOP<sub>2</sub>Pt requires C, 48·0; H, 2·9; F, 21·8; N, 1·3; P, 5·9%; M, 1049];  $\nu_{max}$ . 3420w, 3060w, 1575w, 1475m, 1432m, 1310w, 1253s, 1226s, 1208s, 1182s, 1150vs, 1099m, 1061w, 1003w, 949m, 933m, 915w, 750m, 719m, 703s, and 695s cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>): 64·1 p.p.m. (6F, m, which collapsed to d with <sup>195</sup>Pt satellites on <sup>19</sup>F<sup>-19</sup>F decoupling,  $J_{FF} 2·5$ ,  $J_{PF} 6·0$ ,  $J_{PtF} 86·0$  Hz) and 81·0 (6F, m, collapsed to singlet on <sup>19</sup>F<sup>-19</sup>F decoupling,  $J_{FF} 2·5$  Hz).

Reactions of (VIII).---(a) With trifluoracetic acid. An excess of trifluoracetic acid (0.10 g, 0.88 mmol) was added to a solution of (VIII) (0.10 g, 0.11 mmol) in methylene chloride (5 ml). After 5 min at room temperature the solvent was removed in vacuo and the residue was successively triturated with diethyl ether (5 ml) and hexane (5 ml) affording white crystals of (XI) (0.06 g, 55%), m.p. 199° (Found: C, 50.5; H, 3.7.  $C_{42}H_{34}F_9NO_2P_2Pt$  requires C, 50.0; H, 3.4%);  $\nu_{max}$  3060w, 2760w, 1722m, 1581w, 1475m, 1435s, 1315m, 1280s, 1196s, 1180s, 1140s, 1119s, 1099s, 1030w, 1001w, 936w, 799w, 750m, 731w, 710s, and 689s cm<sup>-1</sup>; <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>): 57.5 p.p.m. (3F, m, collapsed to d with 195Pt satellites on 19F-19F decoupling,  $J_{FF}$  9.0,  $J_{PF}$ 8.5,  $J_{PtF}$  64.0 Hz), 61.1 (3F, m, collapsed to d with 195Pt satellites on 19F-19F decoupling,  $J_{\rm FF}$  9.0,  $J_{\rm PF}$  8.0,  $J_{\rm PtF}$  68.0 Hz), and 75.0 br (3F, s).

(b) Hexafluoroacetone. A similar reaction of (VIII) (0.10 g, (0.88 mmol) with hexafluoroacetone (10 mmol) in diethyl ether (10 ml) gave hexafluoroacetonebis(triphenylphosphine)platinum (0.085 g, 80%), identical (i.r. and n.m.r. spectrum) with an authentic sample.<sup>4</sup>

Reaction Between (I) and Hexafluoroacetone.—Similarly, reaction of (I) (0.10 g, 0.13 mmol) with hexafluoroacetone (10 mmol) in diethyl ether (10 ml) gave hexafluoroacetonebis(triphenylphosphine)nickel (0.075 g, 76%) identical (i.r. and n.m.r.) with an authentic sample.<sup>2</sup>

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