Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XXV.[1] Phosphine, Phosphite and Cyclo-octa-1,5-diene Platinum Complexes

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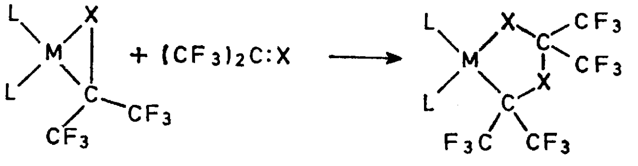
Treatment of $Pt{\cdot}C(CF_3)_2O{\cdot}L_2$ with hexafluoroacetone affords the five-membered ring complexes $Pt{\cdot}C(CF_3)_2O{\cdot}C(CF_3)_2OL_2$ ($L = PMePh_2$; $L_2 = Ph_2PCH_2CH_2PPh_2$). Hexafluoroisopropylideneamine reacts with $Pt{\cdot}C(CF_3)_2OL_2$ to form complexes with the probable structure $Pt{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2OL_2$, and with $Pt{\cdot}C(CF_3)_2NH(Ph_2PCH_2)_2$ to give $Pt{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2NH(Ph_2PCH_2)_2$. With hexafluoroacetone, $Pt[P(OMe)_3]_4$ reacts to give $Pt{\cdot}C(CF_3)_2O{\cdot}C(CF_3)_2O[P(OMe)_3]_2$, whereas $Pt[P(OPh)_3]_4$ yields only $Pt{\cdot}C(CF_3)_2O[P(OPh)_3]_2$. Di-isopropyl(cyclo-octa-1,5-diene)platinum reacts with $(CF_3)_2CO$, $(CF_3)_2C{:}C(CN)_2$, or C_2F_4 to give $Pt{\cdot}C(CF_3)_2O{\cdot}C(CF_3)_2O(1,5\text{-}C_8H_{12})$, $PtC(CF_3)_2C(CN)_2(1,5\text{-}C_8H_{12})$, or $Pt{\cdot}CF_2CF_2CF_2CF_2(1,5\text{-}C_8H_{12})$, respectively. Hexafluoroisopropylideneamine reacts with $PtPr^i_2(1,5\text{-}C_8H_{12})$ to give $Pt[N{:}C(CF_3)_2]_2(1,5\text{-}C_8H_{12})$, while hexafluorobut-2-yne yields $Pt[C(CF_3){:}C(CF_3)H]_2(1,5\text{-}C_8H_{12})$.

EARLIER it has been shown that both nickel- and palladium-hexafluoroacetone and -hexafluoroisopropylideneamine complexes can undergo ring-expansion reactions on treatment with $(CF_3)_2C{:}X$ ($X = O$ or NH) (Scheme 1); the reaction is also extendable to provide a route to the corresponding O,N-heterocyclic complexes, *e.g.* $Ni{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2O(Bu^tNC)_2$,[2] and $Pt{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2O(PPh_3)_2$.[7] Qualitative observations indicated that the ease of ring expansion depends on the nature of the ligands L, electronic and steric factors both effecting the rate of reaction. With a view to understanding more fully the role of the metal we have studied some related platinum chemistry.



SCHEME 1 $M = Ni$; $L = Bu^tNC$,[2] $PhNC$,[2] $o\text{-}C_6H_4(AsMe_2)_2$,[3] $(Ph_2PCH_2)_2$,[3,4] $M = Pd$; $L = Bu^tNC$,[5] $P(OMe)_3$,[6] $AsMe_2Ph$,[5] PPh_2Me,[6] $(Ph_2PCH_2)_2$,[6] $AsMe_2(CH_2Ph)$,[6] $P(OMe)_2Ph$ [6]

Previously three-membered ring complexes $Pt{\cdot}C(CF_3)_2OL_2$ ($L = PPh_3$ or PPh_2Me) have been reported[8] as the only products of the reactions of PtL_4 with hexafluoroacetone, there being no evidence for the formation of five-membered platinum heterocyclic ring complexes. In contrast, $Pt{\cdot}C(CF_3)_2NH(PPh_3)_2$ was found[7] to react readily with hexafluoroacetone to form (I). The discovery of several three- to five-membered ring expansion reactions led us to re-examine the earlier result. The complex $Pt{\cdot}C(CF_3)_2O(PPh_3)_2$ was found to be unreactive towards hexafluoroacetone (60°/30 days) but $Pt{\cdot}C(CF_3)_2O(PPh_2Me)_2$ reacted slowly (3 weeks) with the ketone to give complex (II). The latter is assigned the illustrated head-to-tail five-membered ring structure on the basis of its ^{19}F n.m.r. spectrum.[2,3,7] Similarly, $Pt{\cdot}C(CF_3)_2O[Ph_2PCH_2CH_2PPh_2]$ (IV), prepared by displacement of triphenylphosphine from $Pt{\cdot}C(CF_3)_2O(PPh_3)_2$ by 1,2-bis(diphenylphosphino)ethane, reacted with hexafluoroacetone to afford the five-membered ring compound (V).

Thus, as with the corresponding nickel chemistry, the three- to five-membered ring expansion reaction: $M{\cdot}C(CF_3)_2OL_2 \longrightarrow M{\cdot}C(CF_3)_2O{\cdot}C(CF_3)_2OL_2$ can be promoted by replacement of ligands such as triphenylphosphine by phosphines with better σ donor properties. This suggests that the second molecule of hexafluoroacetone π-complexes to the platinum prior to reaction with the already co-ordinated hexafluoroacetone, the increased electron density on the platinum with the better σ-donor but poorer π-acceptor ligands being required for increased back-donation into the π^* orbital of the incoming hexafluoroacetone molecule.

In contrast with hexafluoroacetone, hexafluoroisopropylideneamine reacts with $Pt{\cdot}C(CF_3)_2O(PPh_3)_2$ to give in good yield the O,N-heterocyclic complex (I) with identical properties to the complex previously[7] obtained by treatment of $Pt{\cdot}C(CF_3)_2NH(PPh_3)_2$ with hexafluoroacetone. As illustrated, this complex can have either structure (Ia) or (Ib), however, on the present evidence

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[1] Part XXIV, J. Clemens, M. Green, and F. G. A. Stone, preceding paper.

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

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

[4] J. Browning, Ph.D. Thesis, Bristol University, 1971.

[5] H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3472.

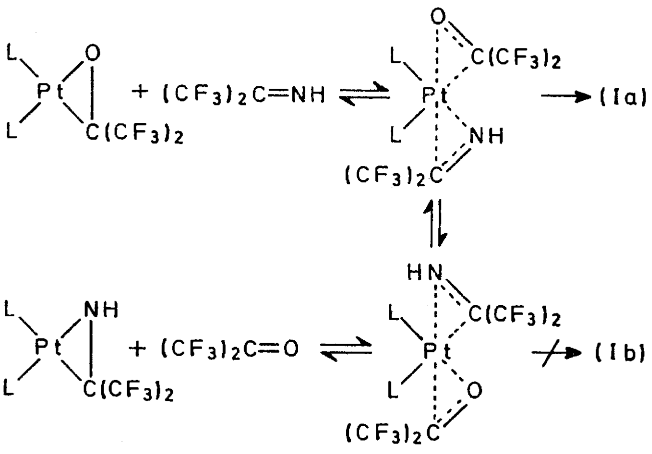
[6] H. D. Empsall, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 96.

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

[8] B. A. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 168.

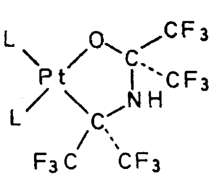
it is not possible to decide between these two alternatives. Interestingly, $\overline{Ni{\cdot}C(CF_3)_2O}(Bu^tNC)_2$ reacts with hexafluoroisopropylideneamine to give only the one isomer $\overline{Ni{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2O}(Bu^tNC)_2$.[2,9]

The formation of (Ia) or (Ib) from either $\overline{Pt{\cdot}C(CF_3)_2NH}(PPh_3)_2$ or $\overline{Pt{\cdot}C(CF_3)_2O}(PPh_3)_2$ may be explained if these reactions proceed *via* formally six-co-ordinate intermediates of the kind postulated for the related nickel[2] and palladium[6] systems [Scheme 2].

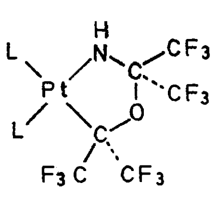


SCHEME 2 (L = PPh$_3$)

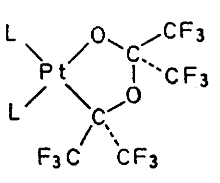
Then either by a conventional rotation [*] about an axis through the platinum and perpendicular to the C–N or C–O bond of the co-ordinated $(CF_3)_2C{:}NH$ or $(CF_3)_2C{:}O$, or by a Bailar twist[10] or related polytopal rearrangement,[11] the preferential formation of one isomer, which is arbitrarily assumed to be (Ia), may be understood.



(Ia) L = PPh$_3$
(IIIa) L = PMePh$_2$



(Ib) L = PPh$_3$
(IIIb) L = PMePh$_2$



(II) L = PMePh$_2$
(V) L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
(IX) L = P(OMe)$_3$
(XI) L$_2$ = 1,5-C$_8$H$_{12}$

As might have been anticipated, $\overline{Pt{\cdot}C(CF_3)_2O}[PPh_2Me]_2$ readily ring expands with hexafluoroisopropylideneamine to give the O,N-heterocyclic complex (III); which as in the case of the bis(triphenylphosphine) complex (I) can have either structure (IIIa) or (IIIb).

The inertness of $\overline{Pt{\cdot}C(CF_3)_2O}(PPh_3)_2$ towards $(CF_3)_2C{:}O$ in contrast to the reactivity towards $(CF_3)C{:}NH$ may possibly be explained if it is assumed that the ketone is a stronger π-acceptor and poorer σ donor than the imine, so that co-ordination of two hexafluoroacetone molecules onto the Pt(PPh$_3$)$_2$ moiety does not readily occur due to the lack of electron density on the platinum, but complex formation with one molecule of $(CF_3)_2C{:}O$ and one molecule of $(CF_3)_2C{:}NH$ is possible as a prerequisite for heterocyclic ring formation. In accord with this argument, as mentioned above, substitution of PPh$_3$ in $\overline{Pt{\cdot}C(CF_3)_2O}(PPh_3)_2$ by the more nucleophilic PPh$_2$Me apparently overcomes the difficulty of bonding a second molecule of the ketone and ring expansion occurs. The role of the more basic phosphines in promoting five-membered ring formation is further shown by the following observations. It has been previously observed[7,12] that $\overline{Pt{\cdot}C(CF_3)_2NH}(PPh_3)_2$ does not readily react with hexafluoroisopropylideneamine; however, replacement of triphenylphosphine by 1,2-bis(diphenylphosphino)ethane affords $\overline{Pt{\cdot}C(CF_3)_2NH}(Ph_2PCH_2)_2$ (VI), which readily reacts with $(CF_3)_2C{:}NH$ to form the N,N-heterocyclic platinum complex (VII).

In the above discussion the electronic effects of the phosphine ligands and the fluorocarbon substrates have been emphasised as determining the relative nucleophilicity of the three-membered ring complexes. Other factors must be involved, since if it is assumed that the metal in $\overline{Pt{\cdot}C(CF_3)_2NH}(PPh_3)_2$ is more electron rich than in $\overline{Pt{\cdot}C(CF_3)_2O}(PPh_3)_2$, on account of the imine being less electrophilic than the ketone, it would be expected that the former complex would react more readily with $(CF_3)_2C{:}NH$ to form a five-membered ring complex than the latter complex, whereas the reverse is the case. However, the relative rates of collapse of the transition states (Scheme 2) may be different so that whereas $Pt[C(CF_3)_2O][C(CF_3)_2NH](PPh_3)_2$ may irreversibly form (Ia) more rapidly than reverting to $Pt[C(CF_3)_2O](PPh_3)_2$, an adduct $Pt[C(CF_3)_2NH][C(CF_3)_2NH](PPh_3)_2$ might release imine in preference to five-membered ring formation. Moreover, experiments with phosphite–platinum complexes strongly suggest that steric effects may also be of critical importance. Although tetrakis(triphenyl phosphite)platinum and tetrakis(trimethyl phosphite)-

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[*] The barrier to rotation would be less than in three-ring complexes because there would be a relative reduction in back bonding to the π* levels resulting from the introduction of a second π-acceptor, *i.e.* $(CF_3)_2C{:}NH$ or $(CF_3)_2C{:}O$, into the co-ordination sphere.

[9] R. Countryman and B. R. Penfold, *Chem. Comm.*, 1971, 1598.

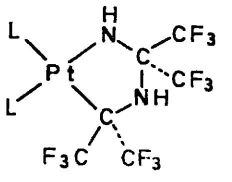
[10] J. C. Bailar, *J. Inorg. Nuclear Chem.*, 1958, **8**, 165.

[11] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1968, **90**, 5097; and references cited therein.

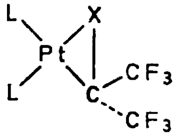
[12] J. Ashley-Smith, Ph.D. Thesis, Bristol University, 1970.

platinum do not react with hexafluoroisopropylideneamine, it was found that hexafluoroacetone reacted with $[\mathrm{Pt\{P(OPh)_3\}_4}]$ to afford the three-membered ring complex (VIII). Attempts to form a five-membered ring complex by treating (VIII) with hexafluoroacetone were unsuccessful. In contrast, $[\mathrm{Pt\{P(OMe)_3\}_4}]$ reacts with $\mathrm{(CF_3)_2C{:}O}$ to afford, directly, the five-membered ring compound (IX); it was not possible to isolate the presumed intermediate $\overline{\mathrm{Pt{\cdot}C(CF_3)_2O}}\mathrm{[P(OMe)_3]_2}$. Similar ligand effects have been observed in the corresponding palladium chemistry.[6]

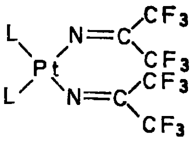
The complex $\overline{\mathrm{Ni{\cdot}C(CF_3)_2O}}\mathrm{(1,5\text{-}C_8H_{12})}$ prepared by treating $\mathrm{Ni(1,5\text{-}C_8H_{12})_2}$ with $\mathrm{(CF_3)_2C{:}O}$ proved to be a valuable intermediate for the synthesis of $\overline{\mathrm{Ni{\cdot}C(CF_3)_2O}}\mathrm{L_2}$ complexes,[13] which, in turn, have been useful in obtaining an understanding of three- to five-membered ring-expansion reactions. Although $\mathrm{Pt(1,5\text{-}C_8H_{12})_2}$ has been prepared in low yield by the photochemical reaction of $\mathrm{PtPr^i_2(1,5\text{-}C_8H_{12})}$ with cyclo-octa-1,5-diene[14] we have found this synthesis difficult to reproduce and accordingly have examined the reaction of molecules like hexafluoroacetone directly with $\mathrm{PtPr^i_2(1,5\text{-}C_8H_{12})}$.



(VII) $\mathrm{L_2 = Ph_2PCH_2CH_2PPh_2}$



(IV) $\mathrm{L_2 = Ph_2PCH_2CH_2PPh_2,\ X = O}$
(VI) $\mathrm{L_2 = Ph_2PCH_2CH_2PPh_2,\ X = NH}$
(VIII) $\mathrm{L = P(OPh)_3,\ X = O}$

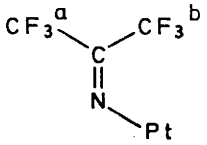


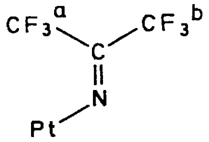
(XV) $\mathrm{L_2 = 1,5\text{-}C_8H_{12}}$

Either u.v. irradiation or simple thermal reaction of an excess of hexafluoroacetone with a light petroleum solution of di-isopropyl(cyclo-octa-1,5-diene)platinum gave compound (XI) in good yield, which showed bands in its i.r., ^{1}H, and ^{19}F n.m.r. spectra characteristic of a five-membered head-to-tail ring structure.

In contrast, the corresponding reaction between $\mathrm{PtPr^i_2(1,5\text{-}C_8H_{12})}$ and hexafluoroisopropylideneamine affords yellow crystals of (XV), which, as illustrated, is formulated as a bis-hexafluoroisopropylideneamido complex of $\mathrm{Pt^{II}}$. The reaction may well involve protolysis by the acidic $\mathrm{(CF_3)_2C{=}NH}$ of the platinum–carbon σ-bond. Alternatively, two molecules of the imine might add oxidatively and successively to $\mathrm{PtPr^i_2(C_8H_{12})}$ with loss of propane. The i.r. spectrum of (XV) showed a strong band at 1685 cm^{-1} attributable to a N:C stretching frequency. Recently,[15] related transition-metal compounds including *cis*-$[\mathrm{Pt\{N{:}C(CF_3)_2\}_2(PMe_2Ph)_2}]$, have been prepared by reaction of hexafluoroisopropylideneamidolithium with transition-metal chlorides. Similar $\nu_{\mathrm{N:C}}$ absorptions were observed in the i.r. spectra. The reaction of $\mathrm{(CF_3)_2C{:}NLi}$ with the respective halides has also been used as a route to group IIIa and IVa hexafluoroisopropylidineamido-compounds.[16]

The ^{19}F n.m.r. spectrum of (XV) showed a singlet resonance at 69·4 p.p.m.; on cooling to −90° there was no change in the sharp line. This suggests that rapid isomerisation is occurring about the C:N bond rendering magnetically equivalent (on a time average) the fluorine atoms of the *syn*- and *anti*-trifluoromethyl groups. At the present time it is not possible to account for the low-energy barrier to inversion or to decide on a probable mechanism[17] of inversion. A lateral-shift mechanism involving a progressive increase in the *p* character of the nitrogen orbital having the lone-pair until the *sp* hybridisation of a transition state is reached might be favoured by back bonding from the nitrogen to a vacant metal orbital. Normal inversion barriers of *N*-alkyl and *N*-aryl imines range from 17—27 kcal mol^{-1}, but recently a much lower barrier to pyramidal inversion has been observed[18] when germanium is attached to the inversion centre as in $p\text{-}\mathrm{CF_3C_6H_4(Ph)C{:}NGeMe_3}$, and this has been related to an electronegativity effect. However, a simple extension of this correlation based on an electronegativity of 2·28 for Pt,[19] would imply a barrier to inversion of at least 17 kcal/mol for (XV) which is not in accord with the ^{19}F n.m.r. result.





1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene, which has previously been shown to form three-membered Ni[2] and Pd[5] complexes, *i.e.* $\mathrm{L_2}\overline{\mathrm{M{\cdot}C(CF_3)_2C}}\mathrm{(CN)_2}$, reacts at room temperature with di-isopropyl(cyclo-octa-1,5-diene)platinum to form only (XII), which on the basis of the i.r. ^{1}H and ^{19}F n.m.r. spectra is formulated as the illustrated three-membered platinum ring complex.

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

[14] J. Muller and P. Gose, *Angew. Chem. Internat. Edn.*, 1967, **6**, 364.

[15] B. Cetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215.

[16] R. F. Swindell, D. P. Babb, T. J. Ouellette, and J. M. Shreeve, *Inorg. Chem.*, 1972, **11**, 242.

[17] J. M. Lehn, *Fortschr. Chem. Forsch.*, 1970, **15**, 311; H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219; M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, 1971, **93**, 685.

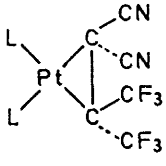
[18] R. J. Cook and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6703.

[19] A. L. Allred, *J. Inorg. Nuclear Chem.*, 1961, **17**, 215.

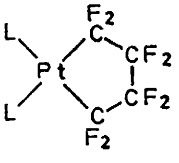
From a study[20,21] of the reactions of tetrafluoroethylene with zerovalent nickel complexes it became clear that a three- to five-membered ring-expansion reaction was possible *i.e.* $L_2Ni{\cdot}CF_2CF_2 \longrightarrow L_2Ni{\cdot}CF_2CF_2CF_2CF_2$, which would be analogous to the ring-expansion reactions observed with $(CF_3)_2C{:}O$ and $(CF_3)_2C{:}NH$. However, treatment of a variety of phosphine-substituted platinum(0) complexes with tetrafluoroethylene gave only compounds of the type $Pt{\cdot}CF_2CF_2L_2$[22] indicating that platinum did not activate fluoro-olefins as well as nickel. It was therefore of interest to study the reaction of fluoro-olefins with $PtPr^{i}_{2}(1,5\text{-}C_8H_{12})$.

When a solution of di-isopropyl(cyclo-octa-1,5-diene)platinum was irradiated in the presence of tetrafluoroethylene, crystals of the five-membered ring complex (X) separated out; a similar reaction involving hexafluorobuta-1,3-diene yielded the complex (XIII). These two complexes provided the first example of five-membered ring formation between platinum and a fluoro-olefin. Although compounds of type (XIII) are known for nickel,[2,3] the three-co-ordinate species $Pt(PPh_3)_3$ reacts with hexafluorobuta-1,3-diene to yield a three-membered ring complex $PtCF_2CFCF{:}CF_2(PPh_3)_2$.[22]

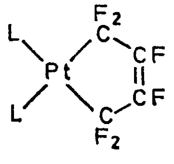
The ^{19}F n.m.r. chemical shifts for (X) and (XIII) are characteristic of compounds of these structural types,[2,3,20] and the high ^{195}Pt–^{19}F coupling constants are noteworthy.[23] No ^{19}F–^{19}F coupling was resolved in the spectrum of (X), and it is interesting that in the wide range of analogous octafluoronickelacyclopentanes the largest observed coupling of this type was only 2·5 Hz.[20] An *X*-ray crystallographic study on the complex $Ni{\cdot}CF_2CF_2CF_2CF_2(AsMe_2Ph)_2$ has confirmed the existence of the metallocyclopentane ring which is very nearly planar.[24] The ^{19}F n.m.r. spectrum of (XIII) consists of two resonances, each with a very intense central line surrounded by 4 pairs of doublets. This symmetrical pattern is consistent with that of an $X_2AA'X_2'$ system where $|J_{AX} + J_{AX'}|$ is zero, and it seems likely that the low ^{19}F–^{19}F coupling exhibited in the octafluorometallocyclopentanes may be due to second order effects, in which certain coupling constants are equal in magnitude but opposite in sign.



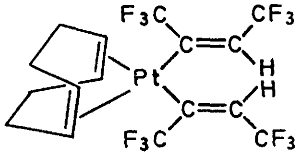
(XII) $L_2 = 1,5\text{-}C_8H_{12}$



(X) $L_2 = 1,5\text{-}C_8H_{12}$



(XIII) $L_2 = 1,5\text{-}C_8H_{12}$



(XIV)

Reaction of bis(cyclo-octa-1,5-diene)nickel with hexafluorobut-2-yne yields two complexes $\{Ni[C_6(CF_3)_6](1,5\text{-}C_8H_{12})\}$ and $\{Ni_2[C_6(CF_3)_6](1,5\text{-}C_8H_{12})_2\}$.[25] It was therefore of interest to examine the reaction of $CF_3C{\equiv}CCF_3$ with $PtPr^{i}_{2}(1,5\text{-}C_8H_{12})$, although it is to be recognised that the metal atoms in the two cyclo-octa-1,5-diene complexes are in different formal oxidation states. Irradiation of a light petroleum solution of di-isopropyl(cyclo-octa-1,5-diene)platinum in the presence of an excess of hexafluorobut-2-yne gave a high yield of a white crystalline complex (XIV). Examination of the i.r., ^{1}H, and ^{19}F n.m.r. spectra clearly established that (XIV) is a divinyl Pt^{II} complex. The ^{19}F n.m.r. spectrum showed two resonances at 53·6 and 59·3 p.p.m.; the low-field resonance was attributed to the CF_3 group α to the platinum. The magnitude of the ^{19}F–^{19}F coupling established a relative *cis*-configuration for the trifluoromethyl groups.[26,27] The presence of a band in the i.r. spectrum at 1628 cm^{-1} confirms the presence of the vinyl group $Pt{\cdot}C(CF_3){:}C(CF_3)H$.[27] Thus the formation of (XIV) formally corresponds to the capture by hexafluorobut-2-yne of an intermediate hydride. The formation of the *cis*-vinyl complex parallels the formation of the *cis*-olefin isomer of *trans*-$[PtCl\{C(CF_3){:}C(CF_3)H\}(PEt_3)_2]$ from $PtHCl(PEt_3)_2$ and $CF_3C{\equiv}CCF_3$,[27] but contrasts with the formation of the *trans*-olefinic product on reaction of the carbonyl hydrides of manganese and rhenium with hexafluorobut-2-yne.[28]

The implied involvement of a hydridic species in a photochemical reaction of $PtPr^{i}_{2}(1,5\text{-}C_8H_{12})$, makes it difficult at this point to relate mechanistically the reactions of di-isopropyl(cyclo-octa-1,5-diene)platinum to those of Pt^0 complexes. However, it seems possible that the formation of (X) and (XI) involves capture of the co-ordinatively unsaturated species $Pt(1,5\text{-}C_8H_{12})$ and the subsequent ring-expansion of complexes $Pt{\cdot}C(CF_3)_2O(1,5\text{-}C_8H_{12})$ and $Pt{\cdot}CF_2CF_2(1,5\text{-}C_8H_{12})$ respectively.

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 are relative to Me_4Si (τ 10·00)

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and CCl_3F (0·00 p.p.m.). I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer using Nujol and hexachlorobutadiene mulls. All operations were carried out in a dry nitrogen atmosphere. Light petroleum refers to the fraction b.p. 40—60°. All solvents were dried over sodium, and redistilled prior to use. Diethyl ether was distilled from calcium hydride. Di-isopropyl(cyclo-octa-1,5-diene)platinum was prepared by addition of isopropylmagnesium bromide to cyclo-octa-1,5-dieneplatinum dichloride.

Reaction of Hexafluoroisopropylideneamine with Hexafluoroacetonebis(triphenylphosphine)platinum. Reaction of an excess of hexafluoroisopropylideneamine (6 mmol) with a solution of hexafluoroacetonebis(triphenylphosphine)-platinum (0·20 g, 0·23 mmol) in benzene (10 ml) for 1 week at 60 °C yielded white crystals, which were recrystallised from methylene chloride–light petroleum to give (I) (0·21 g, 89%) identical (i.r. and n.m.r. spectroscopy) with the material obtained from $(CF_3)_2C{:}O$ and $[(Ph_3P)_2\overline{Pt{\cdot}C(CF_3)_2N}H]$.[7]

Reaction of Hexafluoroacetone with Hexafluoroacetonebis(diphenylmethylphosphine)platinum.—Similarly, reaction (room temperature, 3 weeks) of an excess of hexafluoroacetone (6 mmol) with a solution of hexafluoroacetonebis(diphenylmethylphosphine)platinum [22] (0·30 g, 0·39 mmol) in benzene (13 ml) gave, after removal of solvent *in vacuo* and crystallisation of the residue from methylene chloride–light petroleum, white *crystals* of (II) (0·32 g, 90%), m.p. 173—174° [Found: C, 41·5; H, 2·8; P, 6·6%; *M*, 844 ($CHCl_3$). $C_{32}H_{26}F_{12}O_2P_2Pt$ requires C, 41·4; H, 2·8; P, 6·7%; *M*, 928], $\nu_{max.}$ 3080w, 3055w, 3015w, 2940w, 1586w, 1570w, 1480m, 1440s, 1302m, 1284m, 1275s, 1253s, 1234s, 1199vs, 1184vs, 1166vs, 1159vs, 1143sh, 1114sh, 1104s, 1075m, 1030w, 1006m, 966s, 938m, 929m, 920w, 910s, 901s, 893m, 802w, 758s, 755s, 740s, 731m, 723s, 718sh, 711s, 705sh, and 699s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 64·9 p.p.m. [m, with ^{195}Pt satellites, 6F, α-$C(CF_3)_2$] and 80·6 [m, 6F, β-$C(CF_3)_2$]. Double irradiation of the high-field signal caused the other signal to collapse to a doublet of doublets with *J*(FF) 3·0, J_{trans}(PF) 6·0, J_{cis}(PF) 1·0, and *J*(PtF) 76 Hz; irradiation of the low-field signal caused the high-field resonance to collapse to a singlet. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·27 (m, 10H, C_6H_5P), 2·65 (m, 10H, C_6H_5), 7·99 (d with ^{195}Pt satellites, 3H, CH_3P *trans* to oxygen), and 8·51 (d with ^{195}Pt satellites, 3H, CH_3P *cis* to oxygen).

Reaction of Hexafluoroisopropylideneamine with Hexafluoroacetonebis(diphenylmethylphosphine)platinum.— Reaction of an excess of hexafluoroisopropylideneamine (6·0 mmol) with a solution of hexafluoroacetone bis(diphenylmethylphosphine)platinum (0·30 g, 0·39 mmol) in benzene (12 ml) at 60 °C for 1 week yielded white *crystals* of (III) (0·29 g, 81%) from methylene chloride–light petroleum, m.p. 180—182° [Found: C, 41·6; H, 2·9; N, 1·6%; *M*, 840 ($CHCl_3$). $C_{32}H_{27}F_{12}NOP_2Pt$ requires C, 41·5; H, 2·9; N, 1·5%; *M*, 927], $\nu_{max.}$ 3420w, 3082w, 3055w, 3021w, 2995vw, 2938vw, 1587w, 1572w, 1490sh, 1481m, 1465w, 1440s, 1436sh, 1429w, 1418w, 1330w, 1300w, 1281sh, 1278sh, 1265m, 1254m, 1230m, 1219m, 1198s, 1184m, 1160m, 1149s, 1130m, 1115w, 1104m, 1074sh, 1055w, 1030w, 1019w, 1001w, 998sh, 973w, 958sh, 943m, 935sh, 925sh, 919m, 905m, 895sh, 892m, 861w, 853w, 809w, 758sh, 750m, 743m, 735m, 720m, 711m, 705m, and 699m cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) shows resonances at 63·9 p.p.m. [m with ^{195}Pt satellites, 6F, α-$C(CF_3)_2$] and 80·9 [m, 6F, β-$C(CF_3)_2$]. Double irradiation of the high-field signal caused the low-field signal to collapse to a doublet of doublets with *J*(FF) 2·0, J_{trans}(PF) 6·0, J_{cis}(PF) 2·0, and *J*(PtF) 88 Hz; irradiation of the low-field signal caused the high-field resonance to collapse to a singlet. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·28 (m, 10H, C_6H_5P), 2·72 (m, 10H, C_6H_5P), 8·05 (m with ^{195}Pt satellites, 3H, CH_3P *trans* to oxygen) and 8·56 (m with ^{195}Pt satellites, 3H, CH_3P *cis* to oxygen).

Preparation of Hexafluoroacetone-1,2-bis(diphenylphosphino)ethaneplatinum (IV).—Hexafluoroacetonebis(triphenylphosphine)platinum (0·5 g, 0·56 mmol) and 1,2-bis-(diphenylphosphino)ethane (0·23 g, 0·56 mmol) were refluxed together in benzene (20 ml) for 1 h. Solvent was removed *in vacuo* and the residue was crystallised from methylene chloride–light petroleum to give white *crystals* of (IV) (0·41 g, 94%), m.p. 253—254° [Found: C, 45·7; H, 3·2%; *M*, 788 ($CHCl_3$). $C_{29}H_{24}F_6OP_2Pt$ requires C, 45·9; H, 3·2%; *M*, 760], $\nu_{max.}$ 3050w, 2950sh, 2920w, 2850vw, 1587vw, 1485w, 1442sh, 1438s, 1407w, 1313s, 1271vs, 1245m, 1207m, 1170vs, 1163sh, 1130sh, 1120vs, 1109s, 1104sh, 1089sh, 1081sh, 1073sh, 1029vw, 1000w, 974vw, 939s, 926sh, 878m, 863s, 829m, 765m, 759m, 755m, 750m, 726m, 720s, 712s, 700sh, and 670w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 66·2 p.p.m. [d of d with ^{195}Pt satellites, 6F, J_{trans}(PF) 12·0, J_{cis}(PF) 2·0, *J*(PtF) 71·0 Hz]. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·40 (m, 20H, C_6H_5P) and 7·55 (m, 4H, CH_2P).

Reaction of Hexafluoroacetone with Complex (IV).—Reaction of an excess of hexafluoroacetone (6·0 mmol) with a solution of complex (IV) (0·50 g, 0·66 mmol) in benzene (20 ml) for 1 week at 60 °C, afforded, after removal of the solvent *in vacuo*, a white solid which gave white *crystals* of complex (V) (0·49 g, 80%) from methylene chloride–light petroleum, m.p. 234—235° [Found: C, 41·6; H, 2·6; P, 6·7%; *M*, 910 ($CHCl_3$). $C_{32}H_{24}F_{12}O_2P_2Pt$ requires C, 41·5; H, 2·6; P, 6·7%; *M*, 926], $\nu_{max.}$ 3090w, 3080w, 3060w, 3010vw, 2960vw, 2915w, 1592w,br, 1484w, 1442s, 1437s, 1415w, 1409w, 1338w, 1303w, 1284m, 1260m, 1250sh, 1240sh, 1228m, 1210sh, 1200s, 1194s, 1188sh, 1169s, 1164s, 1157s, 1149sh, 1110m, 1102m, 1056m, 1029sh, 1009m, 1001sh, 978sh, 967m, 936m, 920w, 885m, 830m, 758m, 752m, 729m, 723m, 720m, 712m, 704m, 694m, 689sh, and 660w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 66·6 p.p.m. [m with ^{195}Pt satellites, 6F, α-$C(CF_3)_2$] and 80·7 [m, 6F, β-$C(CF_3)_2$]. Double irradiation of the high-field signal caused the low-field signal to collapse to a doublet with *J*(FF) 3·0, *J*(PF) 4·5, and *J*(PtF) 72·0 Hz; irradiation of the low-field signal caused the high-field signal to collapse to a singlet. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·43 (m, 20H, C_6H_5P) and 7·86 (m, 4H, CH_2P).

Complex (V) was also obtained by heating a suspension of dicarbonylbis(triphenylphosphine)platinum (0·50 g, 0·65 mmol) and 1,2-bis(diphenylphosphino)ethane (0·26 g, 0·65 mmol) in diethyl ether (20 ml) with an excess of hexafluoroacetone (6·0 mmol) at room temperature for 2 days. The solvent was removed *in vacuo* and the residue was crystallised to give (V) (0·34 g, 56%).

Preparation of Hexafluoroisopropylideneamine-1,2-bis(diphenylphosphino)ethaneplatinum (VI).—A solution in benzene (15 ml) of 1,2-bis(diphenylphosphino)ethane (0·17 mmol) and hexafluoroisopropylideneaminebis(triphenylphosphine)platinum (0·15 g, 0·17 mmol) was refluxed for

2 h. The solvent was removed *in vacuo* and the residue was crystallised from methylene chloride–light petroleum to give white *crystals* of complex (VI) (0·12 g, 91%), m.p. 241—243° [Found: C, 46·0; H, 3·3; P, 8·1%; *M*, 740 ($CHCl_3$). $C_{29}H_{25}F_6NP_2Pt$ requires C, 45·9; H, 3·3; P, 8·2%; *M*, 759], $\nu_{max.}$ 3045w, 3000sh, 2920vw, 2910vw, 1586w, 1572w, 1482w, 1472w, 1435s, 1403w, 1305s, 1272s, 1241sh, 1203m, 1185sh, 1170s, 1161sh, 1128s, 1099s, 1069sh, 1025m, 999m, 971w, 935sh, 882m, 859s, 819m, 760sh, 753m, 743m, 711s, 698sh, 692s, and 658w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 66·6 p.p.m. [d of d with ^{195}Pt satellites, 6F, J_{trans}(PF) 11·0, J_{cis}(PF) 1·0, *J*(PtF) 71·0 Hz]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·5 (m, 20H, C_6H_5P) and 7·70 (m, 4H, CH_2P).

Reaction of Complex (VI) *with Hexafluoroisopropylideneamine.*—An excess of hexafluoroisopropylideneamine (6·0 mmol) was condensed into a tube containing complex (VI) (0·15 g, 0·2 mmol) in benzene (15 ml). After 1 week at 60 °C the solvent was removed *in vacuo* and the residue was crystallised from methylene chloride–light petroleum to give white *crystals* of (VII) (0·16 g, 90%), m.p. 249—250° [Found: C, 41·7; H, 2·8; P, 6·7%; *M*, 931 (C_6H_6). $C_{32}H_{26}F_{12}N_2P_2Pt$ requires C, 41·6; H, 2·8; P, 6·7%; *M*, 924], $\nu_{max.}$ 3440m, 3080w, 3060w, 2930w, 1573w, 1495sh, 1485sh, 1474m, 1459sh, 1441s, 1415w, 1312sh, 1300sh, 1287m, 1272s, 1262s, 1245sh, 1231s, 1208vs, 1188s, 1182s, 1150vs, 1145sh, 1135sh, 1109s, 1091w, 1068sh, 1060m, 1030w, 1003m, 977w, 950m, 938sh, 922m, 891m, 852w, 839s, 812w, 766m, 760sh, 756s, 730s, 725s, 715s, 707s, 700s, and 671w cm^{-1}. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 66·1 p.p.m. [m, with ^{195}Pt satellites, 6F, α-C(CF_3)$_2$] and 81·65 [m, 6F, β-(CF_3)$_2$]. Double-irradiation of the high-field signal caused the low-field signal to collapse to a doublet of doublets with *J*(FF) 3·0, J_{cis}(PF) 3·0, J_{trans}(PF) 7·0, and *J*(PtF) 80·0 Hz; irradiation of the low-field signal caused the high-field resonance to collapse to a singlet. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·40 (m, 20H, C_6H_5P) and 7·90 (m, 4H, CH_2P).

Reaction of Hexafluoroacetone with Tetrakis(triphenyl phosphite)platinum.—Hexafluoroacetone (6·0 mmol) was treated with a suspension of tetrakis(triphenyl phosphite)-platinum (0·50 g, 0·35 mmol) in light petroleum (30 ml) at 60 °C for 1 week. The solvent was removed *in vacuo*, the oily residue was triturated with light petroleum, and the resultant solid was crystallised from diethyl ether to give white crystals of complex (VIII) (0·32 g, 92%), m.p. 115—116° [Found: C, 47·6; H, 3·2; P, 6·0%; *M*, 960 ($CHCl_3$). $C_{39}H_{30}F_6O_7P_2Pt$ requires C, 47·7; H, 3·1; P, 6·3%; *M*, 982], $\nu_{max.}$ 3090vw, 3070vw, 3040vw, 1592sh, 1584s, 1575sh, 1507vw, 1489sh, 1483s, 1450w, 1311s, 1292s, 1220sh, 1190sh, 1185s, 1175s, 1161sh, 1158s, 1142s, 1103sh, 1071m, 1025s, 1008m, 982w, 942s, 920s, 911s, 900sh, 862m, 828w, 785sh, 778s, 770sh, 765s, 748s, 734vw, 726m, 706m, and 691s cm^{-1}. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 66·5 p.p.m. [d of d with ^{195}Pt satellites, 6F, J_{trans}(PF) 17·0 Hz, J_{cis}(PF) 3·0 Hz, and *J*(PtF) 60·0 Hz]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed a resonance at τ 2·81 (m, 30H, C_6H_5OP).

Reaction of Hexafluoroacetone with Tetrakis(trimethyl phosphite)platinum.—Similarly, reaction of hexafluoroacetone (6·0 mmol) with tetrakis(trimethyl phosphite)-platinum (0·50 g, 0·72 mmol) in light petroleum–diethyl ether (20 ml; 10 : 1) gave, after 60 °C for 1 week and removal of the solvent *in vacuo*, an orange oil. Chromatography on a Florisil-packed column and elution with light petroleum gave white *crystals* of (IX) (0·16 g, 29%), m.p. 83—85° [Found: C, 18·5; H, 2·4; P, 8·0%; *M*, 819 ($CHCl_3$). $C_{12}H_{18}F_{12}O_8P_2Pt$ requires C, 18·6; H, 2·3; P, 8·0%; *M*, 775], $\nu_{max.}$ 3010vw, 2960m, 2910vw, 2860m, 1451m, 1363m, 1298s, 1275s, 1250sh, 1231sh, 1215vs, 1199vs, 1178vs, 1165sh, 1150s, 1112m, 1091sh, 1079s, 1030vs, 1014sh, 965sh, 961s, 945w, 934w, 928w, 845s, 830s, 802m, 770s, 757m, 753sh, 733s, 725m, 715sh, 710m, and 698m cm^{-1}. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 66·0 p.p.m. [m with ^{195}Pt satellites, 6F, α-C(CF_3), *J*(PtF) 79·0 Hz] and 82·5 [m, 6F, β-C(CF_3)$_2$]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed a resonance at τ 6·25 (apparent t, 18H, CH_3OP, $|J|_{POCH}$ 8·0 Hz).

*Reactions of Di-isopropyl(cyclo-octa-*1,5-*diene)platinum.*—(a) *With tetrafluoroethylene.* A solution of di-isopropyl-(cyclo-octa-1,5-diene)platinum (0·39 g, 1·0 mmol) in light petroleum (10 ml) was sealed in a Carius tube with tetrafluoroethylene (0·80 g, 8·00 mmol). After irradiation with u.v. light (250 W; Hanovia lamp) for 5 days, the tube was opened, and the solvent was removed *in vacuo*. Chromatography on a Florisil-packed column and elution with diethyl ether gave, after recrystallisation from diethyl ether–light petroleum, white *crystals* of complex (X) (0·11 g, 22%), m.p. 164° [Found: C, 28·9; H, 2·1; F, 30·6%; *M*, 493 (C_6H_6). $C_{12}H_{12}F_8Pt$ requires C, 28·6; H, 2·4; F, 30·2%; *M*, 503], $\nu_{max.}$ 2963m, 2938m, 2918m, 2844w, 1555w, 1487m, 1436m, 1351w, 1328s, 1261s, 1236m, 1163s, 1142m, 1113s, 1091m, 1053m, 1028s, 1008m, 1003m, 980s, 974s, 934s, 863m, 828w, 786w, 769w, and 729w cm^{-1}. The ^{19}F n.m.r. spectrum (Et_2O) showed resonances 98·9 p.p.m. [s,br, 4F, α-CF_2, *J*(PtF) 422·0 Hz] and 137·8 [s,br, 4F, β-CF_2, *J*(PtF) 60·0 Hz]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·19 [s,br, 4H, CH=CH, *J*(PtH) 40·0 Hz] and 7·44 (m, 8H, CH_2).

(b) *With hexafluoroacetone.** A solution of di-isopropyl-(cyclo-octa-1,5-diene)platinum (0·39 g, 1·00 mmol) in light petroleum (10 ml) was sealed in a Carius tube with hexafluoroacetone (1·33 g, 8·00 mmol) and exposed to u.v. radiation for 24 h. After removal of the solvent *in vacuo* from the mixture and elution of the residue from a Florisil column with diethyl ether, recrystallisation of the product from this solvent gave white *crystals* of (XI) (0·42 g, 66%), m.p. 183—184° (Found: C, 26·8; H, 2·1; F, 34·3. $C_{14}H_{12}F_{12}O_2Pt$ requires C, 26·5; H, 1·9; F, 35·9%), $\nu_{max.}$ 2990w,br, 2964w, 2939w, 2866w, 1541w, 1491w, 1439m, 1354m, 1335m, 1309s, 1298s, 1283s, 1260s,br, 1235s, 1216s, 1183s, 1172s, 1160s, 1135s, 1105s, 1037m, 1016s, 973s, 953s, 930s, 874w, 858w, 832m, 811w, 802w, 785m, 758w, 734s, 725s, 711s, and 700m cm^{-1}. The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 67·1 p.p.m. [septet with ^{195}Pt satellites, 6F, α-C(CF_3)$_2$, *J*(FF) 3·0, *J*(PtF) 68·5 Hz] and 80·4 [septet, 6F, β-C(CF_3)$_2$, *J*(FF) 3·0 Hz]. The ^{1}H n.m.r. spectrum [$(CD_3)_2CO$] showed resonances at τ 4·08 [s, br,2H, C*H trans* to O, *J*(PtH) 46·0 Hz], 4·89 [s,br, 2H, C*H trans* to C(CF_3)$_2$, *J*(PtH) 67·0 Hz], and 7·36 (m, 8H, CH_2).

(c) *With* 1,1-*dicyano*-2,2-*bis(trifluoromethyl)ethylene.* Di-isopropyl(cyclo-octa-1,5-diene)platinum (0·39 g, 1·00 mmol) in light petroleum (10 ml) was added with stirring to 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (0·43 g, 2·00 mmol) in diethyl ether (5 ml). After 12 h the solvent was removed *in vacuo* and the product was eluted from a Florisil-packed column with diethyl ether. Recrystallisation from diethyl

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* This reaction, leading to the isolation of (XI), was first studied by Dr. D. J. Cook.

ether–light petroleum yielded white *crystals* of (XII) (0·19 g, 37%), m.p. 198—202° (decomp.) (Found: C, 32·7; H, 2·7; F, 22·3; N, 5·3. $C_{14}H_{12}F_6N_2Pt$ requires C, 32·5; H, 2·4; F, 22·1; N, 5·4%), $\nu_{max.}$ 2962m, 2948m, 2930m, 2905m, 2859m,sh, 2241m, 2172s, 1481w, 1451w, 1372s, 1353s, 1291s, 1263s, 1245vs, 1233vs, 1223vs, 1183w, 1144vs, 1094s, 1030m, 1001m, 959w, 920w, 903m, 887m, 872w, 847w, 824w, 803w, 769w, 743m, 725m, and 698s cm^{-1}. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 56·7 p.p.m. [s with ^{195}Pt satellites, 6F, *J*(PtF) 88·0 Hz]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·03 [s,br, 2H, C*H* *trans* to $C(CN)_2$, *J*(PtH) 62·0 Hz], 4·13 [s,br, 2H, C*H* *trans* to $C(CF_3)_2$, *J*(PtH) 71·0 Hz], 7·51 [s,br, 4H, CH_2 *trans* to $C(CN)_2$], and 7·65 [s,br, 4H, CH_2 *trans* to $C(CF_3)_2$].

(d) *With hexafluorobuta*-1,3-*diene*. A solution of di-isopropyl(cyclo-octa-1,5-diene)platinum (0·39 g, 1·00 mmol) in light petroleum (10 ml) was sealed in a tube with hexafluorobuta-1,3-diene (0·65 g, 4·00 mmol). U.v. irradiation (10 h) led to the separation of white *crystals* of (XIII) (0·35 g, 75%), from diethyl ether–light petroleum, m.p. 165—167° (decomp.) (Found: C, 31·2; H, 2·7; F, 24·9; Pt, 41·6. $C_{12}H_{12}F_6Pt$ requires C, 31·0; H, 2·6; F, 24·5; Pt, 41·9%), $\nu_{max.}$ 2983m, 2945m, 2908s, 2844m, 1755s, 1722w, 1711w, 1655w, 1548w, 1491m, 1455w, 1430m, 1381w, 1372w, 1348m, 1330s, 1323s, 1316s, 1289w, 1241w, 1202w, 1184w, 1156w, 1142w, 1121s, 1092w, 1083w, 1046m, 1010s, 1002s, 957s, 949s, 865m, 843m, 829m, 789m, 772m, 732w, and 703w cm^{-1}. The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 84·1 p.p.m. [m, 4F, α-CF_2 ($X_2AA'X_2'$ system), *J*(PtF) 417·0 Hz] and 147·8 [m, 2F, α-CF ($X_2AA'X_2'$ system), *J*(PtF) 240·0 Hz]; each resonance consists of a strong central line symmetrically surrounded by 4 pairs of lines *i.e.* $|J_{AX} + J_{AX'}| = 0$. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·17 (s,br, 4H, CH=CH, *J*(PtH) 41·0 Hz) and 7·42 [s,br, 8H, CH_2, *J*(PtH) 18·0 Hz].

(e) *With hexafluorobut*-2-*yne*. Di-isopropyl(cyclo-octa-1,5-diene)platinum (0·39 g, 1·00 mmol) and hexafluorobut-2-yne (1·30 g, 8·00 mmol) in light petroleum (10 ml) were irradiated in a sealed tube at room temperature. Large crystals formed in the tube, and these were purified by chromatography on Florisil. Elution with diethyl ether–light petroleum (3 : 1) gave white *crystals* of (XIV) (0·52 g, 83%), from diethyl ether, m.p. 148° [Found: C, 30·5; H, 2·2; F, 36·3%; *M*, 584 ($CHCl_3$). $C_{16}H_{14}F_{12}Pt$ requires C, 30·5; H, 2·2; F, 36·2%; *M*, 629], $\nu_{max.}$ 3025w, 2978m, 2947m, 2925w, 2906w, 2859w, 1628s, 1535w, 1493w, 1456w, 1438s, 1386w, 1353s, 1322w, 1268s, 1221s, 1202m, 1130s,br, 1025m, 1013m, 928m, 924m, 912w, 868m, 850w, 832m, 801m, 777m, 774m, 732w, 730w, 706w, and 652s cm^{-1}. The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 53·6 p.p.m. [q with ^{195}Pt satellites, 6F, α-$C(CF_3)$, *J*(FF) 12·0, *J*(PtF) 111·0 Hz] and 59·3 [m with ^{195}Pt satellites, 6F, β-$C(CF_3)$, *J*(FF) 12·0, *J*(PtF) 12·0, J_{gem}(HF) 9·0 Hz]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·26 [q, 2H, $C{=}C(CF_3)H$, *J*(PtH) 100·0 Hz, J_{gem}(HF) 9·0 Hz], 4·80 [s, 4H, CH=CH, *J*(PtH) 44·0 Hz], and 7·48 [s, 8H, CH_2, *J*(PtH) 19·0 Hz].

(f) *With hexafluoroisopropylideneamine*. Di-isopropyl-(cyclo-octa-1,5-diene)platinum (0·39 g, 1·00 mmol) in light petroleum (10 ml) and hexafluoroisopropylideneamine (1·32 g, 8·00 mmol) were sealed together and irradiated with u.v. light for 3 days. The solid which separated was filtered off to yield yellow *crystals* of (XV) (0·49 g, 78%), from diethyl ether–light petroleum, m.p. 144—146° (decomp.) (Found: C, 26·8; H, 2·0; F, 36·2; N, 4·5. $C_{14}H_{12}F_{12}N_2Pt$ requires C, 26·6; H, 1·9; F, 36·1; N, 4·5%), $\nu_{max.}$ 3370w,br, 3041w, 3003m, 2986m, 2940s, 2912m, 2862m, 1685s, 1668w, 1511w, 1487w, 1441m, 1349m, 1314vs, 1283s, 1228vs,br, 1203vs, 1161vs, 1121s, 1099m, 1082m, 1020s, 961vs, 914w, 875m, 862w, 835w, 816w, 784w, 743m, 724s, 711w, and 691m cm^{-1}. The ^{19}F n.m.r. spectrum (Et_2O) showed a resonance at 69·4 p.p.m. [s, 12F, $(CF_3)_2C{=}N$]. The ^{1}H n.m.r. spectrum [$(CD_3)_2CO$] showed resonances at τ 4·94 [s,br, 4H, CH=CH, *J*(PtH) 56·0 Hz] and 7·30 [s,br, 8H, CH_2, *J*(PtH) 24·0 Hz].

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