Reactions of Low-valent Metal Complexes with Fluorocarbons. Part 31.[1] Bis(η-cyclo-octa-1,5-diene)-platinum and -palladium, with Fluoro-olefins

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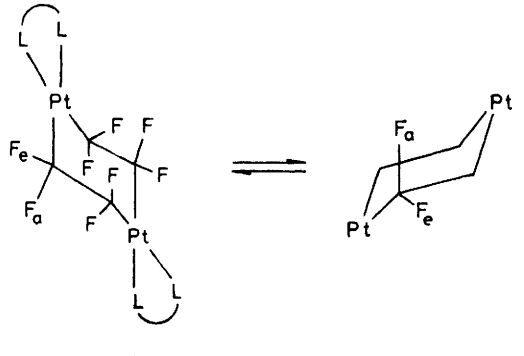
Reaction of bis(η-cyclo-octa-1,5-diene)platinum with C_2F_4 gives an octafluorodiplatinacyclohexane complex $[Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(1,5\text{-}C_8H_{12})_2]$, which undergoes ligand-displacement reactions to form $[Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2L_4]$ [$L = PEt_3$; $L_2 = 1,2\text{-}C_6H_4(AsMe_2)_2$]. Tris(η-bicyclo[2.2.1]heptene)platinum reacts with C_2F_4 to give the mononuclear species $[Pt(CF_2{\cdot}CF_2)(C_7H_{10})_2]$, which with $P(OMe)_3$ and with $1,5\text{-}C_8H_{12}$ forms, respectively, $[Pt(CF_2{\cdot}CF_2)\{P(OMe)_3\}_2]$ and $[Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(1,5\text{-}C_8H_{12})_2]$. In contrast, $[Pd(1,5\text{-}C_8H_{12})_2]$ and C_2F_4 afford the four-ring system $[(1,5\text{-}C_8H_{12})Pd(CF_2{\cdot}CF_2)Pd(1,5\text{-}C_8H_{12})]$. Chlorotrifluoroethylene undergoes a vinyl-rearrangement reaction on treatment with $[Pt(1,5\text{-}C_8H_{12})_2]$ yielding $[PtCl(CF{:}CF_2)(1,5\text{-}C_8H_{12})]$. Hexafluoropropene rearranges on treatment with $[M(1,5\text{-}C_8H_{12})_2]$ (M = Pt or Pd) to form $[(1,5\text{-}C_8H_{12})M\{C(CF_3)_2\}M(1,5\text{-}C_8H_{12})]$. In the case of the palladium system, the complex $[Pd\{CF_2{\cdot}CF(CF_3)\}(1,5\text{-}C_8H_{12})]$ has also been isolated, and shown to be the precursor of the binuclear complex. Octafluorobut-2-ene, hexafluoroacetone, and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene react with $[Pd(1,5\text{-}C_8H_{12})_2]$ to give the conventional products $[Pd\{CF(CF_3){\cdot}CF(CF_3)\}(1,5\text{-}C_8H_{12})]$, $[Pd\{C(CF_3)_2{\cdot}O\}(1,5\text{-}C_8H_{12})]$, and $[Pd\{C(CN)_2{\cdot}C(CF_3)_2\}(1,5\text{-}C_8H_{12})]$.

We have previously shown that both bis(η-cyclo-octa-1,5-diene)-palladium and -platinum readily react with ethylene with displacement of cyclo-octa-1,5-diene to form respectively tris(η-ethylene)-palladium and -platinum.[2] It was thought worthwhile to carry out comparative studies with fluoro-olefins. Some aspects of this investigation have been mentioned in a preliminary communication.[3] In this paper we describe a detailed study of such reactions.

RESULTS AND DISCUSSION

Bis(η-cyclo-octa-1,5-diene)platinum,[2] suspended in diethyl ether, reacted at room temperature with an excess of tetrafluoroethylene to afford in high yield a white crystalline complex (1), which on the basis of elemental analysis and mass spectroscopy is formulated as a binuclear species with the illustrated structure. The i.r. and n.m.r. spectra are in agreement with such a formulation, and in particular the temperature dependence of the ^{19}F n.m.r. spectrum can be interpreted in terms of a chair structure with axial (F_a) and equatorial (F_e) fluorine environments. At 90 °C the ^{19}F spectrum showed a single line *ca.* 30-Hz broad with two pairs of ^{195}Pt satellites. On cooling to −60 °C the spectrum collapsed to an approximate AB system, which on analysis afforded coupling constants in agreement with the formulation of the complex as an octafluoro-1,4-diplatinacyclohexane. The dynamic behaviour can be explained in terms of a degenerate ring-inversion process of the type well known with cyclohexanes and heterocyclic six-membered ring systems. Additional support for these ideas derives from the reaction of (1) with 1,2-bis(dimethylarsino)benzene or triethylphosphine, which leads to displacement of both cyclo-octa-1,5-diene ligands, and the formation of complexes (2) and (3), respectively. The ^{19}F n.m.r. spectrum of (3) showed a similar temperature dependence to (1) and at −80 °C collapsed to an AB system.



(1) L-L = $1,5\text{-}C_8H_{12}$
(2) L-L = $C_6H_4(AsMe_2)_2$
(3) L = PEt_3

Some insight into the reaction which affords (1) was obtained from a study of the reaction of tetrafluoroethylene with tris(bicyclo[2.2.1]heptene)platinum.[2] The crystalline product (4) of this reaction was characterised by elemental analysis and n.m.r. spectroscopy as bis(η-bicyclo[2.2.1]heptene)(tetrafluoroethylene)platinum, and, in agreement, treatment of (4) with trimethyl phosphite led to the displacement of both bicyclo[2.2.1]heptene ligands and the formation of (tetrafluoroethylene)bis(trimethyl phosphite)platinum (5). In contrast, cyclo-octa-1,5-diene reacted (room temperature) with the mononuclear complex (4) to give (70%) the previously obtained binuclear species (1).

Before discussing the implications of these observations it is necessary to consider the related reaction of

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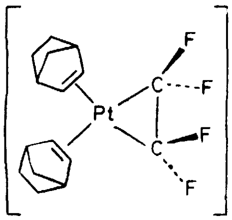
[1] Part 30, M. Green, J. A. K. Howard, A. C. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 278.

[2] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

[3] M. Green, J. A. K. Howard, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 451.

tetrafluoroethylene with bis(η-cyclo-octa-1,5-diene)palladium.[2] Treatment at low temperature of $[Pd(1,5\text{-}C_8H_{12})_2]$ with an excess of tetrafluoroethylene afforded the yellow crystalline complex (6), which analysed for $[Pd_2(C_2F_4)(1,5\text{-}C_8H_{12})_2]$. Since we had previously[1] established by a single-crystal *X*-ray diffraction study that the product of the reaction of hexafluoroacetone with $[Pt(1,5\text{-}C_8H_{12})_2]$ contained the four-membered ring structure $[\overline{Pt\cdot Pt\cdot C(CF_3)_2\cdot O}(1,5\text{-}C_8H_{12})_2]$, it was considered that the palladium complex (6) also had the same structural feature, and that a tetrafluoroethylene molecule and two palladium atoms are combined together as illustrated. In agreement, the ^1H n.m.r. spectrum showed the expected resonances due to co-ordinated cyclo-octa-1,5-diene, and the ^{19}F n.m.r. *spectrum* showed a single sharp resonance at low field (76.2 p.p.m., relative to CCl_3F) consistent with the presence of a $\overline{Pd\cdot CF_2\cdot CF_2\cdot Pd}$ system.



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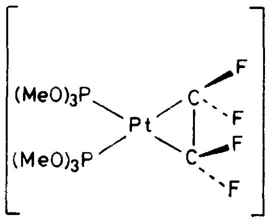

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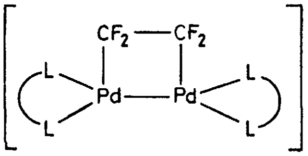
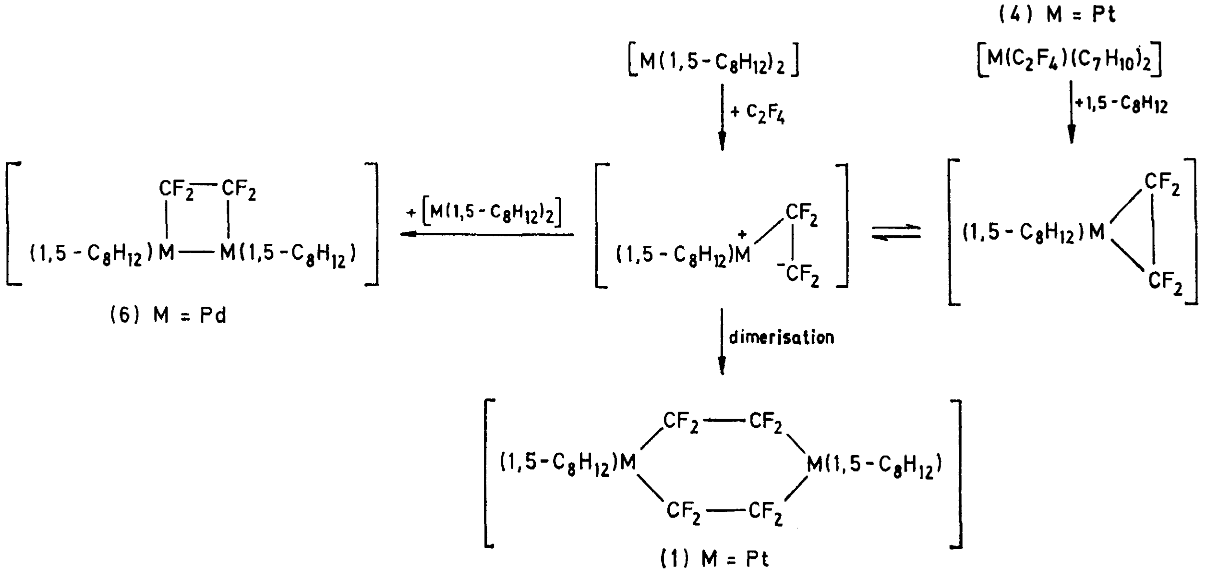


(6)

L - L = 1,5 - C_8H_{12}

We have discussed the possibility that in the reaction of d^8 or d^{10} metal complexes with fluoro-olefins the metal species functions as a nucleophile, and reacts with the fluoro-olefin *via* a two-electron-transfer step to afford a 1,3-dipolar species.[4,5,*] The reversibility of this process is indicated by a recent study[6] of the pyrolysis of stereochemically pure $[Fe(\textit{trans}\text{-}CF_3CH{:}CHCF_3)(CO)_4]$ and $[Fe(\textit{cis}\text{-}CHF{:}CFCF_3)(CO)_4]$. In the pyrolysis, small amounts of geometric isomers of the olefins were obtained, suggesting[6] the involvement of an intermediate 1,3-dipolar species with single-bond character, in which rotation about the formal carbon–carbon double bond may occur. Thus the reaction of $[Pt(1,5\text{-}C_8H_{12})_2]$ with tetrafluoroethylene may be pictured as involving the formation of a 1,3-dipolar species (Scheme 1), which *via* a dimerisation process affords directly the binuclear six-membered ring complex (1). The results with the bicyclo[2.2.1]heptene complex (4) suggest that treatment with cyclo-octa-1,5-diene leads to reversal of three-membered-ring formation and generation of the same 1,3-dipolar intermediate, which then dimerises. A difficulty with this suggestion is that there is no obvious rationale as to why replacement of two bicyclo[2.2.1]heptene ligands by cyclo-octa-1,5-diene leads to formation of a 1,3-dipole. In the reaction of tetrafluoroethylene with $[Pd(1,5\text{-}C_8H_{12})_2]$ it is suggested that a



Scheme 1

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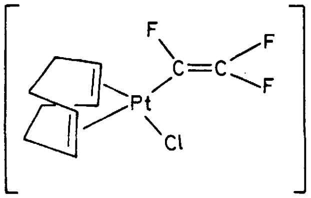
[*] The reactions reported in this paper can, in principle, also be explained in terms of a diradical (singlet on triplet) species, *e.g.* $\dot{M}{-}CF_2{-}\dot{C}F_2$, which would be accessible either directly from the fluoro-olefin and the metal(0) species *via* a one-electron-transfer process, or by electron transfer within a 1,3 dipolar intermediate. However, the absence of products arising from hydrogen-abstraction reactions, which might be expected to occur, lead us to tentatively favour the involvement of dipolar intermediates.

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

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

[6] R. Fields, G. L. Godwin, and R. N. Haszeldine, *J.C.S. Dalton*, 1975, 1867.

competitive process intervenes, in which the initially formed 1,3-dipolar species is captured by a further molecule of the nucleophilic reagent [Pd(1,5-C_8H_{12})$_2$]. A similar mechanism has been suggested [1] to explain the formation of [Pt$_2${(CF_3)$_2$CO}(1,5-C_8H_{12})$_2$].



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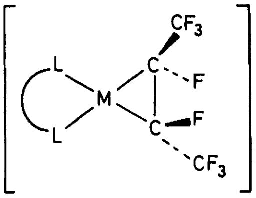
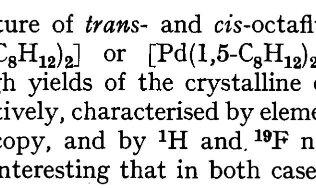


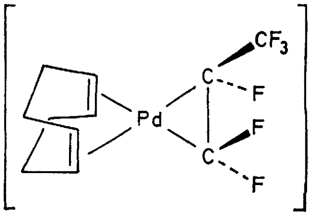
(8) M = Pt, L-L = 1,5-C_8H_{12}
(9) M = Pd, L-L = 1,5-C_8H_{12}

Chlorotrifluoroethylene reacts with [Pt(1,5-C_8H_{12})$_2$] to give white crystals of the trifluorovinyl complex (7). The presence of the arrangement Pt·CF:CF_2 was suggested by the appearance of a strong band in the i.r. spectrum at 1 728 cm^{-1}, and this structural feature was confirmed by the ^{19}F n.m.r. spectrum which exhibited characteristic [7] chemical shifts and coupling constants. Previous studies [8-10] on the reaction of chlorotrifluoroethylene with (tertiary phosphine)platinum(0) complexes have demonstrated that the vinyl complexes are formed from fluoro-olefin π complexes (metallacyclopropanes), the vinyl rearrangement being assisted by polar solvents. However, in the formation of (7) in diethyl ether as solvent there was no evidence for the intermediacy of [Pt(CF_2·CFCl)(1,5-C_8H_{12})]. Although a reaction occurred between [Pd(1,5-C_8H_{12})$_2$] and chlorotrifluoroethylene, the only product isolated was [PdCl_2(1,5-C_8H_{12})]. However, η^2-fluoro-olefin complexes can be formed and this was demonstrated by the observation that reaction of a 3 : 1 mixture of *trans*- and *cis*-octafluorobut-2-ene with [Pt(1,5-C_8H_{12})$_2$] or [Pd(1,5-C_8H_{12})$_2$] in diethyl ether gave high yields of the crystalline complexes (8) and (9), respectively, characterised by elemental analysis, mass spectroscopy, and by ^{1}H and ^{19}F n.m.r. spectroscopy. It is interesting that in both cases, as deduced from the relative simplicity of the ^{19}F spectra, only one isomer is formed, presumably [9] the *trans* isomer.



(10) M = Pt, L-L = 1,5-C_8H_{12}
(11) M = Pd, L-L = 1,5-C_8H_{12}

The products of the reactions of hexafluoropropene with bis(η-cyclo-octa-1,5-diene)-platinum or -palladium provide an interesting contrast with those obtained from tetrafluoroethylene. Crystalline diplatinum and dipalladium complexes (10) and (11) were obtained. The ^{19}F n.m.r. spectrum of the species (10) is fully consistent with the illustrated structure, suggested by elemental analysis and mass and i.r. spectroscopy, showing a single resonance at 47.6 p.p.m. which appeared as a 1 : 8 : 18 : 8 : 1 multiplet. The splitting arises from ^{195}Pt–^{19}F coupling [*J*(PtF) 153 Hz], this being confirmed by the observation that irradiation at 21.405 3 MHz (^{195}Pt) collapsed the multiplet to a singlet. Thus in the formation of (10) and (11) from hexafluoropropene a fluorine-migration reaction occurs to give a bridged bis(trifluoromethyl)methylene system.



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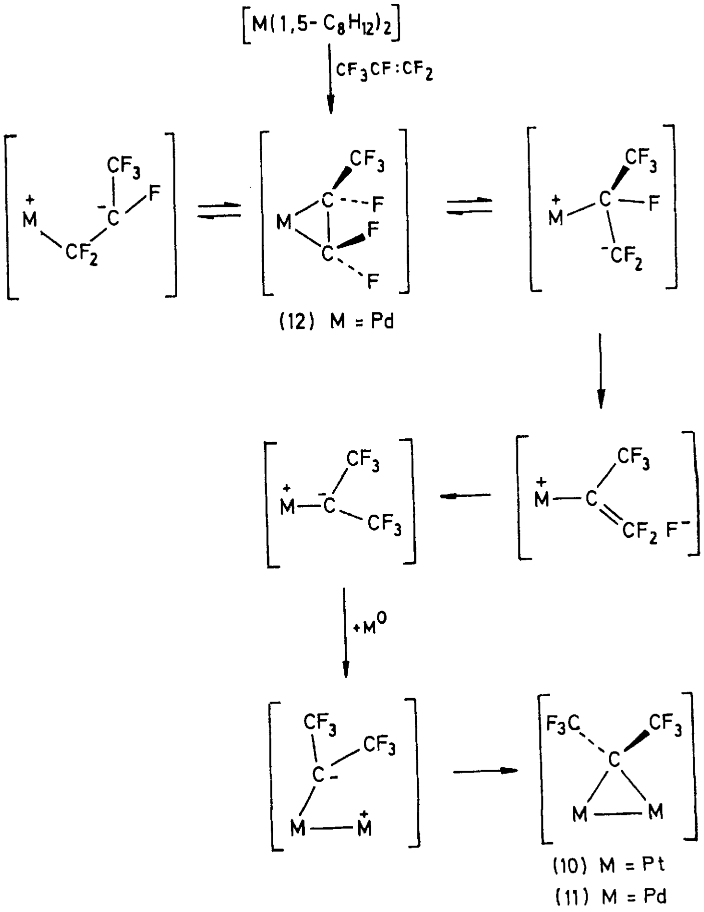

SCHEME 2 C_8H_{12} ligands are omitted

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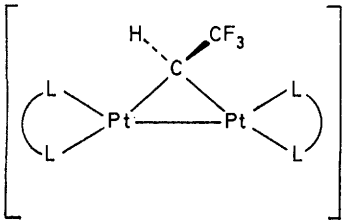
[7] A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 66.

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

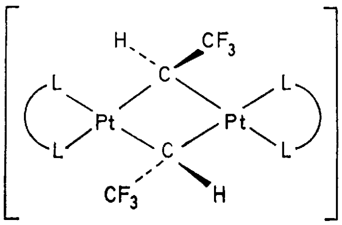
[9] M. Green, P. K. Maples, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 2069 and refs. therein.

[10] M. Green and G. J. Parker, *J.C.S. Dalton*, 1973, 2099.

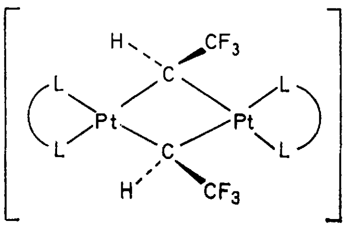
When the reaction of $[\mathrm{Pd}(1,5\text{-}\mathrm{C_8H_{12}})_2]$ with $\mathrm{CF_3CF{:}CF_2}$ was carried out for less time (1.5 h, 0 °C) a crystalline complex $[\mathrm{Pd}\{\mathrm{CF_2{\cdot}CF(CF_3)}\}(1,5\text{-}\mathrm{C_8H_{12}})]$ (12) was obtained. The ^{19}F n.m.r. spectrum confirmed this formulation showing typical[8,11] chemical shifts and coupling constants for an η^2-bonded hexafluoropropene system. Of considerable interest was the observation that a solution of (12) in diethyl ether at room temperature afforded the binuclear complex (11).



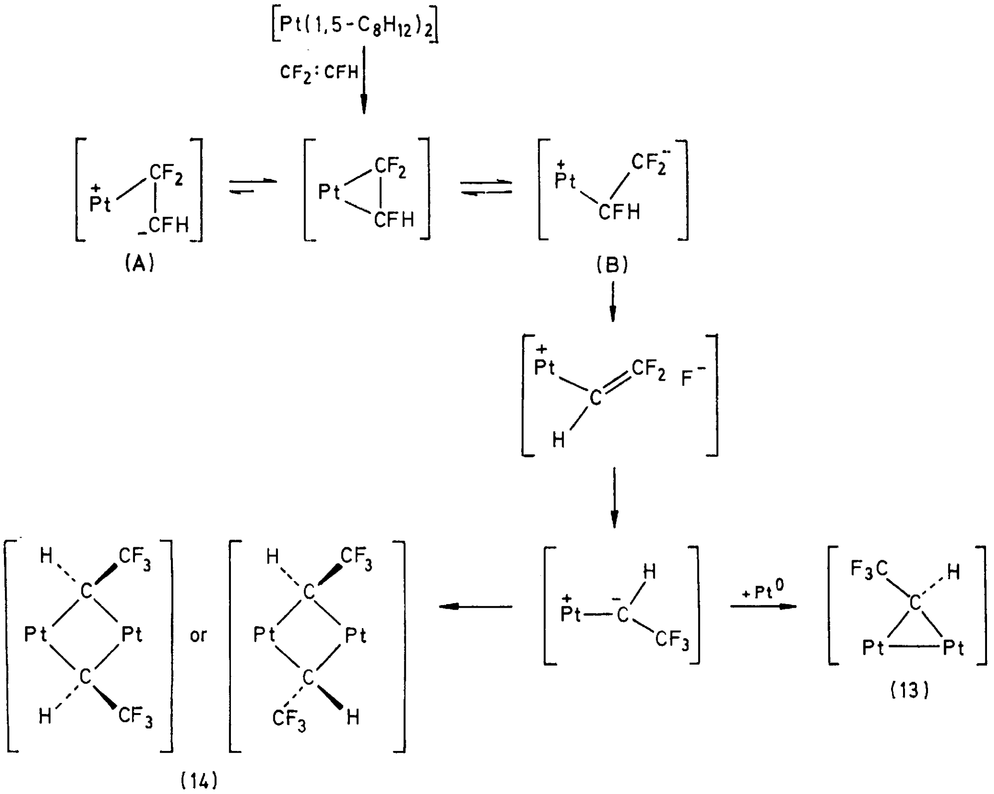
(13) L-L = 1,5-$\mathrm{C_8H_{12}}$



(14a) L-L = 1,5-$\mathrm{C_8H_{12}}$



(14b) L-L = 1,5-$\mathrm{C_8H_{12}}$



SCHEME 3 $\mathrm{C_8H_{12}}$ ligands are omitted

It is assumed that the first step in the formation of (10) and (11) involves nucleophilic attack by Pt^0 or Pd^0 on hexafluoropropene to give *via* dipolar intermediates an η^2 complex (a metallacyclopropane in valence-bond terms). Fluoride-anion elimination, followed by recombination with F$^-$ could give an ylide (Scheme 2) which could serve as the precursor to (10) or (11) by reaction with a further molecule of bis(η-cyclo-octa-1,5-diene)-platinum or -palladium. Fluoride-migration reactions are well established in reactions of nucleophilic carbonylmetal anions with perfluoroallyl chloride,[12,13] and in reactions of pentacarbonylhydridomanganese with hexafluorobuta-1,3-diene[14] and perfluorocyclopentadiene.[15]

Trifluoroethylene reacted at room temperature with $[\mathrm{Pt}(1,5\text{-}\mathrm{C_8H_{12}})_2]$ in toluene or diethyl ether to give a mixture of products which we were unable to separate. However, ^{19}F n.m.r. studies on mixtures provide strong evidence for the presence of binuclear platinum complexes with bridging $\mathrm{C(CF_3)H}$ groups. Thus one product showed a resonance at 45.9 p.p.m. with *J*(PtF) 150 Hz,

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

[12] W. R. McClellan, *J. Amer. Chem. Soc.*, 1961, **83**, 1598.

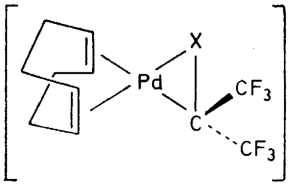
[13] H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 1960, **B15**, 763.

[14] B. W. Tattershall, A. J. Rest, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 899.

[15] R. Fields, M. Green, T. Harrison, R. N. Haszeldine, A. Jones, and A. B. P. Lever, *J. Chem. Soc.* (*A*), 1970, 49.

and is assigned structure (13) on the basis of the close similarity of this data with that of (10) (see above), and a characteristic[16] coupling *J*(HF) 17 Hz for a $C(CF_3)H$ group. Two other fluorine-containing platinum complexes were present in the mixture, the spectrum of each species showing one multiplet, *viz.* 40.2 [*J*(PtF) 210 and *J*(HF) 13.5] and 40.4 p.p.m. [*J*(PtF) 204 and *J*(HF) 13.5 Hz]. It is suggested that these two complexes are the two possible isomers (14a) and (14b) in which the trifluoromethyl groups have a relative *trans* or *cis* configuration. It is proposed that (13) and (14) might form according to the processes indicated in Scheme 3. However, a difficulty arises. Namely, the normal direction of addition of a nucleophilic reagent to trifluoroethylene would preferentially give the 1,3-dipolar species (A). In order to explain the formation of the complexes it is necessary to assume that the 1,3-dipolar (B) is also formed, possibly in a subsequent thermodynamically controlled step, which then undergoes a fluoride-anion-elimination reaction as discussed above for the corresponding reaction with hexafluoropropene.

We have previously described reactions of $[Pt(1,5\text{-}C_8H_{12})_2]$ with $(CF_3)_2CO$ and $(CF_3)_2C{:}C(CN)_2$.[1] In order to make a comparison, reactions of $[Pd(1,5\text{-}C_8H_{12})_2]$ with these dipolar reagents were studied, and in this manner the mononuclear complexes (15) and (16) were isolated. In neither reaction was there evidence for either the formation of binuclear metal species or products arising from linking of the reactant with cyclo-octa-1,5-diene.



(15) X = O
(16) X = $C(CN)_2$

EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 and 94.1 MHz, respectively. Fluorine-19 shifts are relative to CCl_3F (0.0 p.p.m.), positive values indicating a shift to high field. Infrared spectra were obtained with a Perkin-Elmer 457 instrument using Nujol mulls. Mass spectra for molecular-weight determinations were recorded on an MS 902 spectrometer operating at 70 eV.* Solvents were dried and distilled under nitrogen, and all the operations were conducted in an atmosphere of dry oxygen-free nitrogen.

Reactions of Bis(η-*cyclo-octa*-1,5-*diene*)*platinum*.[2]—(*a*) *With tetrafluoroethylene*. A suspension of $[Pt(1,5\text{-}C_8H_{12})_2]$ (0.4 g, 1.0 mmol) in diethyl ether (30 cm³) was introduced into a Carius tube (100 cm³) and C_2F_4 (0.17 g, 1.7 mmol) was condensed (−196 °C) into the vessel. After 4 h at room temperature, white *crystals* were deposited. A further crop was obtained on reduction of the volume (10 cm³) of the solvent *in vacuo* to give white *crystals* of $[Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(1,5\text{-}C_8H_{12})_2]$ (1) (0.39 g, 96%), m.p. 140 °C [Found: C, 29.4; H, 3.0%; *M* 806 (mass spectrum), 826 ($CHCl_3$ solution). $C_{20}H_{24}F_8Pt_2$ requires C, 29.8; H, 3.0%; *M* 806], $\nu_{max.}$ at 1 435s, 1 340m, 1 318w, 1 260w, 1 255w, 1 235w, 1 205w, 1 192w, 1 128s, 1 098w, 1 052s, 1 022s, 1 002s, 948s, 940s, 895w, 872m, 832s, 785m, 745w, 732w, 700w, 678m, 458w, and 398w cm⁻¹. The ¹H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.25 (m, 4 H, CH:CH) and 7.53 (m, 8 H, CH_2). The ^{19}F n.m.r. spectrum is temperature dependent. At 90 °C (C_6D_6—$CH_3C_6H_5$) the spectrum showed a single line (δ 86.2 p.p.m.) *ca.* 30-Hz broad with two pairs of satellite peaks [*J*(PtF) 388 and 98 Hz]. At −60 °C ($CDCl_3$) the spectrum collapsed into an approximate AB system where δ_A 81.6 and δ_B 93.3 p.p.m. [*J*(AB) 230, *J*(APt) 398, *J*(APt′) 80, *J*(BPt) 356, and *J*(BPt′) 140 Hz].

(*b*) *With chlorotrifluoroethylene*. An excess of chlorotrifluoroethylene (1.9 g, 17 mmol) was condensed into a Carius tube containing $[Pt(1,5\text{-}C_8H_{12})_2]$ (0.4 g, 1.0 mmol) in diethyl ether (100 cm³). A dark brown precipitate formed on warming to room temperature. After 10 h the volatile material was removed *in vacuo*, and the volume of solvent was reduced (10 cm³). Addition of light petroleum (20 cm³), followed by cooling (−40 °C), gave white *crystals* of $[PtCl(CF{:}CF_2)(1,5\text{-}C_8H_{12})]$ (7) (0.24 g, 57%), m.p. 129 °C (decomp.) (Found: C, 28.3; H, 2.9%; *M* 419. $C_{10}H_{12}ClF_3Pt$ requires C, 28.6; H, 2.9%; *M* 419), $\nu_{max.}$ at 1 728s, 1 550w, 1 545w, 1 435s, 1 348m, 1 318m, 1 312m, 1 305w, 1 292w, 1 255s, 1 235m, 1 220w, 1 202w, 1 188w, 1 158w, 1 102s, 1 092s, 1 080s, 1 032m, 1 012m, 998s, 985s, 918w, 895w, 872m, 860m, 830m, 805m, 778m, 700w, 655w, 585w, 518w, 482m, 445w, 420w, 335s, 318w, and 280w cm⁻¹. The ¹H n.m.r. spectrum in C_6D_6 showed resonances at τ 4.56 (s, 2 H, CH=CH), 5.37 (s, 2 H, CH=CH), and 8.42 (m, 8 H, CH_2). The ^{19}F n.m.r. spectrum in CH_2Cl_2 showed resonances ($Pt{\cdot}CF^3{:}CF^1F^2$ with F^2 *trans* to F^3) at 96.7 [d of d, 1 F, F^1, *J* (PtF^1) 72.0], 121.9 [d of d, 1 F, F^2, *J*(PtF^2) 10.5], and 159.2 p.p.m. [d of d, 1 F, F^3, *J*(PtF^3) 429 Hz], where *J*(F^1F^2) 90, *J*(F^2F^3) 107, and *J*(F^1F^3) 40 Hz.

(*c*) *With Hexafluoropropene*. An excess of hexafluoropropene (0.52 g, 3.5 mmol) was condensed into a tube containing $[Pt(1,5\text{-}C_8H_{12})_2]$ (0.50 g, 1.25 mmol) suspended in light petroleum (40 cm³). The tube and contents were allowed to warm to room temperature with shaking. After 12 h the reaction mixture was filtered, the solid residue being washed (4 × 20 cm³) with diethyl ether. The filtrate and combined washings were filtered through a column (2 cm) of alumina, and the volume of the solvent was reduced (10 cm³) *in vacuo*. The solution was cooled (−40 °C) giving yellow *crystals* of $[Pt_2\{\mu\text{-}C(CF_3)_2\}(1,5\text{-}C_8H_{12})_2]$ (10) (0.12 g, 21%), m.p. 170 °C (decomp.) (Found: C, 30.5; H, 3.5%; *M* 756. $C_{19}H_{24}F_6Pt_2$ requires C, 30.2; H, 3.2%; *M* 756), $\nu_{max.}$ at 1 520w, 1 435m, 1 340w, 1 315w, 1 272s, 1 250m, 1 230m, 1 208vs, 1 175s, 1 080vs, 1 070s, 1 050m, 998w, 972m, 945s, 912s, 865w, 828w, 790ms, 780m, 772m, 762w, 752w, 745w, 688m, 530w, and 460w cm⁻¹. The ¹H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.42 [m, 4 H, CH=CH, *J*(PtH) 60 Hz] and 7.84 (m, 8 H, CH_2). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed a single resonance at 47.6 p.p.m. [five peak multiplet 1 : 8 : 18 : 8 : 1, *J*(PtF) 153 Hz]; irradiation at 21.405 3 MHz reduced the multiplet to a singlet.

(*d*) *With octafluorobut*-2-*ene*. A similar reaction (10 h,

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* 1 eV ≈ 1.60×10^{-19} J.

[16] J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1872.

room temperature) of a *cis–trans* (1 : 3) mixture of octafluorobut-2-enes (1 g, 5 mmol) with $[\mathrm{Pt(1,5\text{-}C_8H_{12})_2}]$ (0.40 g, 1.0 mmol) in diethyl ether (60 $\mathrm{cm^3}$) gave a colourless reaction mixture. Reduction of the volume (5 $\mathrm{cm^3}$) of the solvent followed by the addition of light petroleum and cooling (−40 °C) gave white *crystals* of $[\overline{\mathrm{Pt\{CF(CF_3)\cdot CF}}\mathrm{(CF_3)\}(1,5\text{-}C_8H_{12})}]$ (8) (0.40 g, 80%), m.p. 89 °C (Found: C, 28.3; H, 2.6%; *M* 503. $\mathrm{C_{12}H_{12}F_8Pt}$ requires C, 28.6; H, 2.4%; *M* 503). The ^{1}H n.m.r. spectrum in $\mathrm{CDCl_3}$ showed resonances at τ 4.04 [m, 4 H, CH=CH, *J*(PtH) 56] and 7.61 [m, 8 H, $\mathrm{CH_2}$, *J*(PtH) 28 Hz]. The ^{19}F n.m.r. spectrum in $\mathrm{CDCl_3}$ showed resonances at 68.5 [s with ^{195}Pt satellites, 6 F, $\mathrm{CF_3}$, *J*(PtF) 106] and 194.3 p.p.m. [s with ^{195}Pt satellites, 2 F, CF:CF, *J*(PtF) 114 Hz].

*Displacements of Cyclo-octa-*1,5-*diene from* (1).—(*a*) *With* 1,2-*bis(dimethylarsino)benzene.* The arsine $\mathrm{1,2\text{-}C_6H_4(AsMe_2)_2}$ (0.15 $\mathrm{cm^3}$, 0.78 mmol) was added dropwise with stirring to a solution of (1) (0.30 g, 0.37 mmol) in methylene chloride (20 $\mathrm{cm^3}$). After 1.5 h the volume of the solvent was reduced (5 $\mathrm{cm^3}$) *in vacuo*, light petroleum (20 $\mathrm{cm^3}$) was added, and the solution was cooled (−40 °C) to give yellow *crystals* of $[\mathrm{Pt_2(\mu\text{-}CF_2\cdot CF_2)_2\{1,2\text{-}C_6H_4(AsMe_2)_2\}_2}]$ (2) (0.41 g, 95%) (Found: C, 24.6; H, 3.0. $\mathrm{C_{24}H_{32}As_4F_8Pt_2}$ requires C, 24.8; H, 2.8%).

(*b*) *With triethylphosphine.* A solution of $\mathrm{PEt_3}$ (0.23 g, 2 mmol) in diethyl ether (5 $\mathrm{cm^3}$) was added to a suspension of (1) (0.30 g, 0.37 mmol) in diethyl ether (50 $\mathrm{cm^3}$). After 10 h at room temperature the volume of the solvent was reduced (5 $\mathrm{cm^3}$), and the solution was cooled (−30 °C) to give white *crystals* of $[\mathrm{Pt_2(\mu\text{-}CF_2\cdot CF_2)_2(PEt_3)_4}]$ (3) (0.39 g, 94%), isolated with 0.5 mol of diethyl ether, m.p. 108 °C (Found: C, 32.9; H, 6.0. $\mathrm{C_{28}H_{60}F_8P_4Pt_2\cdot 0.5Et_2O}$ requires C, 32.8; H, 6.0%). The ^{1}H n.m.r. spectrum in $\mathrm{C_6D_6}$ showed resonances at τ 6.73 [q, 2 H, $\mathrm{CH_3}$*$\mathrm{CH_2}$*O, *J*(HH) 8.0], 8.30 (m, 24 H, $\mathrm{CH_3}$*$\mathrm{CH_2}$*P), 8.88 [t, 3 H, *$\mathrm{CH_3}$*$\mathrm{CH_2}$O, *J*(HH) 8.0] and 9.02 (m, 36 H, *$\mathrm{CH_3}$*$\mathrm{CH_2}$P). The ^{19}F n.m.r. spectrum ($\mathrm{CH_3C_6H_5\text{–}C_6D_6}$, −80 °C) showed an AB pattern with the parameters δ_A 71.1 and δ_B 82.5 p.p.m. [*J*(AB) 245, *J*(APt) 402, *J*(BPt) 299, and *J*(BP) + *J'*(BP) 41 Hz]. At room temperature broadening occurred. The ^{31}P n.m.r. spectrum in $\mathrm{C_6D_6}$ showed a resonance at −5.6 p.p.m. [m, *J*(PtP) 1 990, *J*(PF) 41.0 Hz], relative to external $\mathrm{H_3PO_4}$.

Reactions of Bis(η-*cyclo-octa*-1,5-*diene)palladium*.[2]—(*a*) *With tetrafluoroethylene.* An excess of tetrafluoroethylene (8.0 mmol) was condensed (−196 °C) into a Carius tube containing a suspension of $[\mathrm{Pd(1,5\text{-}C_8H_{12})_2}]$ (0.8 g, 2.5 mmol) in diethyl ether (30 $\mathrm{cm^3}$). The tube and contents were agitated at −30 °C for 1 h. The resulting yellow solid was collected and recrystallised from diethyl ether–light petroleum to give yellow *crystals* of $[\mathrm{Pd_2(\mu\text{-}CF_2\cdot CF_2)(1,5\text{-}C_8H_{12})_2}]$ (6) (0.6 g, 90%) (Found: C, 40.8; H, 4.6. $\mathrm{C_{18}H_{24}F_4Pd_2}$ requires C, 40.9; H, 4.6%), $\nu_{\max.}$ at 3 010w, 1 570w, 1 430m, 1 345w, 1 322w, 1 282s, 1 268w, 1 240w, 1 202w, 1 192w, 1 160w, 1 145w, 1 122w, 1 090w, 1 060w, 1 025s, 1 002m, 995w, 975w, 968w, 948m, 898vs, 860s, 828m, 755m, 735m, 728m, 662w, 552w, 545w, and 535w $\mathrm{cm^{-1}}$. The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$, −30 °C) showed resonances at τ 3.84 (m, 4 H, CH=CH), 4.05 (m, 4 H, CH=CH), and 7.58 (m, 16 H, $\mathrm{CH_2}$). The ^{19}F n.m.r. spectrum ($\mathrm{CDCl_3}$, −30 °C) showed a resonance at 76.2(s) p.p.m.

(*b*) *With hexafluoropropene.* An excess of hexafluoropropene (1.2 g, 8 mmol) was condensed into a tube containing a suspension of $[\mathrm{Pd(1,5\text{-}C_8H_{12})_2}]$ (0.8 g, 2.5 mmol) in diethyl ether (30 $\mathrm{cm^3}$). The tube and contents were allowed to warm slowly (12 h) to room temperature and filtered. The red solution was filtered through a short (2 cm) column of alumina, and the volume of the solvent was reduced (8 $\mathrm{cm^3}$) *in vacuo*. The solution was cooled (−40 °C) to give brown-red *crystals* of $[\mathrm{Pd_2\{\mu\text{-}C(CF_3)_2\}(1,5\text{-}C_8H_{12})_2}]$ (11) (0.5 g, 69%), m.p. 160 °C (decomp.) (Found: C, 39.3; H, 4.4. $\mathrm{C_{19}H_{24}F_6Pd_2}$ requires C, 39.4; H, 4.2%), $\nu_{\max.}$ at 1 550w, 1 475m, 1 430s, 1 340w, 1 318w, 1 262s, 1 238m, 1 230m, 1 218m, 1 182vs, 1 158s, 1 072s, 1 058s, 1 040s, 992w, 975w, 960m, 912m, 900s, 858m, 822m, 765s, 748s, 730s, 722s, 680m, 630m, 522w, and 435w $\mathrm{cm^{-1}}$. The ^{1}H n.m.r. spectrum in $\mathrm{CDCl_3}$ showed resonances at τ 4.08 (br m, 8 H, CH=CH) and 7.62 (m, 16 H, $\mathrm{CH_2}$). The ^{19}F n.m.r. spectrum in $\mathrm{CDCl_3}$ showed a resonance at 46.8(s) p.p.m.

If the reaction was terminated after a shorter reaction time then a different product was obtained. Bis(η-cyclo-octa-1,5-diene)palladium (0.37 g, 1.15 mmol) was suspended in diethyl ether (15 $\mathrm{cm^3}$) contained in a large Schlenk tube (100 $\mathrm{cm^3}$), and hexafluoropropene (3.5 mmol) was condensed (−196 °C) into the tube. On warming the mixture slowly from −78 to 0 °C (1.5 h) the grey suspension dissolved to give a yellow solution, which was filtered through Celite and evaporated to dryness. The residue was extracted with light petroleum (b.p. 40—60 °C), and the extract was filtered and cooled (−78 °C) giving off-white *crystals* of $[\overline{\mathrm{Pd\{CF_2\cdot CF}}\mathrm{(CF_3)\}(1,5\text{-}C_8H_{12})}]$ (12) (0.19 g, 45%) (Found: C, 35.7; H, 3.4. $\mathrm{C_{11}H_{12}F_6Pd}$ requires C, 36.2; H, 3.3%), $\nu_{\max.}$ at 1 490m, 1 435m, 1 418m, 1 343w, 1 313s, 1 271w, 1 245w, 1 184vs, 1 139s, 1 110s, 1 079s, 1 007w, 973s, 918w, 906w, 861w, 831m, 770s, 739m, and 681s $\mathrm{cm^{-1}}$. The ^{19}F n.m.r. spectrum in $\mathrm{CDCl_3}$ showed resonances [$\mathrm{Pd(F^1F^2C{:}CF^3CF_3{}^4)}$, $\mathrm{F^2}$ and $\mathrm{F^3}$ assumed *trans* [11]] at 66.2 (3 F, $\mathrm{CF_3}$), 100.6 (1 F, $\mathrm{F^1}$), 108.8 (1 F, $\mathrm{F^2}$), and 199 p.p.m. (1 F, $\mathrm{F^3}$) [*J*($\mathrm{F^1F^2}$) 147, *J*($\mathrm{F^2F^3}$) 80, *J*($\mathrm{F^2F^4}$) 10, and *J*($\mathrm{F^3F^4}$) 10 Hz].

(*c*) *With octafluorobut-2-ene.* Similarly, reaction of octafluorobut-2-ene (1.6 g, 8.0 mmol) with $[\mathrm{Pd(1,5\text{-}C_8H_{12})_2}]$ (0.8 g, 2.5 mmol) in diethyl ether (30 $\mathrm{cm^3}$) gave (3 h) a colourless solution. Removal of the solvent *in vacuo* and recrystallisation from diethyl ether–light petroleum afforded white *crystals* of $[\overline{\mathrm{Pd\{CF(CF_3)\cdot CF}}\mathrm{(CF_3)\}(1,5\text{-}C_8H_{12})}]$ (9) (0.9 g, 87%), m.p. 67 °C (decomp.) (Found: C, 35.3; H, 3.0. $\mathrm{C_{12}H_{12}F_8Pd}$ requires C, 34.8; H, 2.9%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$, −30 °C) showed resonances at τ 3.90 (m, 8 H, CH=CH) and 7.52 (m, 16 H, $\mathrm{CH_2}$). The ^{19}F n.m.r. spectrum ($\mathrm{CDCl_3}$, −30 °C) showed resonances at 67.3 (s, 6 F, $\mathrm{CF_3}$) and 190.4 p.p.m. (s, 2 F, CF=CF).

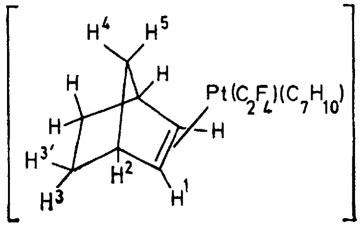
(*d*) *With hexafluoroacetone.* Hexafluoroacetone (0.42 g, 2.5 mmol) was condensed into a tube containing a suspension of $[\mathrm{Pd(1,5\text{-}C_8H_{12})_2}]$ (0.8 g, 2.5 mmol) in diethyl ether (30 $\mathrm{cm^3}$). The tube and contents were allowed to warm slowly (2 h) to 0 °C. After 1 h at 0 °C the resulting colourless solution was evaporated to dryness and the solid was recrystallised from diethyl ether–light petroleum to give white *crystals* of $[\overline{\mathrm{Pd\{C(CF_3)_2\cdot O}}\mathrm{\}(1,5\text{-}C_8H_{12})}]$ (15) (0.8 g, 84%), m.p. 110 °C (decomp.) (Found: C, 34.8; H, 3.2. $\mathrm{C_{11}H_{12}F_6OPd}$ requires C, 34.7; H, 3.2%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$, −30 °C) showed resonances at τ 4.03 (br s, 2 H, CH=CH), 4.43 (br s, 2 H, CH=CH), and 7.51 (m, 8 H, $\mathrm{CH_2}$). The ^{19}F n.m.r. spectrum ($\mathrm{CDCl_3}$, −30 °C) showed a resonance at 67.3(s) p.p.m.

(*e*) *With* 1,1-*dicyano*-2,2-*bis(trifluoromethyl)ethylene.* A similar reaction (−40 °C) of $\mathrm{(CF_3)_2C{:}C(CN)_2}$ (0.3 g, 1.5 mmol) and $[\mathrm{Pd(1,5\text{-}C_8H_{12})_2}]$ (0.46 g, 1.5 mmol) in diethyl ether

(30 cm^3) gave on recrystallisation from diethyl ether–light petroleum white *crystals* of [$Pd\{C(CN)_2{\cdot}C(CF_3)_2\}(1,5\text{-}C_8H_{12})$] (16) (0.4 g, 63%), m.p. 280 °C (decomp.) (Found: C, 39.1; H, 2.9; N, 6.4. $C_{14}H_{12}F_6N_2Pd$ requires C, 39.2; H, 2.8; N, 6.5%). The ^1H n.m.r. spectrum ($CDCl_3$, −30 °C) showed resonances at τ 3.89 (br s, 4 H, CH=CH) and 7.38 (m, 8 H, CH_2). The ^{19}F n.m.r. spectrum ($CDCl_3$, −30 °C) showed a resonance at 55.1(s) p.p.m.

Reaction of Tris(η-*bicyclo*[2.2.1]*heptene*)*platinum with Tetrafluoroethylene*.—An excess of tetrafluoroethylene (4.0 mmol) was condensed into a tube containing tris(η-bicyclo[2.2.1]heptene)platinum (1.5 g, 3.1 mmol) in light petroleum (50 cm^3). After 1 h at room temperature, the reaction mixture was filtered and the solvent was removed *in vacuo*. Recrystallisation of the white solid from light petroleum–bicyclo[2.2.1]heptene (5 : 1) afforded white *crystals* of [$Pt(CF_2{\cdot}CF_2)(C_7H_{10})_2$] (4) (1.25 g, 83%), m.p. 95—96 °C (Found: C, 39.7; H, 4.3. $C_{16}H_{20}F_4Pt$ requires C, 39.8; H, 4.2%), $\nu_{max.}$ at 2 510w, 2 470w, 1 328m, 1 298w, 1 281m, 1 252w, 1 210w, 1 172w, 1 149s, 1 131s, 1 124s, 1 117m, 1 085(sh), 1 070s, 1 060(sh), 1 002w, 970w, 940w, 911w, 889w, 870w, 850w, 798s, and 780s cm^{-1}. The ^1H n.m.r. spectrum in C_6D_6 showed resonances at τ 6.1 [s, with ^{195}Pt satellites, 4 H, H^1, CH=CH, $J(PtH^1)$ 53 Hz], 7.2 (m, 4 H, H^2), 8.8 (m, 8 H, H^3 and $H^{3'}$), and 9.8 (AB multiplet, 4 H, H^4 and H^5). The ^{19}F n.m.r. spectrum in C_6D_6 showed a resonance at 127.6 p.p.m. [s, with ^{195}Pt satellites, J(PtF) 252 Hz].

Reaction of Cyclo-octa-1,5-*diene with* (4).—An excess of cyclo-octa-1,5-diene (10 cm^3) was added to a solution of (4) (1.35 g, 2.8 mmol) in light petroleum (70 cm^3). After 10 h at room temperature the resulting white crystals were collected and washed with light petroleum. Elemental analysis and i.r. and n.m.r. spectroscopy showed the material to be complex (1) (0.8 g, 71%).



Reaction of Trimethyl Phosphite with (4).—Trimethyl phosphite (0.7 g, 5.6 mmol) in light petroleum (10 cm^3) was added to a solution of (4) (1.35 g, 2.8 mmol) in light petroleum (30 cm^3). After 10 h at room temperature the volume of the solvent was reduced *in vacuo*, and the solution was cooled (−30 °C) to give white *crystals* of (tetrafluoroethylene)-bis(trimethyl phosphite)platinum (5) (0.94 g, 62%), m.p. 30—31 °C (Found: C, 18.6; H, 3.6. $C_8H_{18}F_4O_6P_2Pt$ requires C, 17.7; H, 3.3%). The ^{19}F n.m.r. spectrum in C_6D_6 showed a resonance at 126.7 p.p.m. [where J(PtF) 271 and $J(PtF_{cis}) + J(PtF_{trans})$ 112 Hz].

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