Reactions of Low-valent Metal Complexes with Fluorocarbons. Part 32.[1] Tris-μ-(t-butyl isocyanide)-tris(t-butyl isocyanide)-*triangulo*-triplatinum

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Reaction of [Pt$_3$(Bu^{t}NC)$_6$] (1) with hexafluoroacetone affords the five-membered ring metallacycle [{Pt·O·C(CF$_3$)$_2$·O·C(CF$_3$)$_2$}(Bu^{t}NC)$_2$], but with tetrafluoroethylene an octafluorodiplatinacyclohexane complex [(Bu^{t}NC)$_2$Pt·CF$_2$·CF$_2$·Pt(Bu^{t}NC)$_2$·CF$_2$·CF$_2$] is formed, which undergoes dynamic behaviour in solution. Treatment of (1) with hexafluoropropene, octafluorobut-2-ene, and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene yields the three-membered ring complexes [{Pt·CF$_2$·CF(CF$_3$)}(Bu^{t}NC)$_2$], [{Pt·CF(CF$_3$)·CF(CF$_3$)}(Bu^{t}NC)$_2$], and [{Pt·C(CF$_3$)$_2$·C(CN)$_2$}(Bu^{t}NC)$_2$], respectively. Whereas bromotrifluoroethylene and (1) form *trans*-[PtBr(CF:CF$_2$)(Bu^{t}NC)$_2$], chlorotrifluoroethylene affords [(Pt·CF$_2$·CFCl)(Bu^{t}NC)$_2$] which in solution rearranges to *cis*-[PtCl(CF:CF$_2$)(Bu^{t}NC)$_2$] and subsequently to *trans*-[PtCl(CF:CF$_2$)(Bu^{t}NC)$_2$]. Fluorine-19 n.m.r. and i.r. studies reveal that *cis*-[PtCl(CF:CF$_2$)(Bu^{t}NC)$_2$] reverts to the η^2-chlorotrifluoroethylene complex [(Pt·CF$_2$·CFCl)(Bu^{t}NC)$_2$] on recrystallisation of the former from solutions.

OXIDATIVE-ADDITION reactions readily occur between d^{10} platinum complexes [PtL$_4$] or [PtL$_2$(*trans*-PhCH:CHPh)] [L = Ph$_3$P, Ph$_2$PMe, Ph$_2$PCH$_2$CH$_2$PPh$_2$, or (MeO)$_3$P] and electrophilic fluoro-organic compounds (CF$_3$)$_2$CX [X = O, NH, NMe, or C(CN)$_2$], CF$_2$·CFX (X = F, CF$_3$, CF:CF$_2$, Cl, or Br), CF$_3$CF:CFCF$_3$, and (CF$_3$)$_2$CN$_2$.[2-5] The complexes so formed are either three- or five-membered metallacycles, depending on the nature of L and the electrophilic reagent. In these reactions hexafluoroacetone and hexafluoroisopropylideneamine have a marked tendency to afford initially a three-membered ring adduct [{Pt·C(CF$_3$)$_2$·X}L$_2$] which subsequently undergoes ring expansion to yield complexes [{Pt·C(CF$_3$)$_2$·X·C(CF$_3$)$_2$·X}L$_2$]. In contrast, the olefins CF$_2$:CFX, (CF$_3$)$_2$C:C(CN)$_2$, and CF$_3$CF:CFCF$_3$ give adducts [Pt(fluoro-olefin)L$_2$]. Moreover, related reactions between [Pt(cod)$_2$] (cod = 1,5-C$_8$H$_{12}$)[6] and hexafluoroacetone,[7] tetrafluoroethylene, or perfluoropropene[1] show a different pattern of behaviour. In particular, binuclear platinum species are formed, *viz.* [(cod)Pt·C(CF$_3$)$_2$·O·Pt(cod)], [(cod)Pt·CF$_2$·CF$_2$·Pt(cod)·CF$_2$·CF$_2$], and [(cod)Pt·C(CF$_3$)$_2$·Pt(cod)].

Since the structures of the organoplatinum complexes produced depend so much on the nature of the ligands present in the nucleophilic reactants [PtL$_4$] (L = phosphine or phosphite, L$_2$ = cod), it seemed useful to investigate the behaviour of the cluster compound [Pt$_3$(Bu^{t}NC)$_6$][8] towards unsaturated fluoro-organic compounds in order to establish the effect of isocyanide ligands on the course of the reactions. It has previously been observed[9] that [Pt$_3$(Bu^{t}NC)$_6$] has the capacity to cleave a carbon–carbon bond of hexakis(trifluoromethyl)benzene.

RESULTS AND DISCUSSION

Hexafluoroacetone and [Pt$_3$(Bu^{t}NC)$_6$] (1) react to give the five-membered ring complex (2), the structure of which is established by two characteristic[10] ^{19}F n.m.r. signals at 66.9 and 80.1 p.p.m. The product (2) is thus similar to that obtained[4] from [Pt(PPh$_2$Me)$_4$], or related phosphineplatinum complexes and hexafluoroacetone. A similar head-to-tail five-membered ring complex was one of the products from [Pt(cod)$_2$] and (CF$_3$)$_2$CO, although in this reaction other products including the diplatinum species [(cod)Pt·C(CF$_3$)$_2$·O·Pt(cod)] were isolated.[7] No complexes containing platinum–platinum bonds were obtained from the reaction of (1) with hexafluoroacetone.

Reaction of (1) with hexafluoropropene, octafluorobut-2-ene, and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene gave the three-membered ring compounds (3), (4), and (5), respectively, characterised by elemental analyses, the appearance of two ν(NC) bands in the i.r. spectrum of each complex, and very typical ^{19}F n.m.r. spectra for species of this structural type.[1,3-5,11]

Whereas tetrafluoroethylene reacts with tetrakis(tertiary phosphine)platinum complexes to give the platinacyclopropane-type adducts [(Pt·CF$_2$·CF$_2$)L$_2$],[3] in

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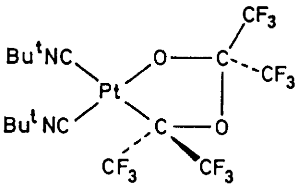
contrast bis(cyclo-octa-1,5-diene)platinum affords[1] an unusual octafluorodiplatinacyclohexane complex [$Pt_2C_4F_8(1,5\text{-}C_8H_{12})_2$]. Reaction of (1) with tetrafluoroethylene also yields a diplatinum six-membered ring compound (6), presumably similarly formed by dimerisation of a dipolar intermediate,[1] *viz.* [$(Bu^tNC)_2\overset{+}{P}t\cdot CF_2\cdot\overset{-}{C}F_2$]. The ^{19}F n.m.r. spectrum of (6) indicates dynamic behaviour similar to that found[1] with the cyclo-octa-1,5-diene complex mentioned above, the spectra of these two compounds being very different from those shown by the mononuclear complexes [$(Pt\cdot CF_2\cdot CF_2)L_2$].[3] Thus the spectra of the octafluorodiplatinacyclohexane complex (6) and [$Pt_2C_4F_8(1,5\text{-}C_8H_{12})_2$] are characterised by a single peak with two pairs of satellite peaks at elevated temperature (30 and 60 °C, respectively), with limiting spectra having an AB pattern being observed at low temperatures (−90 and −40 °C, respectively). Application of the Eyring rate equation to the variable-temperature n.m.r. spectra gave values for the free energy of activation of the ring-inversion process of 9.3 kcal mol^{-1} for (6) (at 218 K) and 12.9 kcal mol^{-1} for the cyclo-octadiene analogue (at 303 K).* Although these values are subject to an error of ± 0.5 kcal mol^{-1}, they do show that the inversion process is more facile in (6) than in the cyclo-octadiene analogue.



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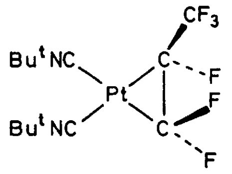

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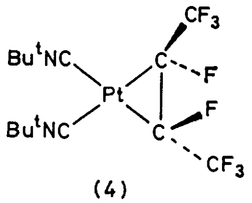

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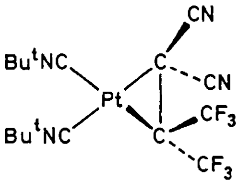

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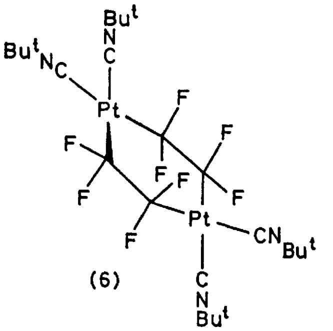

η^2-Complexes formed between chloro- or bromo-trifluoroethylene and the metal(0) complexes [$M(R_3P)_4$] (M = Ni, Pd, or Pt) readily rearrange to their vinyl isomers.[10] In this context the complexes [$Pt(CF_2{:}CFX)(Ph_3P)_2$] (X = Cl or Br), although isolable, afford the species *trans*-[$PtX(CF{:}CF_2)(Ph_3P)_2$],[3] particularly in polar solvents. Mechanistic studies of this ' vinyl rearrangement ' are compatible with a mechanism in which fission of the carbon–halogen bond occurs to give a tight ion pair.[12]

Treatment of (1) with bromotrifluoroethylene affords *trans*-[$PtBr(CF{:}CF_2)(Bu^tNC)_2$] (7), no intermediate η^2-complex [$(Pt\cdot CF_2\cdot CFBr)(Bu^tNC)_2$] being identified as a product. The i.r. [$\nu(C{:}C)_{max.}$ at 1 710s cm^{-1}] and ^{19}F spectra of (7) are in accord with the structure proposed. The ^{19}F spectra of trifluorovinylplatinum complexes show a characteristic pattern of three quartets with chemical shifts centred near 100, 125, and 150 p.p.m. (relative to CCl_3F).[3,13] In (7) these quartets appear at 98.8, 124.4, and 146.5 p.p.m., with *J*(FF) couplings as expected (Table).

It is well established that the vinyl rearrangement occurs more readily with bromotrifluoroplatinacyclopropane compounds than with the corresponding chloro-complexes.[3] Following this trend, and in contrast to the formation of (7), chlorotrifluoroethylene and (1) react in toluene at room temperature to give a three-membered ring complex [$(Pt\cdot CF_2\cdot CFCl)(Bu^tNC)_2$] (8). This formulation follows from the absence in the i.r. spectrum (Nujol) of any $CF{:}CF_2$ band near 1 700 cm^{-1}.[13] If the ^{19}F n.m.r. spectrum of (8) is measured at −40 °C (C_6H_5Me–C_6D_6) on a freshly prepared sample the signals observed are in good agreement with those reported earlier[3] for similar complexes (Table). However, if (8) is dissolved (C_6H_6–C_6D_6) at room temperature and the ^{19}F spectrum measured only peaks characteristic of a $Pt\cdot CF{:}CF_2$ group are seen. These same peaks may sometimes be detected as very weak signals in the spectrum recorded at −40 °C.

When solutions used to study ^{19}F spectra at room temperature are evaporated and the solids recrystallised from light petroleum, the i.r. spectra (Nujol) are identical with that for the initial product (8). However, repeated dissolution and recrystallisations of samples from benzene leads to the appearance of two i.r. bands at 1 710 and 1 705 cm^{-1} which grow in intensity, the latter being assigned to *trans*-[$PtCl(CF{:}CF_2)(Bu^tNC)_2$].

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* Throughout this paper: 1 cal = 4.184 J.

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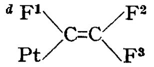
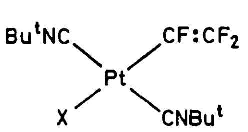
Fluorine-19 chemical shifts and coupling constants

	δ [a]/p.p.m.			J/Hz					
	F^1	F^2	F^3	F^1F^2	F^1F^3	F^2F^3	PtF^1	PtF^2	PtF^3
$[Pt(CF^1F^2{:}CF^3Cl)(Bu^tNC)_2]$	114.6	115.4	138.4	186.8	<1	52.6	297	257	211
$[Pt(CF^1F^2{:}CF^3Cl)(Ph_3P)_2]$ [b]	114.3	114.3	137.4						
$[Pt(CF^1F^2{:}CF^3C_2F_3)(Ph_3P)_2]$ [c]	109.0	113.9	184.5	176	*ca.* 1	56.3			
cis-$[PtCl(CF^1{:}CF^2F^3)(1,5\text{-}C_8H_{12})]$ [d,e]	159.2	96.7	121.9	40	107	90.0	429	72	11
cis-$[PtCl(CF^1{:}CF^2F^3)(Bu^tNC)_2]$ [d]	162.3	96.8	125.7	35	107	91.6	396	84	49
cis-$[PtBr(CF^1{:}CF^2F^3)(Et_3P)_2]$ [d,f]	155.1	98.6	127.0	34	104	104	348	88	51
trans-$[PtCl(CF^1{:}CF^2F^3)(Bu^tNC)_2]$ [d]	146.0	98.3	125.6	38	109	92.7	568	66	44
trans-$[PtBr(CF^1{:}CF^2F^3)(Bu^tNC)_2]$ [d]	146.5	98.8	124.4	40	109	92	598	73	39
trans-$[PtCl(CF^1{:}CF^2F^3)(Ph_3P)_2]$ [b,d]	147.0	101.2	128.7	31	105	98	452	64	49

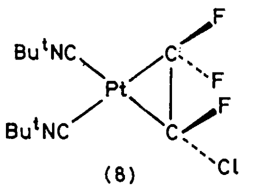
[a] Relative to CCl_3F (δ 0.00 p.p.m.). [b] Data from ref. 3. [c] Data from ref. 5. [d] 

[e] Data from ref. 1. [f] Data from ref. 13.

These results suggest that as a solid, or in solution at −40 °C, complex (8) is stable, but at room temperature in solution *cis*-$[PtCl(CF{:}CF_2)(Bu^tNC)_2]$ (9) is produced and that (9) reverts to (8) on recrystallisation. However, in time this interconversion ceases as (9) is converted into another isomer, presumably *trans*-$[PtCl(CF{:}CF_2)(Bu^tNC)_2]$ (10). Fluorine n.m.r. bands due to isomer (10) were observed, as well as signals due to (9), in spectra recorded after several hours at room temperature (Table). The reversible reaction (9) $\rightleftharpoons$ (8) involving Cl transfer is particularly interesting in the context of the previously observed migration of hydrogen,[14] methyl,[15] and allyl [16] groups from metals to σ-bonded vinyl groups, and formally corresponds to an intramolecular reductive process, the fluoro-olefin remaining bonded to platinum (Scheme).



(7) X = Br
(10) X = Cl



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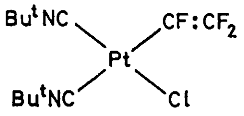

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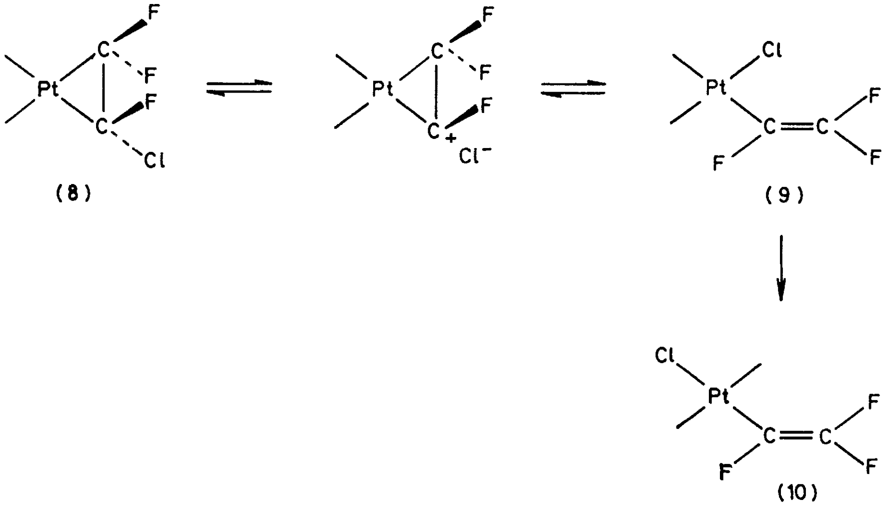

SCHEME

EXPERIMENTAL

The instrumentation employed and general experimental techniques were as described earlier.[1] Fluorine-19 n.m.r. chemical shifts are relative to CCl_3F (0.0 p.p.m.).

Reactions of Tris-μ-(t-butyl isocyanide)-tris(t-butyl isocyanide)-triangulo-*triplatinum* (1).—(*a*) *With hexafluoroacetone.* An excess of hexafluoroacetone (0.64 g, 4 mmol) was condensed into a Carius tube containing (1) (0.4 g, 0.37 mmol) in diethyl ether (80 cm^3). After 4 h at room temperature the resulting white crystals were collected and recrystallised from diethyl ether–light petroleum to give *crystals* of (2)

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(0.60 g, 78%), m.p. 175 °C (Found: C, 27.5; H, 2.6; N, 3.7%; *M*, 693. $C_{16}H_{18}F_{12}N_2Pt$ requires C, 27.7; H, 2.6; N, 4.0%; *M*, 693), $\nu_{max.}$ (Nujol) at 2 258s and 2 228s cm^{-1} (NC). N.m.r. spectra in $CDCl_3$: ^1H, τ 8.40 (s, 9 H, Bu^tNC) and 8.50 (s, 9 H, Bu^tNC); ^{19}F, 66.9 [septet, 6 F, α-$C(CF_3)_2$, *J*(FF) 3.5, *J*(PtF) 91.3 Hz] and 80.1 p.p.m. [septet, 6F, β-$C(CF_3)_2$, *J*(FF) 3.5 Hz].[10]

(*b*) *With hexafluoropropene*. A solution of (1) (0.22 g, 0.20 mmol) in diethyl ether (60 cm^3) was introduced into a Carius tube and hexafluoropropene (0.15 g, 1.0 mmol) was condensed into the tube. After 3 h at room temperature, the colourless solution was filtered and the solvent was removed *in vacuo*. The white solid was recrystallised from diethyl ether–light petroleum to give white crystals of (3) (0.25 g, 83%), m.p. 101 °C (Found: C, 31.1; H, 3.7; N, 5.4%; *M* 511. $C_{13}H_{18}F_6N_2Pt$ requires C, 30.5; H, 3.5; N, 5.5%; *M* 511), $\nu_{max.}$ (Nujol) at 2 220vs and 2 200vs cm^{-1} (NC). N.m.r. spectra in $CDCl_3$: ^1H, τ 8.74 (s, 18 H, Bu^tNC); ^{19}F, [$Pt(F^1F^2C{:}CF^3CF_3{}^4)$, F^2 and F^3 assumed *trans* [11]], 68.7 [d of d of d, 3 F, CF_3, $J(F^3F^4)$ 14, $J(F^2F^4)$ 9, $J(F^1F^4)$ 3, $J(PtF^4)$ 126 Hz], 111.5 [d of q, 1 F, F^1, $J(F^1F^4)$ 3, $J(F^1F^3)$ 6.5, $J(F^1F^2)$ 200, $J(PtF^1)$ 285 Hz], 120.0 [d of q, 1 F, F^2, $J(F^2F^4)$ 9, $J(F^2F^3)$ 51, $J(F^1F^2)$ 200, $J(PtF^2)$ 212 Hz], and 205.0 p.p.m. [d of d of q, 1 F, F^3, $J(F^3F^4)$ 13, $J(F^1F^3)$ 6.5, $J(PtF^3)$ 118 Hz].

(*c*) *With octafluorobut-2-ene*. Similarly, reaction of (1) (0.35 g, 0.32 mmol) with $(CF_3)CF{:}CF(CF_3)$ (1.0 g, 5.0 mmol) in diethyl ether (60 cm^3) gave, after recrystallisation from diethyl ether–light petroleum, white *crystals* of (4) (0.42 g, 78%), m.p. 72 °C (Found: C, 30.1; H, 3.5; N, 5.1. $C_{14}H_{18}F_8N_2Pt$ requires C, 30.1; H, 3.2; N, 5.0%), $\nu_{max.}$ (Nujol) at 2 230s and 2 200s cm^{-1} (NC). N.m.r. spectra in $CDCl_3$: ^1H, τ 8.42 (s, 18 H, Bu^tNC); ^{19}F, 68.9 and 200.5 p.p.m. [$J(PtCF_3)$ 97, *J*(PtF) 65 Hz].

(*d*) *With* 1,1-*dicyano*-2,2-*bis*(*trifluoromethyl*)*ethylene*. A solution of $(CN)_2C{:}C(CF_3)_2$ (0.21 g, 1.0 mmol) in diethyl ether (5 cm^3) was added (dropwise) to a solution of (1) in diethyl ether (10 cm^3). After 2 h at room temperature the solvent was removed *in vacuo* from the colourless solution. The residue was recrystallised from diethyl ether–light petroleum to give white *crystals* of (5) (0.32 g, 72%), m.p. 147 °C (Found: C, 34.0; H, 3.5; N, 9.6%; *M* 575. $C_{16}H_{18}F_6N_4Pt$ requires C, 33.4; H, 3.2; N, 9.7%; *M* 575), $\nu_{max.}$ (Nujol) at 2 238s and 2 210s cm^{-1} (NC). N.m.r. spectra in $CDCl_3$: ^1H, τ 8.42 (s, 9 H, Bu^tNC) and 8.38 (s, 9 H, Bu^tNC); ^{19}F, 56.1 p.p.m. [s, 6 F, CF_3, *J*(PtF) 85.9 Hz].

(*e*) *With Tetrafluoroethylene*. A Schlenk tube fitted with a Westef stopcock was charged with (1) (0.4 g, 0.37 mmol), diethyl ether (80 cm^3), and tetrafluoroethylene (0.2 g, 2 mmol). On warming to room temperature an orange solid appeared. After 5 h the solid was recovered and recrystallised from dichloromethane–diethyl ether to give yellow *crystals* of (6) (0.22 g, 49%), m.p. 134—135 °C (decomp.) (Found: C, 30.7; H, 4.0; N, 5.9. $C_{24}H_{36}F_8N_4Pt_2$ requires C, 31.2; H, 3.9; N, 6.1%), $\nu_{max.}$ (Nujol) at 2 223s, 2 199s, 1 268w, 1 243s, 1 213m, 1 150m, 1 053s, 1 023m, 982m, 945s, 868w, 853m, 840s, 633w, 570m, 548w, 533w, and 451w cm^{-1}. N.m.r. spectra: ^1H, τ 8.44(m); ^{19}F in CH_2Cl_2–CD_2Cl_2; (*a*) 35 °C, 80.4 p.p.m. [s, with two pairs of satellite peaks, *J*(PtF) 94.7 and 416 Hz], (*b*) −90 °C, AB pattern, δ_A 76.4, δ_B 85.6 p.p.m. [*J*(AB) 243, *J*(APt) 473, *J*(APt′) *ca*. 95, and *J*(BPt) 370 Hz].

(*f*) *With bromotrifluoroethylene*. Reaction (5 h, room temperature) of (1) (0.30 g, 0.28 mmol) with bromotrifluoroethylene (0.24 g, 1.5 mmol) in toluene (50 cm^3) afforded a clear colourless solution. Removal of solvent *in vacuo* gave a yellow oil which was extracted with diethyl ether. Addition of light petroleum to the extract and cooling (−40 °C) produced white *crystals* of (7) (0.25 g, 54%), m.p. 98 °C (Found: C, 28.1; H, 3.7; N, 5.0%; *M* 522. $C_{12}H_{18}BrF_3N_2Pt$ requires C, 27.6; H, 3.5; N, 5.4%, *M* 522). $\nu_{max.}$ (Nujol) at 2 225vs and 2 180s (NC) and 1 710ms (C:C); (Nujol, CsI plates) 288m, 228m, and 208m cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: τ 8.48 (s, 18 H, Bu^t).

(*g*) *With chlorotrifluoroethylene*. Complex (1) (0.5 g, 0.46 mmol) in toluene (60 cm^3) was treated with chlorotrifluoroethylene (4 mmol) in a Schlenk tube fitted with a Westef stopcock. The mixture was stirred (2 h) and solvent was removed *in vacuo* to give a yellow residue. The latter was partially dissolved in diethyl ether (65 cm^3) and the solution so obtained was partially evaporated to 30 cm^3. Light petroleum was added (5 cm^3) and the mixture was cooled (−40 °C) giving pale yellow *crystals* of (8) (0.3 g, 45.5%), m.p. 88 °C (Found: C, 30.6; H, 4.0; N, 5.7. $C_{11}H_{18}ClF_3N_2Pt$ requires C, 30.2; H, 3.8; N, 5.9%). Complex (8) showed no i.r. band near 1 700 cm^{-1}; $\nu_{max.}$ (Nujol, CsI plates) at 2 215s, 2 195s (NC), 1 478m, 1 402w, 1 378s, 1 332s, 1 312w, 1 238s, 1 100s,br, 1 080s, 1 040s, 998m, 920s, 862w, 778m, 742s, 730s, 585w, 530w, 520w, 458w, 430w, 393w, and 338w cm^{-1}. The ^{19}F n.m.r. spectrum of (8) (C_6D_6–C_6H_5Me) at −40 °C gave data (Table) in accord with the structure proposed, together with weak signals corresponding to (9). Samples of (8) dissolved in C_6D_6 at room temperature, with the spectrum being recorded immediately, showed only ^{19}F n.m.r. signals corresponding to (9). However, recrystallisation of the residue [$\nu_{max.}$(C:C) at 1 710s cm^{-1}] from light petroleum afforded (8).

Repeated dissolution of the solid in benzene and recrystallisation led to the appearance of ^{19}F n.m.r. signals corresponding (Table) to a second complex containing a $Pt{\cdot}CF{:}CF_2$ group and assumed to be the *trans* complex (10) [$\nu_{max.}$ at 2 230s (NC) and 1 705s cm^{-1} (C:C)].

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