Reaction of Low-valent Metal Complexes with Fluorocarbons. Part XXVII.[1] Zerovalent Nickel, Palladium, and Platinum, and Iridium(I), Palladium(II), and Platinum(II) Complexes with Bis(trifluoromethyl)-diazomethane

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Reaction of $[Pt(stilbene)(PPh_3)_2]$, $[Pt(PEt_3)_3]$, $[Pd(t\text{-}BuNC)_2]$, $[Pd(C_6H_{11}NC)_2]$, $[Ni(t\text{-}BuNC)_4]$ and $[Ni(PMePh_2)_4]$ with $(CF_3)_2CN_2$ affords the perfluoroacetone azine complexes $[MC(CF_3)_2N{\cdot}N{=}C(CF_3)_2L_2]$. The complexes $[M(PhCN)_2Cl_2]$ (M = Pd or Pt) undergo insertion reactions into the M–Cl bond with $(CF_3)_2CN_2$, whereas, *trans*-$[IrCl(N_2)(PPh_3)_2]$ gives the adduct, $[Ir(Cl)N{=}NC(CF_3)_2(PPh_3)_2]$. Minor products in the reaction of Pt^0 complexes with $(CF_3)_2CN_2$ include $[PtCH(CF_3)CF_2(PPh_3)_2]$ and *cis*- and *trans*-$[PtF\{CH(CF_3)_2\}(PPh_3)_2]$.

EARLIER[2] it was shown that bis(trifluoromethyl)diazomethane underwent insertion reactions of the $C(CF_3)_2$ group with metal–hydrogen and metal–metal bonds. Here we report reactions of $(CF_3)_2CN_2$ with some d^8 and d^{10} complexes.

An excess of bis(trifluoromethyl)diazomethane[3] reacts rapidly at room temperature with a diethyl ether solution of *trans*-stilbenebis(triphenylphosphine)platinum to give *trans*-stilbene and bright yellow crystals of the air-stable complex (I). The latter was initially assigned the illustrated structure on the basis of elemental analyses, a solution molecular weight determination, i.r. and n.m.r. spectroscopy; and the molecular geometry was subsequently confirmed by *X*-ray crystallography. The i.r. spectrum showed a strong band at 1560 cm^{-1}, which was assigned to the stretching mode of the unco-ordinated C=N group of the azine ligand; the free ligand shows a band at 1665 cm^{-1}.[4] Reaction of (I) with iodine in benzonitrile afforded $[PtI_2(PPh_3)_2]$ and perfluoroacetone azine,† $(CF_3)_2C{=}N{\cdot}N{=}C(CF_3)_2$, identified by its i.r. spectrum. Treatment of the azine with *trans*-stilbenebis(triphenylphosphine)platinum regenerated complex (I); no evidence could be found by ^{19}F n.m.r. spectroscopy for other products corresponding to co-ordination of both C=N bonds either in a 1,4-addition (as in related tetra-azadiene complexes of iron[5] or iridium[6]), or to two separate $Pt(PPh_3)_2$ groups. During the course of our work, (I) was independently prepared from $(CF_3)_2CN_2$ and $[Pt(PPh_3)_3]$.[7]

The ^{19}F n.m.r. spectrum of (I) showed three multiplets of relative intensity 2 : 1 : 1 with increasing field (rel. CCl_3F, 0·00 p.p.m.); a resonance at 59·5 p.p.m. was assigned to the two apparently equivalent CF_3 groups attached to the carbon adjacent to platinum, with a doublet splitting (10·0 Hz) due to *trans*-^{19}F–^{31}P coupling, and platinum satellite peaks due to ^{19}F–^{195}Pt coupling (79·0 Hz). These values compare well with those observed[8] for similar compounds, *e.g.* $Pt{\cdot}C(CF_3)_2NMe(PPh_3)_2$, δ_F 59·7 p.p.m. [J(PF) 13·0, J(PtF) 81·0 Hz]. The remaining 1 : 1 multiplets at 63·5 and 65·8 p.p.m. in the spectrum of (I) were assigned to the inequivalent CF_3 groups of the $N{=}C(CF_3)_2$ moiety. Double irradiation experiments showed that each of these coupled multiplets

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† This compound has also been called 1,1,4,4-tetrakis(trifluoromethyl)buta-1,3-azine in the past.

[1] Part XXVI, P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 388.

[2] J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1969, 1872; *Chem. Comm.*, 1968, 170.

[3] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1966, **88**, 3617.

[4] W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, 1965, **30**, 1398.

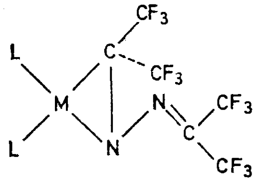
[5] R. J. Doedens, *Chem. Comm.*, 1968, 1271.

[6] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1971, **93**, 1826.

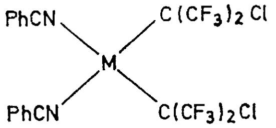
[7] D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.

[8] J. Clemens, R. E. Davis, M. Green, J. D. Oliver, and F. G. A. Stone, *Chem. Comm.*, 1971, 1095.

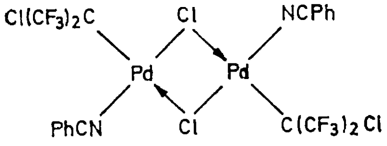
[J(FF) 6·0 Hz] was split unequally by the ^{31}P nuclei into a doublet (2·5 and 6·0 Hz, respectively), although interestingly, no ^{19}F–^{195}Pt coupling was observed.



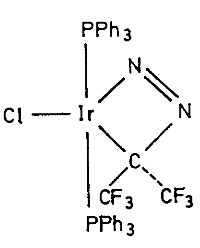
(I, M = Pt, L = PPh_3)
(II, M = Pt, L = PEt_3)
(III, M = Pd, L = ^tBuNC)
(IV, M = Pd, L = $C_6H_{11}NC$)
(V, M = Ni, L = ^tBuNC)
(VI, M = Ni, L = $PMePh_2$)



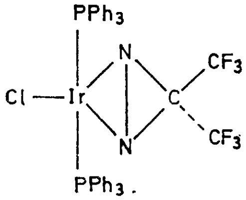
(VII, M = Pd)
(IX, M = Pt)



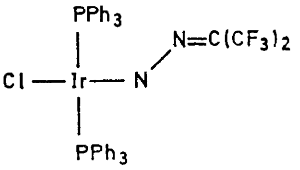
(VIII)



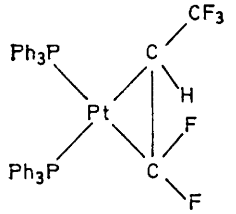
(Xa)



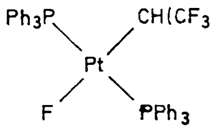
(Xb)



(Xc)



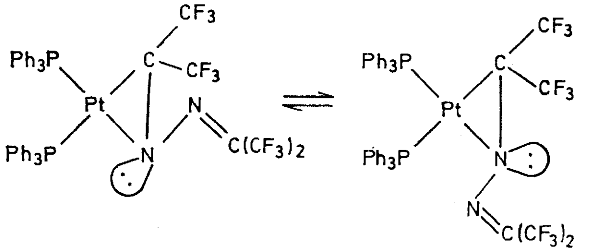
(XI)



(XII)
(XIII) *cis* isomer

The crystal structure determination[8] showed that in (I) the nitrogen bonded to the platinum is formally sp^3 hybridised. Since the ^{19}F n.m.r. spectrum showed that the CF_3 groups bonded to the carbon adjacent to the platinum are magnetically equivalent this required that in solution a rapid inversion occurs at nitrogen.

A similar situation has been previously observed and discussed[9] for the related hexafluoroisopropylideneamine complex [$\overline{PtC(CF_3)_2N}Me(PPh_3)_2$]. Unfortunately even at −95° there was no change in the ^{19}F n.m.r. line shapes of the spectrum of (I), and therefore at the present time it is not possible to say anything further about the nature of this process.



Complexes of the type [M(azine)L_2] (M = Ni, Pd, or Pt) were also formed in reactions of excess of bis(trifluoromethyl)diazomethane with tris(triethylphosphine)platinum, bis(t-butyl isocyanide)palladium, bis(cyclohexyl isocyanide)palladium, tetrakis(t-butyl isocyanide)nickel and tetrakis(methyldiphenylphosphine)nickel. The products, (II)—(VI) respectively, all showed a band in their i.r. spectra close to 1560 cm^{-1} [ν-(C=N)], and a characteristic 2 : 1 : 1 intensity ^{19}F n.m.r. spectrum of a singlet and two coupled quartets with additional ^{19}F–^{31}P coupling in (II) and (VI) (see the Table).

When compound (I) was prepared from $Pt(PPh_3)_n$ (n = 3 or 4) variation of reaction conditions (solvent, time) resulted in formation of minor products discussed below.

The triethylphosphine complex (II) showed stability similar to that of (I), whereas the isocyanide complexes of palladium and nickel (III)—(V) were air-sensitive, particularly in solution. The red methyldiphenylphosphine–nickel complex (VI) showed greater thermal stability, although this also decomposed slowly in solution to [$MePh_2PN_2C(CF_3)_2$].

In order to extend these studies to d^8 systems, the reaction of bis(trifluoromethyl)diazomethane with chlorodinitrogenbis(triphenylphosphine)iridium[10] was examined. In benzene solution at room temperature green-black crystals of air-stable complex (X) were obtained in high yield. This compound decomposed slowly in solution but could be recrystallised with care from benzene. Elemental analyses and a molecular weight measurement in benzene solution indicated that (X) possessed the molecular formula [$Ir(Cl)(C_3F_6N_2)(PPh_3)_2$].

Treatment of (X) with iodine in benzonitrile gave as the only volatile product bis(trifluoromethyl)diazomethane identified[3] by a strong band in the i.r. spectrum at 2135 cm^{-1} as well as characteristic C–F bands, and a singlet ^{19}F n.m.r. resonance at 56·9 p.p.m. The ^{19}F n.m.r. spectrum of (X) showed one triplet resonance due to ^{19}F–^{31}P coupling, which is in accord with a structure in which the phosphines have a relative *trans*-configuration. In agreement the far i.r. spectrum showed bands consistent with a structure containing two relatively *trans* triphenylphosphine ligands and one Ir–Cl bond. The i.r. showed no bands in the 1550 cm^{-1} region where stretching

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

[10] J. P. Collman, M. Kubota, J. Y. Sun, and F. Vastine, *J. Amer. Chem. Soc.*, 1967, **89**, 169.

frequencies due to the $N{=}C(CF_3)_2$ moiety might be expected.

On this basis (X) may be tentatively assigned the illustrated trigonal bipyramidal structure (Xa) with the diazoalkane bonded as a 1,3-dipolar ligand. The alternative formulations (Xb) and (Xc) are not consistent with the available evidence. It is interesting that analogous four-membered ring complexes $\overline{\mathrm{Ir{\cdot}N{=}N{\cdot}N}}\mathrm{{\cdot}COR}$ have been postulated [10,11] as intermediates in the reaction of acyl azides with *trans*-$[IrCl(CO)(PPh_3)_2]$ to give $[IrCl(N_2)(PPh_3)_2]$.

Comparison of ^{19}F n.m.r. chemical shifts (p.p.m.) and coupling constants (Hz) for azine complexes

	Compound	$\delta_{(1)}[6F]$	$\delta_{(2)}[3F]$	$\delta_{(3)}[3F]$	$J(F_2F_3)$	$J(PF_2)$	$J(PF_3)$
(I)	$Pt(azine)(PPh_3)_2$	59·5(d)	63·5(m)	65·8(m)	6·0	2·5	6·0 [a]
(II)	$Pt(azine)(PEt_3)_2$	58·8(d)	61·8(m)	65·8(m)	6·0	2·5	6·0 [b]
(III)	$Pd(azine)(t\text{-}BuNC)_2$	62·5(s)	62·5(q)	66·8(q)	6·0		
(IV)	$Pd(azine)(C_6H_{11}NC)_2$	62·3(s)	62·4(q)	66·7(q)	6·0		
(V)	$Ni(azine)(t\text{-}BuNC)_2$	62·0(s)	62·6(q)	63·7(q)	6·0		
(VI)	$Ni(azine)(MePh_2P)_2$	59·9(d)	60·9(m)	63·4(m)	6·0	2·0	6·0 [c]
	Ni(azine)(cod) [d]	57·0(s)	60·0(q)	63·8(q)	6·0		

[a] $J(PtF_1)$ 79·0, $J(trans\text{-}PF_1)$ 10·0. [b] $J(PtF_1)$ 81·0, $J(trans\text{-}PF_1)$ 10·0. [c] $J(trans\text{-}PF_1)$ 10·0. [d] J. Ashley-Smith, Ph.D. Thesis, Bristol University, 1970.

In diethyl ether solution the reaction takes a different course to give an iridium(IV) species the structure of which is currently being investigated.

In the reaction of $[IrCl(N_2)(PPh_3)_2]$ with $(CF_3)_2CN_2$ there was no evidence for products arising from the formal insertion of the $C(CF_3)_2$ group into the iridium–chlorine bond. This is in contrast to the corresponding reaction of bis(benzonitrile)-palladium and -platinum dichloride.[12] Treatment of a methylene chloride solution of $PdCl_2(PhCN)_2$ with an excess of $(CF_3)CN_2$ at room temperature leads to the formation of the crystalline complexes (VII) and (VIII). The yellow crystalline complex (VII) showed a sharp singlet ^{19}F n.m.r. resonance at 62·3 p.p.m., and no bands in the i.r. spectrum (600—200 cm^{-1}) attributable to Pd–Cl, suggesting the illustrated structure in which the $C(CF_3)_2$ group has formally inserted into both palladium–chlorine bonds. The second less soluble complex (VIII) showed a ^{19}F n.m.r. resonance at 62·9 p.p.m., but had a molecular weight corresponding to the illustrated dinuclear structure. The related reaction of bis(benzonitrile)platinum dichloride with $(CF_3)_2CN_2$ only occurred at higher temperatures (80°) to give (IX). The i.r. spectrum showed bands attributable to co-ordinated benzonitrile, and in the ^{19}F n.m.r. spectrum a single resonance was observed at 63·1 p.p.m. with ^{19}F–^{195}Pt coupling (53·0 Hz) indicating a structure similar to the palladium complex (VII). In these reactions no evidence was obtained for intermediates containing co-ordinated bis(trifluoromethyl)diazomethane.

The reaction of bis(trifluoromethyl)diazomethane with *trans*-stilbenebis(triphenylphosphine)platinum was carefully examined with a view to understanding the reaction path leading to the formation of the azine complexes (I)—(VI). Colourless crystals of a compound (XI) were obtained in low yield from the reaction in diethyl ether, which analysed correctly for a compound with molecular formula $[Pt(C_3HF_5)(PPh_3)_2]$. Although the lone proton could not be located in the ^1H n.m.r. spectrum, the ^{19}F n.m.r. spectrum showed chemical shifts and coupling constants compatible with co-ordinated pentafluoropropene.

When the reaction of *trans*-stilbenebis(triphenylphosphene)platinum with the diazoalkane was carried out over a period of days often small amounts of the isomeric complexes (XII) and (XIII) were isolated in addition to (I). Compound (XIII) formed from (XII) on heating in benzene. Elemental analyses, solution molecular weight measurements, and consideration of the i.r. and n.m.r. spectra of these complexes suggested that they were the illustrated platinum(II) fluorides, and this was confirmed for (XII) by a single crystal *X*-ray diffraction study.[13]

The ^{19}F n.m.r. spectrum of (XII) showed one quartet resonance at 52·8 p.p.m. [$J(PtF)$ 97·0 Hz] due to coupling of the fluorine nuclei to the proton in the group $CH(CF_3)_2$ and to the two *cis*-phosphines. The other isomer (XIII) showed one triplet resonance at 50·1 p.p.m. [$J(PtF)$ 97·0 Hz] with the same line spacing (11·0 Hz). Compounds containing the $M{\cdot}CH(CF_3)_2$ grouping have been reported [2] previously and show consistent ^{19}F n.m.r. spectra, *e.g.* $[MnCH(CF_3)_2(CO)_5]$, doublet (12·0 Hz) at 53·3 p.p.m. and $[FeCH(CF_3)_2(CO)_2(\pi\text{-}C_5H_5)]$, doublet (12·0 Hz) at 53·4 p.p.m. The *cis* and *trans* isomers of $[PtClCH(CF_3)_2(PEt_3)_2]$ showed resonances at 50·0 and 53·9 p.p.m. respectively, each with a coupling to the proton of 12·0 Hz.

Unfortunately attempts to observe a ^{19}F n.m.r. signal attributable to Pt*F* in the spectra of (XII) and (XIII) were unsuccessful. However, it is important to note that the resonance due to Pt*F* would be coupled to several nuclei, and that no ^{19}F resonances have been observed for the species $[MF(CO)(PPh_3)_2]$ (M = Rh or Ir),[14] $[PdFL_2]_2^{2+}$, $[PtFL_3]^+$ (L = PPh_3, $PMePh_2$), and $PtF(X)(PPh_3)_2$ (X = Cl or Br).[15]

The possible reaction path leading the formation of the azine complexes (I)—(VI) requires comment. In the reaction of for example, *trans*-stilbenebis(triphenylphosphine)platinum with bis(trifluoromethyl)diazomethane

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[11] J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, 1968, **90**, 5430.

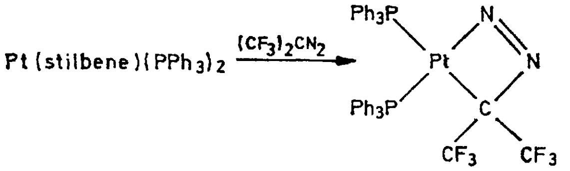
[12] J. Ashley-Smith, J. Clemens, M. Green, and F. G. A. Stone, *J. Organometallic Chem.*, 1969, **17**, P23.

[13] Judith Howard and P. W. Woodward, personal communication.

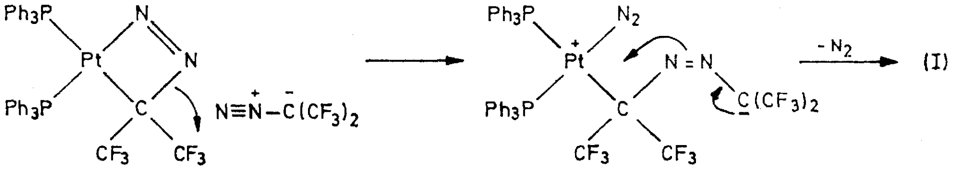
[14] L. Vaska and J. Peone, jun., *Chem. Comm.*, 1971, 418.

[15] R. D. W. Kemmitt, R. D. Peacock, and J. Stocks, *J. Chem. Soc. (A)*, 1971, 846.

the Pt^0 complex probably reacts with the 1,3-dipolarophile to give an adduct with similar structure to that proposed (Xa) for the iridium complex. Unlike the

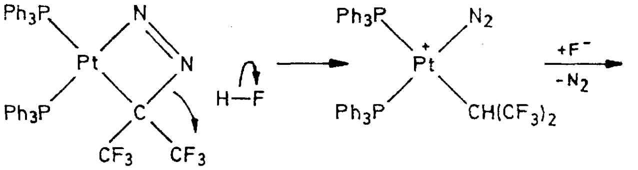


iridium system a further molecule of (CF$_3$)$_2$CN$_2$ could react to give the azine complex (I) *via* a platinum dinitrogen complex:



A similar reaction sequence has been proposed to explain the formation of [(Ph$_3$P)$_2$Pt(OH)NHSO$_2$Ph] from tris-(triphenylphosphine)platinum and the corresponding sulphonyl azide;[16] and also tetra-azadiene nickel complexes from the Ni^0 species [Ni(cod)$_2$] and C$_6$F$_5$N$_3$.[17]

It is interesting that the formation of the platinum(II) fluorides (XII) and (XIII) can be readily understood in terms of the reaction of traces of hydrogen fluoride with the proposed initial adduct with (CF$_3$)$_2$CN$_2$, *viz*:



(XII)

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94·1 MHz, respectively. Chemical shifts are relative to Me$_4$Si (τ 10·0) and CCl$_3$F (0·00 p.p.m.) internal standard. I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using Nujol and hexachlorobutadiene mulls. Molecular weights were determined using a Mechrolab vapour pressure osmometer. Light petroleum refers to the fraction b.p. 30—40°. *trans*-Stilbenebis(triphenylphosphine)platinum was prepared by treating [PtCl$_2$(PPh$_3$)$_2$] with aqueous hydrazine in the presence of *trans*-stilbene;[18] tris(triethylphosphine)platinum[19] by reacting the phosphine with [Pt(π-C$_3$H$_5$)(π-C$_5$H$_5$)], which was itself derived from [PtCl(π-C$_3$H$_5$)]$_4$; bis(isocyanide)palladium[20] complexes were obtained by reacting the respective isocyanide with [Pd(π-C$_3$H$_5$)(π-C$_5$H$_5$)]; tetrakis(t-butyl isocyanide)nickel and tetrakis(methyldiphenylphosphine)nickel were prepared by ligand displacement from bis(cyclo-octa-1,5-diene)-nickel.[21] Chlorodinitrogenbis(triphenylphosphine)iridium was prepared from *trans*-[IrCl(CO)(PPh$_3$)$_2$] and α-furoyl azide.[11] Dichlorobis(benzonitrile)-palladium and -platinum were obtained from benzonitrile and PdCl$_2$ or K$_2$PtCl$_4$, respectively.

Reactions of Bis(trifluoromethyl)diazomethane.—(a) *With* trans-*stilbenebis(triphenylphosphine)platinum.* Bis(trifluoromethyl)diazomethane (0·30 g, 2·00 mmol) was condensed (—196°) into a Carius tube containing *trans*-stilbenebis(triphenylphosphine)platinum (0·91 g, 1·00 mmol) in diethyl ether (20 ml). After 1 h at 25° the yellow solution was reduced in volume *in vacuo* to give yellow *crystals* of (I) (0·95 g, 91%), m.p. 196—197° (dec.) [Found: C, 48·1; H, 3·1; F, 21·9; N, 2·8; Pt, 17·6; *M* (CHCl$_3$), 1061. C$_{42}$H$_{30}$F$_{12}$N$_2$P$_2$Pt requires C, 48·2; H, 2·9; F, 21·8; N, 2·8; Pt, 18·6%; *M*, 1048], $\nu_{max.}$ 3080w, 3050w, 1590w, 1560s, 1482m, 1478m, 1440s, 1436s, 1350s, 1305m, 1278m, 1260s, 1220m, 1180m, 1160s, 1140s, 1120s, 1095s, 1040m, 1000m, 980s, 950s, 850m, 790w, 758s, 751s, 745s, 740s, 731s, 712s, 704s, and 690s cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed a resonance at τ 2·4—3·2 (m, 30H, C$_6$H$_5$P). The ^{19}F n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at 59·5 p.p.m. [d, with ^{195}Pt satellites, 6F, C(CF$_3$)$_2$, *J*(PF) 10·0, *J*(PtF) 79·0 Hz], 63·5 [m, 3F, CF$_3$; irradiation of the high field quintet collapsed this signal to a doublet, *J*(PF) 2·5, *J*(FF) 6·0 Hz] and 65·8 [apparent quintet, 3F, CF$_3$; irradiation of the low-field multiplet collapsed this signal to a doublet, *J*(PF) = *J*(FF) 6·0 Hz]. The spectrum was unchanged at —95°.

(b) *With tris(triethylphosphine)platinum.* Bis(trifluoromethyl)diazomethane (0·6 g, 4·00 mmol) was treated in a flask (100 ml) with tris(triethylphosphine)platinum (0·28 g, 0·50 mmol) dissolved in light petroleum (20 ml) at 0 °C. After 30 min, the volume of the solvent was reduced *in vacuo* and cooled (—78°) to give yellow *crystals* of (II) (0·15 g, 40%), m.p. 94—95° (dec.) (Found: C, 28·2; H, 3·9; F, 30·0; P, 8·2. C$_{18}$H$_{30}$F$_{12}$N$_2$P$_2$Pt requires C, 28·4; H, 4·0; F, 30·0; P, 8·2%), $\nu_{max.}$ 1560s, 1425m, 1385m, 1380m, 1355m, 1305s, 1260s, 1220m, 1200m, 1150vs, 1105s, 1045m, 1030s, 1010w, 975s, 950s, 850m, 775m, 760m, 745s, 730s, 710s, and 700m cm^{-1}. The ^{1}H n.m.r. spectrum (C$_6$D$_6$) showed resonances at τ 8·5 (m, 12H, CH$_2$P) and 9·3 (d, of t, 18H, CH$_3$, *J*(HH) 8·0, *J*(PH) 6·0 Hz). The ^{19}F n.m.r. spectrum (C$_6$D$_6$) showed resonances at 58·8 p.p.m. [d, with ^{195}Pt satellites, 6F, C(CF$_3$)$_2$, *J*(PF) 10·0, *J*(PtF) 81·0 Hz], 61·8 (m, 3F, CF$_3$; irradiation of the high field quintet collapsed this signal to a doublet, *J*(PF) 2·5, *J*(FF) 6·0 Hz) and 65·8 (apparent quintet, 3F, CF$_3$; irradiation of the low-field multiplet collapsed this signal to a doublet, *J*(PF) = *J*(FF) 6·0 Hz). The spectrum was unchanged at —95°.

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[16] W. Beck, M. Bauder, G. La Monnica, S. Cenini, and R. Ugo, *J. Chem. Soc.* (*A*), 1971, 113.

[17] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 1805.

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[19] J. L. Spencer, M. Green, and F. G. A. Stone, unpublished observations.

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(c) *With bis(t-butyl isocyanide)palladium.* Bis(trifluoromethyl)diazomethane (0·60 g, 4·00 mmol) was reacted (at 0°) in a flask with bis(t-butyl isocyanide)palladium (0·33 g, 1·20 mmol) in diethyl ether (40 ml). After 30 min the volume of solvent was reduced *in vacuo* and hexane added; cooling (−78°) gave yellow *crystals* of (III) (0·24 g, 33%), m.p. 145—146° (dec.) (Found: C, 32·2; H, 3·1; F, 37·7; N, 9·5; Pd, 17·6. $C_{16}H_{18}F_{12}N_4Pd$ requires C, 32·0; H, 3·0; F, 38·0; N, 9·3; Pd, 17·7%), $\nu_{max.}$ 2219s, 2200s, 1570s, 1480m, 1460m, 1405w, 1378s, 1360m, 1318s, 1300m, 1270m, 1230m, 1165s, 1145s, 1110m, 1050m, 990s, 968s, 858w, 840m, 795w, 766w, 740s, and 719s cm^{-1}. The ^1H n.m.r. spectrum (C_6D_6) showed a resonance at τ 9·1 [s, 18H, $C(CH_3)_3$]. The ^{19}F n.m.r. spectrum (C_6H_6, external CCl_3F) showed resonances at 62·5 p.p.m. [s, and q coincident, 9F, $C(CF_3)_2$ and CF_3] and 66·8 (q, 3F, CF_3, *J*(FF) 6·0 Hz).

(d) *With bis(cyclohexyl isocyanide)palladium.* Bis(trifluoromethyl)diazomethane (0·30 g, 2·00 mmol) was added (at 0°) to bis(cyclohexyl isocyanide)palladium (0·56 g, 1·80 mmol) in diethyl ether (40 ml). After 1 h, the volume was reduced *in vacuo* and hexane added to give (−78°) yellow *crystals* of (IV) (0·30 g, 25%), m.p. 121° (dec.) (Found: C, 34·1; H, 3·5; N, 8·5. $C_{18}H_{22}F_{12}N_4Pd$ requires C, 34·7; H, 3·5; N, 9·0%), $\nu_{max.}$ 2219s, 2200s, 1570s, 1482m, 1460m, 1445m, 1400m, 1378s, 1360m, 1318s, 1300m, 1273m, 1235m, 1160s, 1145s, 1110m, 1050m, 990s, 968s, 858w, 840m, 795w, 770w, 765w, 740s, and 719s cm^{-1}. The ^{19}F n.m.r. spectrum (C_6H_6, external CCl_3F) showed resonances at 62·3 p.p.m. [s, 6F, $C(CF_3)_2$], 62·4 (q, 3F, CF_3, *J*(FF) 6·0 Hz) and 66·7 (q, 3F, CF_3, *J*(FF) 6·0 Hz).

(e) *With tetrakis (t-butyl isocyanide)nickel.* Bis(trifluoromethyl)diazomethane (0·75 g, 5·00 mmol) was reacted (at 0°) with tetrakis(t-butyl isocyanide)nickel (0·49 g, 1·25 mmol) in diethyl ether (30 ml). After 1 h the solvent was removed *in vacuo* and the resultant brown oil taken up in the minimum volume of diethyl ether, addition of hexane and cooling (−78°) gave yellow *crystals* of (V) (0·50 g, 72%), m.p. 134—135° (dec.) (Found: C, 35·0; H, 3·3; F, 41·3; N, 10·2. $C_{16}H_{18}F_{12}N_4Ni$ requires C, 34·8; H, 3·3; F, 41·2; N, 10·1%), $\nu_{max.}$ 2219s, 2200s, 1570s, 1480m, 1460m, 1405m, 1378s, 1360m, 1318s, 1300m, 1270m, 1230m, 1165s, 1145s, 1110m, 1060m, 990s, 968s, 862w, 840m, 795w, 766w, 740s, and 719s cm^{-1}. The ^1H n.m.r. spectrum (C_6D_6) showed a resonance at τ 9·0 [s, 18H, $C(CH_3)_3$]. The ^{19}F n.m.r. spectrum (C_6H_6, external CCl_3F) showed resonances at 62·0 p.p.m. [s, 6F, $C(CF_3)_2$], 62·6 (q, 3F, CF_3, *J*(FF) 6·0 Hz) and 66·7 (q, 3F, CF_3 *J*(FF) 6·0 Hz).

(f) *With tetrakis(methyldiphenylphosphine)nickel.* Bis(trifluoromethyl)diazomethane (0·60 g, 4·00 mmol) was reacted (at 10°) with tetrakis(methyldiphenylphosphine)-nickel (0·70 g, 0·84 mmol) suspended in ether–hexane (1 : 4, 25 ml). After 1 h the red solution was filtered and the volume reduced *in vacuo*; cooling (−78°) gave first white crystals of $MePh_2PN_2C(CF_3)_2$, followed by red *crystals* of (VI) (0·30 g, 47%), m.p. 122—124° (dec.) (Found: C, 49·0; H, 3·5. $C_{32}H_{26}F_{12}N_2P_2Ni$ requires C, 48·9; H, 3·3%), $\nu_{max.}$ 3050w, 1590s, 1480m, 1438s, 1420m, 1354m, 1304s, 1280s, 1252s, 1220m, 1160vs, 1122s, 1100s, 1023m, 995w, 970s, 950s, 893s, 880s, 810m, 740s, 727s, 711s, and 690s cm^{-1}. The ^1H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·5—3·2 (m, 20H, C_6H_5P), 8·4 (apparent d, 3H, CH_3P, $|J|$(PCH) 8·0 Hz) and 9·1 (apparent d, 3H, CH_3P, $|J|$(PCH) 7·0 Hz). The ^{19}F n.m.r. spectrum (diethyl ether, external CCl_3F) showed resonances at 59·9 p.p.m. [d, 6F, $C(CF_3)_2$, *J*(PF) 10·0 Hz], 60·9 (m, 3F, CF_3 *J*(PF) 2·0, *J*(FF) 6·0 Hz) and 63·4 (apparent q, 3F, CF_3, *J*(PF) = *J*(FF) 6·0 Hz). Recrystallisation of (VI) from diethyl ether led to slow decomposition and deposition of $MePh_2PN_2C(CF_3)_2$.

(g) *With bis(benzonitrile)palladium dichloride.* Bis(trifluoromethyl)diazomethane (0·38 g, 2·50 mmol) was condensed (−196°) into a Carius tube containing bis(benzonitrile)palladium dichloride (1·00 g, 2·63 mmol) in diethyl ether (20 ml). After 9 days at room temperature, yellow and finer orange crystals formed in a red solution. The crystals were separated by hand, and a further quantity of the orange material was obtained by addition of hexane to the diethyl ether solution. Recrystallisation from methylene chloride–hexane gave yellow *crystals* of (VII) (0·60 g, 32%), m.p. 170° (dec.) (Found: C, 35·0; H, 1·5; F, 32·4; N, 4·2. $C_{20}H_{10}F_{12}N_2Cl_2Pd$ requires C, 35·1; H, 1·5; F, 32·8; N, 4·1%), $\nu_{max.}$ 3060w, 2295w, 1597m, 1488m, 1450s, 1370m, 1340w, 1275s, 1250s, 1210s, 1170b,s, 1115s, 1095m, 1070m, 1031m, 1005m, 932s, 895s, 828s, 764s, 734s, 725w, 704s, and 685s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 62·3 p.p.m. [s, 12F, $PdC(CF_3)_2Cl$]. Recrystallisation of the orange material gave orange *crystals* of (VIII) (0·60 g, 28%), m.p. 150° (dec.) [Found: C, 28·2; H, 1·3; Cl, 16·9; N, 3·4; *M* ($CHCl_3$), 810. $C_{20}H_{10}F_{12}N_2Cl_4Pd_2$ requires C, 28·0; H, 1·2; Cl, 16·5; N, 3·3%; *M*, 860], $\nu_{max.}$ 2293s, 1602m, 1493w, 1452s, 1341w, 1300m, 1270s, 1250s,b, 1235s, 1165s, 1128m, 1102w, 1086w, 1073w, 1031m, 930s, 901s, 838s, 761s, 739s, 701s, and 688s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 62·9 p.p.m. [s, 12F, $PdC(CF_3)_2Cl$].

(h) *With bis(benzonitrile)platinum dichloride.* Similarly, bis(trifluoromethyl)diazomethane (0·38 g, 2·50 mmol) was reacted (80°, 4 days) in diethyl ether (25 ml) with bis-(benzonitrile)platinum chloride (0·30 g, 0·64 mmol) to give colourless *crystals* of (IX) (0·18 g, 40%), m.p. 217° (dec.) (Found: C, 31·3; H, 1·3; F, 29·4; Cl, 9·1. $C_{20}H_{10}F_{12}N_2Cl_2Pt$ requires C, 31·1; H, 1·3; F, 29·5; Cl, 9·3%), $\nu_{max.}$ 3070w, 2295m, 1600m, 1454s, 1370m, 1342w, 1297m, 1277s, 1250b,s, 1210b,s, 1170b,s, 1115s, 1098m, 1062m, 1030m, 1003m, 934s, 892s, 828s, 780m, 766s, 737s, 725w, 704s, and 688s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 63·1 p.p.m. [s, with ^{195}Pt satellites, 12F, $PtC(CF_3)_2Cl$, *J*(PtF) 53·0 Hz].

(i) *With chlorodinitrogenbis(triphenylphosphine)iridium.* Bis(trifluoromethyl)diazomethane (0·60 g, 4·00 mmol) was reacted at 0 °C in a flask with chloro(dinitrogen)bis(triphenylphosphine)iridium (2·60 g, 3·33 mmol) suspended in benzene and diethyl ether (1 : 1, 40 ml). There was an instant colour change from yellow to black, and after 10 min the solvent was slowly removed *in vacuo* to give green-black *crystals* of (X) (3·00 g, 95%), m.p. 171—173° (dec.) [Found: C, 50·4; H, 3·5; F, 12·1; Cl, 3·7; N, 3·0; P, 6·5; *M* (C_6H_6), 938. $C_{39}H_{30}F_6N_2ClP_2Ir$ requires C, 50·2; H, 3·2; F, 12·3; Cl, 3·9; N, 3·0; P, 6·7%; *M*, 930], $\nu_{max.}$ 3060w, 1590w, 1575w, 1480m, 1435s, 1370s, 1330s, 1215s, 1190m, 1170m, 1160m, 1100s, 1070m, 1030w, 1000w, 960s, 840w, 755s, 750m, 745m, 710s, 700s, 695s, 675s, and 650s cm^{-1}; (CsI/Nujol) 540—500s, 287m, and 272 m cm^{-1}.[22] The ^1H n.m.r. spectrum (C_6D_6) showed a resonance at τ 2·8 (m, 30H, C_6H_5P). The ^{19}F n.m.r. spectrum (C_6H_6, external CCl_3F) showed a resonance at 57·2 p.p.m. [t, 6F, $C(CF_3)_2$, $|J(FP) + J(FP')|$ 8·4 Hz]; this spectrum was unchanged down to −90 °C. The same material was also obtained from equimolar quantities of the same starting materials in a Carius tube over 5 days at −5 °C.

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[22] P. L. Goggin, unpublished observations.

Reaction of Bis(trifluoromethyl)diazomethane with trans-*Stilbenebis(triphenylphosphine)platinum under Other Conditions.*—Bis(trifluoromethyl)diazomethane (0·30 g, 2·00 mmol) was condensed (−196°) into a tube containing *trans*-stilbenebis(triphenylphosphine)platinum (0·45 g, 0·50 mmol), suspended in diethyl ether (20 ml). After 5 days at 25° the solvent was removed slowly *in vacuo* to yield white *crystals* of $[(Ph_3P)_2\overline{PtOC(CF_3)_2O}]$ [23] and *trans*-stilbene; addition of hexane gave crystals of (I), and of (XI) (0·06 g, 15%), m.p. 153° (dec.) (Found: C, 54·9; H, 3·7; F, 11·4; P, 7·2. $C_{39}H_{31}F_5P_2Pt$ requires C, 55·0; H, 3·6; F, 11·2; P, 7·3%), $\nu_{max.}$ 3060w, 1585w, 1575w, 1480m, 1438s, 1394s, 1310w, 1265s, 1228m, 1180w, 1160w, 1146s, 1100s, 1073s, 1030m, 1000w, 938s, 890w, 830s, 750s, 736m, 704s, and 670s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 52·8 p.p.m. (m, 3F, CF_3, complex nine-line spectrum, d of t of d, *J* values 5, 10, and 15 Hz respectively, *J*(PtF) 13·0 Hz), 94·1 (d of m, 1F, *J*(gemFF) 168 Hz) and 107·0 (d of m, 1F, *J*(gemFF) 168, *J*(PF) 30·0 Hz). In reactions between bis(trifluoromethyl)diazomethane and *trans*-stilbenebis(triphenylphosphine)platinum carried out over a period of days small quantities of (XII) and (XIII) were obtained; these were also prepared as follows. Bis(trifluoromethyl)diazomethane (1·80 g, 12·00 mmol) was condensed into a tube containing tetrakis(triphenylphosphine)platinum (3·14 g, 3·00 mmol) in benzene (30 ml). The yellow colouration was dispelled after 24 h, and within 3 weeks at room temperature white crystals of $[Ph_3PN_2C(CF_3)_2]$ separated. The volume of the solvent was reduced *in vacuo* and hexane added to give large colourless *crystals* of (XII) (0·60 g, 25%), m.p. 215—216° (dec.) (Found: C, 52·9; H, 3·7; F, 15·3; P, 6·9; *M* ($CHCl_3$), 820. $C_{39}H_{31}F_7P_2Pt$ requires C, 52·7; H, 3·5; F, 15·0; P, 7·0%; *M*, 890), $\nu_{max.}$ 3060w, 1595w, 1570w, 1480m, 1439s, 1435s, 1360m, 1310w, 1275s, 1251s, 1200s, 1162s, 1094s, 1065s, 1049m, 1030m, 1000w, 892m, 870m, 760m, 750s, 721s, 710s, 700s, and 675m cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 52·8 p.p.m. [apparent q, 6F, $CH(CF_3)_2$, *J*(HF) = *J*(PF) 11·0, *J*(PtF) 97·0 Hz]; the complex was too insoluble for useful ^1H n.m.r. data to be collected.

Heating in refluxing benzene (5 min) converted (XII) quantitatively to (XIII), m.p. 272° (dec.) (Found: C, 53·0; H, 3·6; F, 15·2; *M* ($CHCl_3$), 844. $C_{39}H_{31}F_7P_2Pt$ requires C, 52·7; H, 3·5; F, 15·0%; *M*, 890), $\nu_{max.}$ 3055w, 1590w, 1575w, 1482m, 1440s, 1438s, 1369m, 1315w, 1273s, 1250s, 1201s, 1188m, 1176s, 1102s, 1096s, 1065s, 1003w, 893m, 868m, 763m, 754m, 745m, 720s, 703s, 699s, and 675m cm^{-1}. The far-i.r. spectrum showed no bands assignable to a Pt–Cl bond; 490—550s cm^{-1} [*cis*-$(Ph_3P)_2Pt$]. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 50·1 p.p.m. [apparent t, 6F, $CH(CF_3)_2$, *J*(HF) = *J*(PF) 11·0, *J*(PtF) 97·0 Hz].

We thank the S.R.C. for support of this work, and for a research studentship (J. C.).

[2/2634 *Received, 21st November*, 1972]

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