Alkylideneamido-derivatives of Metals and Metalloids. Part V.[1] Complexes of the Late Transition Metals with $(CF_3)_2C{:}N^-$ as Ligand, and a Tautomeric Hydrogen Transfer from Metal to Ligand

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Reaction of $LiN{:}C(CF_3)_2$ or $Me_3SnN{:}C(CF_3)_2$ with a Pt^{II}, Rh^{I}, or Ir^{I} halide generally leads to the appropriate d^8 metal alkylideneamide (reactivity: Li > Me_3Sn). A Pt^{II} derivative, *trans*-$Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2$, is also obtained by an oxidative addition of $Me_3SnN{:}C(CF_3)_2$ to $Pt(PPh_3)_2$(stilbene). *trans*-Pt(H or D)$[N{:}C(CF_3)_2](PPh_3)_2$ rearranges into $Pt[H(D)N{:}C(CF_3)_2](PPh_3)_2$ by heating with PPh_3 under reflux in benzene, or without phosphine in boiling xylene. The latter isomer reacts with an excess of PPh_3 to give $Pt[HN{:}C(CF_3)_2](PPh_3)_3$. The spectra of the new thermally- and hydrolytically-stable compounds, as well as the M–N cleavage by HCl, are discussed.

PARTS I—IV of this series dealt with aspects of the chemistry of alkylideneaminoboranes ($>$B–N:CHR[2] and $>$B–N:CR$_2$[3]) and stannanes,[4] and with other Group IVB derivatives of the type $M[N{:}C(CF_3)_2]_x$ ($x = 1$—4; M = Si, Ge, or Sn).[1] Preliminary publications described the preparation of alkylideneamido-complexes of the early[5] and late[6] transition metals.

Although the chemistry of transition metal amides ($LMNR_2$) has been extensively studied,[7] data are broadly limited to derivatives of early transition metals.[7b] Results for the related alkylideneamido- ($R_2C{:}N^-$, also known as ketimido- or azomethine-) complexes of transition metals are much more sparse.[7a] Complexes of Ti^{IV},[5] Zr^{IV},[5] Hf^{IV},[5] Mo^{II},[8] Fe^{I},[9,10] Rh^{I},[6] and Pt^{II}[6] have now been described but to date, attention has centred on characterisation, structures, and spectral properties of these complexes rather than on their reactions.

Following our earlier study of d^0 derivatives,[5] an extension to the d^8 alkylideneamides was considered of interest for two main reasons. First, it was likely that air-stable products might be obtained, which would simplify manipulative problems, and secondly it was desirable to investigate complexes in which $d_\pi \longrightarrow \pi^*$ bonding was feasible. This paper deals with compounds of the type $LM[-N{:}C(CF_3)_2]_x$ where L represents all ligands other than the alkylideneamido-ligand(s) attached to the central metal atom M (Rh^{I}, Ir^{I}, or Pt^{II}). Some of the Pt^{II} and a Rh^{I} compound have been briefly reported.[6]

Details of the preparations are in Table 1; six reaction types (A—F) have been observed. Data on the compounds are in Table 2.

A factor influencing our choice of the 1,1-bis(trifluoromethyl)methyleneamido-ligand was a belief that the electron-withdrawing CF_3 groups would make this a relatively ' soft ' ligand and hence more compatible with a d^8 metal ' soft ' acceptor centre than a ' hard ' $R_2C{:}N^-$ or $Ar_2C{:}N^-$ ligand.[11] Secondly, the complexes would be amenable to study by ^{19}F n.m.r., spectroscopy. Thirdly, the ligand was expected to confer good hydrocarbon-solubility and high volatility on the derived complexes.

A series of platinum(II) complexes was prepared from 1,1-bis(trifluoromethyl)methyleneamidolithium and various halogeno-platinum(II) compounds (Table 1). Apart from a reaction involving $PtI(Me)(PPh_3)_2$, *ca.* 70% yields (after recrystallisation) were obtained (see Table 1; for an explanation of the low yield of the third compound, see below). Although the stereochemistry of one or two of the complexes is still in doubt, it appears that the reactions proceed without isomerisation.

Alkyl-lithium reagents (unlike corresponding Grignard reagents) normally react with bis(phosphine)platinum dihalides to give disubstituted products. Similarly, in the case of $LiN{:}C(CF_3)_2$, an excess of the reagent with *cis*-$PtCl_2(PMe_2Ph)_2$ led exclusively to *cis*-$Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2$. Using a 1 : 1 ratio of reactants, this was still the major product, although *ca.* 15% of the mono-substituted derivative was obtained. By contrast, *cis*-$PtCl_2(PPh_3)_2$ and $LiN{:}C(CF_3)_2$, gave exclusively the mono-substituted complex. In a related reaction, between *cis*-$PtCl_2(PPh_3)_2$ and $LiCH_2SiMe_3$, a mixture of mono- and di-substituted products was also obtained.[12] It may be that the sparingly-soluble and more sterically crowded triphenylphosphine derivatives require longer reaction times and more forcing conditions [hardly possible (see below) with $LiN{:}C(CF_3)_2$][13] to achieve complete conversion. Surprisingly, there was no re-

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TABLE 1

Preparation of alkylideneamides and related compounds

Reaction type[a]	Reagents	Reaction conditions[b]	Product (yield, %)
A	*cis*-$\mathrm{PtCl_2(PPh_3)_2 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6{-}Et_2O}$; 0°, $\frac{1}{2}$ h; 20°, 3 h	*cis*-$\mathrm{PtCl[N{:}C(CF_3)_2](PPh_3)_2}$ (79)
B	*cis*-$\mathrm{PtCl_2(PPh_3)_2 + Me_3SnN{:}C(CF_3)_2}$[4]	1 : 3, $\mathrm{C_6H_6}$; reflux, 3 h	*cis*-$\mathrm{PtCl[N{:}C(CF_3)_2](PPh_3)_2}$ (90)[4]
A	*cis*-$\mathrm{PtCl_2(PMe_2Ph)_2 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6}$; 1 h, 10°; 4 h, 20°	$\mathrm{PtCl[N{:}C(CF_3)_2](PMe_2Ph)_2}$ (15)
B	*cis*-$\mathrm{PtCl_2(PMe_2Ph)_2 + Me_3SnN{:}C(CF_3)_2}$	1 : 3, $\mathrm{C_6H_6}$; reflux, 5 h	$\mathrm{PtCl[N{:}C(CF_3)_2](PMe_2Ph)_2}$ (>95)
A	*cis*-$\mathrm{PtCl_2(PMe_2Ph)_2 + LiN{:}C(CF_3)_2}$	1 : 2, $\mathrm{C_6H_6}$; 20°, 4 h	*cis*-$\mathrm{Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2}$ (57)
A	*trans*-$\mathrm{PtH(Cl)(PPh_3)_2 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6{-}Et_2O}$; 5°, $\frac{1}{4}$ h; 20°, 2 h	*trans*-$\mathrm{PtH[N{:}C(CF_3)_2](PPh_3)_2}$ (66)
B	*trans*-$\mathrm{PtH(Cl)(PPh_3)_2 + Me_3SnN{:}C(CF_3)_2}$[4]	1 : 1, $\mathrm{Me_2{\cdot}C_6H_4}$; 140°, 5 min	$\mathrm{Pt[HN{:}C(CF_3)_2](PPh_3)_2}$ (67)[4]
B, C	*trans*-$\mathrm{PtH(Cl)(PPh_3)_2 + Me_3SnN{:}C(CF_3)_2}$	1 : 2·5, $\mathrm{C_6H_6}$; reflux, 17 h	*trans*-$\mathrm{Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2}$ (10)
A	*trans*-$\mathrm{PtH(Cl)(PMe_2Ph)_2 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6{-}Et_2O}$; 0°, $\frac{1}{2}$ h; 20°, 2 h	*trans*-$\mathrm{PtH[N{:}C(CF_3)_2](PMe_2Ph)_2}$ (50)
A	*trans*-$\mathrm{PtI(Me)(PPh_3)_2 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6{-}Et_2O}$; 10°, $\frac{1}{2}$ h; 20°, 4 h	$\mathrm{Pt[N{:}C(CF_3)_2](Me)(PPh_3)_2}$ (15)
A	$\mathrm{PtCl(Ph)(PPh_3)_2 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6{-}Et_2O}$; 6°, 2 h; 20°, 2 h	$\mathrm{Pt[N{:}C(CF_3)_2](Ph)(PPh_3)_2}$ (51)
D	$\mathrm{Pt(PPh_3)_3 + (CF_3)_2C{:}NH}$	1 : 2, $\mathrm{C_6H_6}$; 20°, 4 h	$\mathrm{Pt[HN{:}C(CF_3)_2](PPh_3)_2}$ (77)
D	$\mathrm{Pt(Stilbene)(PPh_3)_2 + Me_3SnN{:}C(CF_3)_2}$	1 : 5, $\mathrm{C_6H_6}$; 20°, 1 h	*trans*-$\mathrm{Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2}$ (92)
E	*trans*-$\mathrm{PtH[N{:}C(CF_3)_2](PPh_3)_2}$	$\mathrm{PPh_3}$, $\mathrm{C_6H_6}$, reflux, 1 h; or $\mathrm{Me_2C_6H_4}$, reflux, 1 h	$\mathrm{Pt[HN{:}C(CF_3)_2](PPh_3)_2}$ (>50)
D	$\mathrm{Pt(PPh_3)_3 + Me_3SnN{:}C(CF_3)_2}$	1 : 4, $\mathrm{C_6H_6{-}n{-}C_6H_{14}}$, 40°, 1 h	$\mathrm{Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2}$ (80)
F	$\mathrm{Pt[HN{:}C(CF_3)_2](PPh_3)_2 + PPh_3}$	1 : 1, $\mathrm{C_6H_6}$, 20°, 1 min	$\mathrm{Pt[HN{:}C(CF_3)_2](PPh_3)_3}$ (>95)
A	$\mathrm{RhCl(PPh_3)_3 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6{-}Et_2O}$; 3°, $\frac{1}{2}$ h; 20°, 2 h	$\mathrm{Rh[N{:}C(CF_3)_2](PPh_3)_3}$ (30)
B	$\mathrm{RhCl(PPh_3)_3 + Me_3SnN{:}C(CF_3)_2}$	1 : 2, $\mathrm{C_6H_6}$; 20°, 2 h	$\mathrm{Rh[N{:}C(CF_3)_2](PPh_3)_3}$ (99)
A	*trans*-$\mathrm{IrCl(CO)(PPh_3)_2 + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{C_6H_6}$; 5°, $\frac{1}{2}$ h; 20°, 2 h	*trans*-$\mathrm{Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2}$ (70)
B	*trans*-$\mathrm{IrCl(CO)(PPh_3)_2 + Me_3SnN{:}C(CF_3)_2}$	1 : 3, $\mathrm{C_6H_6}$, 20°, 12 h	*trans*-$\mathrm{Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2}$ (89)

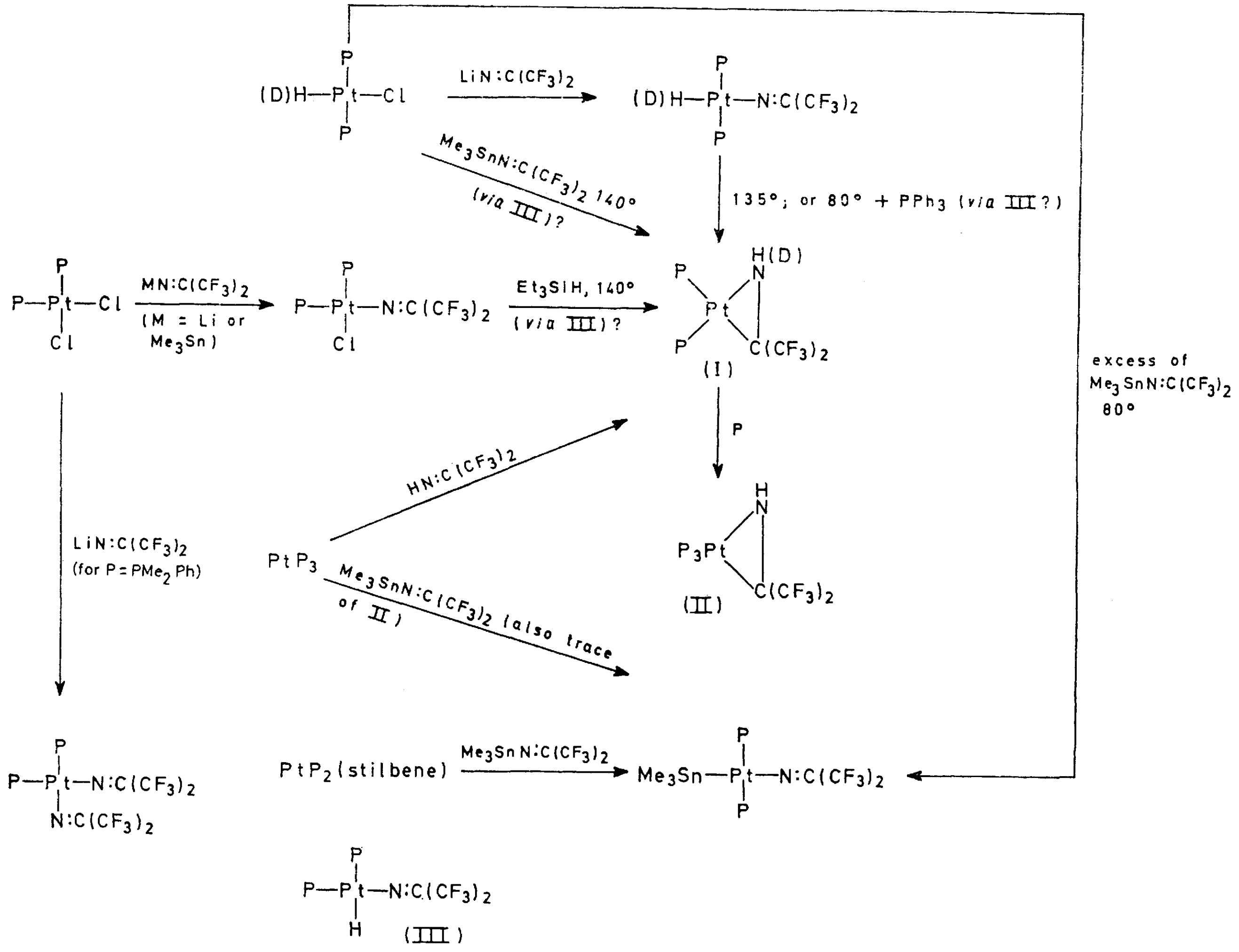
[a] A and B refer to Halogen–$\mathrm{N{:}C(CF_3)_2}$ exchange, using $\mathrm{LiN{:}C(CF_3)_2}$ or $\mathrm{Me_3SnN{:}C(CF_3)_2}$, respectively; C refers to hydrogen–$\mathrm{N{:}C(CF_3)_2}$ exchange; D refers to oxidative addition; E refers to isomerisation; F refers to adduct formation. [b] Ratios refer to molar proportions.

TABLE 2

d^8 Metal 1,1-bis(trifluoromethyl)methyleneamides and related compounds

				Selected n.m.r. data[b]		Analytical data (Calc. data in parentheses)			
Compound	Appearance	ν(C:N)[a]	M.p. (°C)	^{1}H	^{19}F and [^{31}P] ($\mathrm{CHCl_3}$) 68·69(s) [($\mathrm{CDCl_3}$) 100·6(d)]	C (%)	H (%)	N (%)	*M*
cis-$\mathrm{PtCl[N{:}C(CF_3)_2](PPh_3)_2}$	Pale yellow	1673 ± 5	258—261			50·9 (51·0)	3·3 (3·3)	1·7 (1·5)	
cis-$\mathrm{PtCl[N{:}C(CF_3)_2](PMe_2Ph)_2}$	Pale yellow	1670	128—130	($\mathrm{CDCl_3}$) 2·35 (10H, m, PhP), 8·01 (12H, m, $\mathrm{Me_2P}$)		34·4 (34·0)	3·4 (3·3)	2·0 (2·1)	670 (670)[c]
cis-$\mathrm{Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2}$	Yellow	1675 (1650)	102—104	($\mathrm{CDCl_3}$) 2·60 (10H, m, PhP), 8·71 [12H, 3d, $\mathrm{Me_2P}$, $J(^{195}\mathrm{Pt}^1\mathrm{H})$ 29 Hz]	($\mathrm{CHCl_3}$) 69·95(s) [$\mathrm{CHCl_3}$) 140·2(s) $J(^{195}\mathrm{Pt}^{31}\mathrm{P})$ 2·934 KHz]	33·3 (33·1)	2·8 (2·8)	3·5 (3·5)	840 (799)[d]
trans-$\mathrm{PtH[N{:}C(CF_3)_2](PPh_3)_2}$	Yellow	1663	139—140	($\mathrm{C_6H_6}$) 2·36, 2·94 (30H, m, PhP)	($\mathrm{C_6H_6}$) 70·02(m) [($\mathrm{C_6H_6}$) 86·8(s), $J(^{195}\mathrm{Pt}^{31}\mathrm{P})$ 3·148 KHz]	52·4 (52·9)	3·5 (3·5)	1·7 (1·6)	
trans-$\mathrm{PtH[N{:}C(CF_3)_2](PMe_2Ph)_2}$	Yellow	1663	48—50	($\mathrm{C_6D_6}$) 3·10—3·57 (10H, m, PhP), 9·25 [12H, 3t, $J(^{195}\mathrm{PtH})$ **34** Hz, $J(^{31}\mathrm{P}^1\mathrm{H})$ 7 Hz]		35·3 (35·9)	3·6 (3·6)	2·3 (2·2)	636 (636)[c]
trans-$\mathrm{Pt[N{:}C(CF_3)_2](Me)(PPh_3)_2}$	Pale yellow	1660	229—233			53·3 (53·5)	3·7 (3·7)	1·6 (1·6)	
$\mathrm{Pt[N{:}C(CF_3)_2](Ph)(PPh_3)_2}$	Pale yellow	1673	147—149			56·3 (56·3)	4·1 (3·7)	1·6 (1·5)	
$\mathrm{Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2}$[e]	Pale yellow	1663				48·8 (48·2)	3·9 (3·8)	1·5 (1·3)	
$\mathrm{Rh[N{:}C(CF_3)_2](PPh_3)_3}$	Yellow	1664	104—115		($\mathrm{C_6H_6}$) 68·97(s)	64·4 (65·0)	4·4 (4·3)	1·5 (1·3)	
trans-$\mathrm{Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2}$	Yellow	1695	192—193		($\mathrm{C_6H_6}$) 69·95(t) $J(^{31}\mathrm{P}^{19}\mathrm{F})$ 1·5 Hz	52·9 (52·9)	3·4 (3·3)	1·7 (1·5)	
$\mathrm{Pt[HN{:}C(CF_3)_2](PPh_3)_2}$[f]	White	[ν(NH) 3280]	175—180		($\mathrm{C_6H_6}$) 62·3(d), $J(^{31}\mathrm{P}^{19}\mathrm{F})$ 12·0 Hz, $J(^{195}\mathrm{Pt}^{19}\mathrm{F})$ 84·0 Hz	52·9 (52·9)	3·5 (3·5)	1·7 (1·6)	
$\mathrm{Pt[HN{:}C(CF_3)_2](PPh_3)_3}$	Orange-yellow	[ν(NH) 3280]	139—143		($\mathrm{C_6H_6}$) 62·5(d), $J(^{31}\mathrm{P}^{19}\mathrm{F})$ 12·0 Hz, $J(^{195}\mathrm{Pt}^{19}\mathrm{F})$ 83·0 Hz	60·2 (59·7)	4·3 (4·0)	1·2 (1·3)	1179[g] (1147)

[a] Infrared spectra, in $\mathrm{cm^{-1}}$ for Nujol mulls. [b] ^{19}F Shifts in p.p.m. relative to $\mathrm{CFCl_3}$; ^{31}P shifts in p.p.m. relative to $\mathrm{P_4O_6}$; see also Tables 3 and 4. [c] Mass spectrometrically. [d] Isopiestically ($\mathrm{CHCl_3}$). [e] See ref. 4. [f] See ref. 18. [g] By cryoscopy ($\mathrm{C_6H_6}$).



SCHEME The platinum(II)–triphenylphosphine–1,1-bis(trifluoromethyl)methyleneadime system (P = PPh_3)

action between $PtI_2(PPh_3)_2$ and $2LiN:C(CF_3)_2$. *cis*-$Pt[N:C(CF_3)_2]_2(PPh_3)_2$ also proved to be inaccessible from Pt^0 complexes and the azine $(CF_3)_2C:NN:C(CF_3)_2$. [Earlier work had shown that the N–N bond of certain azines, or of related compounds, may readily be cleaved by low-oxidation state transition metal complexes, *e.g.*, $Fe_3(CO)_{12}$, to give alkylideneamides;[9,10] indeed, the first such transition metal complex was obtained by this route.[14]] Green, Stone, and their co-workers have shown[15] that reaction between $Pt(PPh_3)_2$(stilbene) and $(CF_3)_2C:NN:C(CF_3)_2$ gives, instead, the adduct $(Ph_3P)_2Pt\cdot C(CF_3)_2\cdot NN:C(CF_3)_2$,[15] also accessible from the reaction between $Pt(PPh_3)_3$ and $(CF_3)_2CN_2$,[16] or the diazoalkane and other Pt^0 substrates.[15]

The tin reagent $Me_3SnN:C(CF_3)_2$ has a number of advantages over the corresponding lithium compound. The latter is explosively unstable above 20—25°;[13,17] the former is unchanged after 5 h at 100° and, being liquid, is conveniently transferred by syringe.[4] It is less reactive but more selective than the lithium reagent. Thus, the tin reagent reacts with either *cis*-$PtCl_2(PPh_3)_2$[4] or *cis*-$PtCl_2(PMe_2Ph)_2$ to give exclusively the mono-substituted derivative *cis*-$PtCl[N:C(CF_3)_2]P_2$. Other trialkyltin alkylideneamides also react with *cis*-$PtCl_2(PPh_3)_2$ to give only mono-substituted products. In all the reactions in which the lithium reagent was used, explosive hazards were minimised by use of low temperature (<10°) and high dilution.

Although $Ir[N:C(CF_3)_2](CO)(PPh_3)_2$ and $Rh[N:C(CF_3)_2](PPh_3)_3$ were obtained from the appropriate metal halide and $LiN:C(CF_3)_2$, they are best obtained using the d^8 metal chloride and $Me_3SnN:C(CF_3)_2$. In these cases, the alkylideneamides were obtained under particularly mild conditions compared with many of the chloride displacements at these metal centres; this suggests that initial co-ordination of the tin reagent may precede intramolecular trimethyltin chloride elimination.

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[14] M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Comm.*, 1965, 543.

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1,1-Bis(trifluoromethyl)methyleneamine and tris-(triphenylphosphine)platinum(0) yield the adduct (I) (see Scheme),[18] *rather* than the hydrido(alkylideneamido)-isomer.[6] The latter may, however, be a reaction intermediate (see below);[6] such an oxidative addition product would not be unexpected by analogy with the behaviour of imides, such as succinnimide, with Pt^0 substrates.[19] Nevertheless, the related hexafluoroacetone directly forms the oxygen analogue of (I), although the possibility of an intermediate oxidative adduct does not arise; hence it is improbable that it plays a role for the methyleneamine.

An excess of $Me_3SnN{:}C(CF_3)_2$ was reacted with $Pt(PPh_3)_3$ to give mainly *trans*-$Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2$. A minor second product is believed to be $Pt[(CF_3)_2CNH](PPh_3)_3$, (II) (Scheme). Compound (II) is bright yellow-orange and is very soluble in benzene, unlike the white, sparingly-soluble (I). Compound (II) was also formed when an excess of triphenylphosphine was added to a benzene solution of (I); the formation of (II) from $Me_3SnN{:}C(CF_3)_2$ with $Pt(PPh_3)_3$, must be slow relative to that of $Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2$. The trace of (II) probably arose from reaction of $(CF_3)_2CNH$ [formed by adventitious hydrolysis of $Me_3SnN{:}C(CF_3)_2$] with $Pt(PPh_3)_3$, and excess of triphenylphosphine. There was no reaction at 20° between $Pt(PPh_3)_3$ and $Me_3SnN{:}CPh_2$, nor between stilbenebis(triphenylphosphine)platinum(0) and Me_3SnNMe_2. The reactions of tin alkylideneamides with *trans*-$PtH(Cl)(PPh_3)_2$ have been discussed elsewhere.[4]

The platinum alkylideneamides are pale yellow, air-stable solids, soluble in benzene and chloroform, but insoluble (except for the hydrido-derivatives) in diethyl ether or n-hexane. The complexes are somewhat more air-sensitive in solution: *trans*-$Pt[N{:}C(CF_3)_2](SnMe_3)(PPh_3)_2$ and *trans*-$Pt(H)[N{:}C(CF_3)_2](PMe_2Ph)_2$ are rapidly decomposed in chloroform in air, whereas other complexes, including *cis*-$PtCl[N{:}C(CF_3)_2](PPh_3)_2$ and $Pt[(CF_3)_2CNH](PPh_3)_2$, withstand washing with water in air. The rhodium and iridium complexes are slightly air-sensitive in benzene solution but, as solids, are stable in air for at least one day. Physical data are summarised in Tables 2—4.

TABLE 3

Selected spectroscopic data on some platinum(II) hydrido-complexes

Compound	ν(M–H)/ cm^{-1} (Nujol)	τ(H)	*J*(PtH)/ Hz	*J*(PH)/ Hz
trans-$Pt(H)Cl(PEt_3)_2$ [a]	2209	26·9	1276	14·5
trans-$Pt(H)Cl(PPh_3)_2$ [b]	2225	26·1	1194	13·3
trans-$Pt(H)(saccharin)(PPh_3)_2$ [c]	2230	25·7		12·8
trans-$Pt(H)[N{:}C(CF_3)_2](PPh_3)_2$ [d]	2146	22·8	748	16·0
trans-$Pt(H)[N{:}C(CF_3)_2](PMe_2Ph)_2$ [d]	2118	*ca.* 24·3		17·5
trans-$Pt(H)(NO_2)(PEt_3)_2$ [a]	2165	29·7		

[a] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075; J. Powell and B. L. Shaw, *ibid.*, 1965, 3879. [b] J. C. Bailar and H. Itatani, *J. Amer. Chem. Soc.*, 1967, **89**, 1592. [c] Ref. 19. [d] This work.

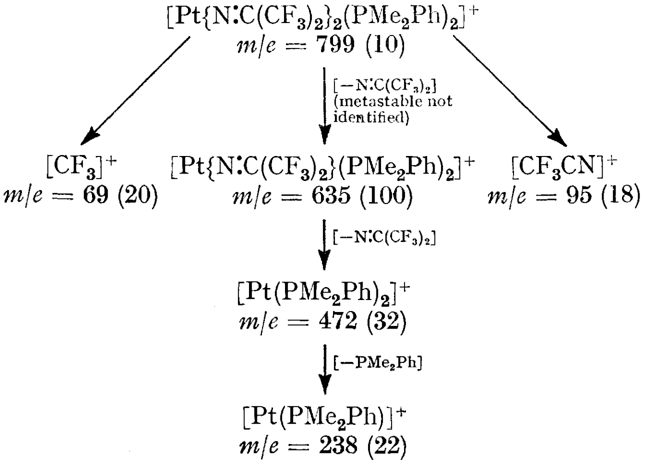
TABLE 4

Variation of $J(^{195}Pt^{31}P)$ with *trans*-ligand

Compound	Solvent	*trans*- Ligand	$J(^{195}Pt^{31}P)$/ KHz
cis-$PtCl_2(PMe_2Ph)_2$ [a]	CH_2Cl_2	Cl	3·549
cis-$PtCl_2(PEt_3)_2$ [a]	CH_2Cl_2	Cl	3·520
cis-$Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2$ [b]	$CDCl_3$	$N{:}C(CF_3)_2$	2·930
trans-$Pt(H)[N{:}C(CF_3)_2](PPh_3)_2$ [b]	C_6D_6	PPh_3	3·150
trans-$Pt(NO_2)[(PhO)_2PO](PBu_3)_2$ [c]	CH_2Cl_2	PBu_3	2·555
trans-$PtCl_2(PEt_3)_2$ [a]	CH_2Cl_2	PEt_3	2·400
cis-$Pt(SiMePh_2)_2(PMe_2Ph)_2$ [d]	CH_2Cl_2	$SiMePh_2$	1·559

[a] S. O. Grim, R. L. Kreiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133. [b] This work. [c] Ref. 23. [d] B. T. Heaton and A. Pidcock, *J. Organometallic Chem.*, 1968, **14**, 235.

Platinum complexes with dimethylphenylphosphine ligands on the metal, show parent-ions in the mass spectra. Complexes with triphenylphosphine ligands, including $Rh[N{:}C(CF_3)_2](PPh_3)_3$ and $Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2$, show only peaks corresponding to fragmentation. A partial fragmentation scheme for *cis*-$Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2$ is given below (relative intensities are indicated in parentheses).



Platinum complexes show ν(CN) at *ca.* 1670 cm^{-1} and strong bands due to ν(C–F) in the 1400—1000 cm^{-1} region.[13] *trans*-$Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2$ and $Rh[N{:}C(CF_3)_2](PPh_3)_3$ also have ν(CN) in the 1670—1690 cm^{-1} range, but these bands are very weak. The Pt–H stretching mode in *trans*-$Pt(H)[N{:}C(CF_3)_2](PPh_3)_2$ occurs at 2146 cm^{-1}; the corresponding deuteride has ν(Pt–D) at 1535 cm^{-1}. This is consistent with a *trans*-arrangement of ligands; *cis*-hydrides normally have ν(Pt–H) <2100 cm^{-1}. Presumably the ligand $(CF_3)_2C{:}N^-$ has a low *trans*-influence compared with triphenylphosphine. The data in Table 3 indicate that NO_2^- and $(CF_3)_2C{:}N^-$ lie close in the *trans*-influence series (see, however, ref. 20 for a critique of such analysis).

^1H N.m.r. data are in Table 2. For $Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2$ in $CDCl_3$, the three doublets [$J(^{31}PH)$ 11 Hz;

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

[19] D. M. Roundhill, *Chem. Comm.*, 1969, 567; *Inorg. Chem.*, 1970, **9**, 254.

[20] D. M. Roundhill, P. B. Tripathy, and B. W. Renoe, *Inorg. Chem.*, 1971, **10**, 727, and references therein.

$J(^{195}Pt^{1}H)$ 29 Hz] associated with PMe_2 are consistent [21] with the *cis*-configuration. For $Pt(H)[N{:}C(CF_3)_2](PMe_2Ph)_2$ in benzene, the P–Me groups appear as three triplets [$J(^{31}P^{1}H)$ 7 Hz; $J(^{195}Pt^{1}H)$ 34 Hz], appropriate for a *trans*-configuration; this is consistent with the splitting of the hydride resonance (τ 22·8) in the related complex $Pt(H)[N{:}C(CF_3)_2](PPh_3)_2$ into a triplet by two equivalent phosphorus nuclei [$J(^{31}P^{1}H)$ 16 Hz] and a further splitting by the platinum [$J(^{195}Pt^{1}H)$ 750 Hz]. The n.m.r. data of Tables 3 and 4 indicate the relatively high *trans*-influence of $(CF_3)_2C{:}N^-$ (see ref. 22).

The stereochemistry of the complexes was confirmed (see ref. 23) using ^{31}P n.m.r. spectroscopy (Table 4). As expected the spectrum of *cis*-$PtCl[N{:}C(CF_3)_2](PPh_3)_2$ shows a doublet (with additional ^{195}Pt satellites), whereas that of *trans*-$Pt(H)[N{:}C(CF_3)_2](PPh_3)_2$ exhibits a single peak. In *cis*-$Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2$, the two phosphorus atoms are in identical environments and a single peak was again observed.

With the exception of *trans*-$Pt(H)[N{:}C(CF_3)_2](PPh_3)_2$ (which upon scale expansion exhibited a complex multiplet for the fluorine resonance), all the platinum complexes show a sharp singlet for the ^{19}F resonance, consistent with a linear PtNC arrangement of atoms (Table 2). There was no evidence for (P–F) coupling in either *cis*-$Pt[N{:}C(CF_3)_2]_2(PMe_2Ph)_2$ or *cis*-$PtCl[N{:}C(CF_3)_2](PPh_3)_2$. However, the ^{19}F n.m.r. spectrum of $Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2$ in benzene solution shows a relatively broad singlet [$\delta = +69{\cdot}95$ p.p.m. (relative to $CFCl_3$)] which upon scale expansion is resolved into a symmetrical triplet [$J(^{31}P^{19}F)$ 1·5 Hz], indicating a *trans*-arrangement of ligands.

The principal details of platinum(II)–1,1-bis(trifluoromethyl)methyleneamido-chemistry, with triphenylphosphine as ligand, are summarised in the Scheme. When $Pt(H)[N{:}C(CF_3)_2](PPh_3)_2$ was heated under reflux in benzene (1 h) with a trace of triphenylphosphine, the complex (I) (see Scheme) was formed in high yield. (The reverse reaction was not effected thermally or photolytically.)

The role of triphenylphosphine (other bases may behave similarly) is probably to catalyse the *trans* ⟶ *cis* (III) isomerisation [^{1}H n.m.r. experiments provided no evidence for (III)]; the *cis*-hydride may rearrange intramolecularly to the cyclic adduct (I). The isomerisation experiment was also carried out on *trans*-$Pt(D)[N{:}C(CF_3)_2](PPh_3)_2$. This furnished the *N*-deuterio-analogue of (I), independently obtained from (I) and D_2O in chloroform.

The isomerisation was alternatively effected, in the absence of added triphenylphosphine, by heating under reflux in xylene. However, at this temperature some thermal decomposition of the hydride occurred, which may have provided traces of free phosphine in solution. Triethylsilane effected the transformation of *cis*-$PtCl[N{:}C(CF_3)_2](PPh_3)_2$ into (I), presumably *via* $PtH[N{:}C(CF_3)_2](PPh_3)_2$, by heating under reflux in xylene; there was no reaction in boiling toluene.

Many examples of hydrogen transfer from ligand to metal are known,[24] as are two cases of tautomerism.[25] Other hydrogen transfers from metal to ligand are rare, but are established for nitrosyl,[26] acetylene,[27] and acetylide [28] ligands. Such tautomerism is often suggested to account *inter alia* for the transition metal-catalysed isomerisation of olefins.[29]

Neither $Pt[N{:}C(CF_3)_2](Me)(PPh_3)_2$ nor $Pt[N{:}C(CF_3)_2](Ph)(PPh_3)_2$ was isomerised to the *N*-methyl or *N*-phenyl analogues of (I), by heating in benzene with triphenylphosphine. This is not due to the inherent instability of the rearrangement product; $[Pt\{(CF_3)_2CNMe\}(PPh_3)_2]$ has been prepared.[18] 1,1-Bis(trifluoromethyl)methyleneamine was not eliminated when $Rh[N{:}C(CF_3)_2](PPh_3)_3$ was heated under reflux for 1 h in benzene, whereas $Rh(Me)(PPh_3)_3$ readily loses methane consequent upon *o*-metallation.[30]

In general, the M–N bond of metal alkylideneamides is cleaved by hydrogen chloride. Thus, *trans*-$Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2$ in benzene reacted instantly with an excess of ethereal hydrogen chloride (1 : 2), presumably *via* $IrCl(CO)(PPh_3)_2$, to give $IrHCl_2(CO)(PPh_3)_2$. Stoicheiometric quantities of $PtCl[N{:}C(CF_3)_2](PMe_2Ph)_2$ and HCl gave *cis*-$PtCl_2(PMe_2Ph)_2$.

EXPERIMENTAL

General procedures have been outlined previously.[1,4] M.p.s were determined in sealed capillaries under nitrogen. Analyses were carried out by Mr. and Mrs. A. G. Olney of the Departmental Microanalytical Laboratory. Spectra were recorded on the following instruments: Perkin-Elmer 457 (i.r.), Varian T 60 and A 60 (^{1}H n.m.r.), Varian HA 100 (^{1}H and ^{19}F n.m.r.), Perkin-Elmer R 10 (^{31}P n.m.r.), and A.E.I. MS 9 (mass): details of i.r. and other spectra are in ref. 31.

$(CF_3)_2C{:}NH$,[13] $(CF_3)_2C{:}NSnMe_3$,[4] $Pt(PPh_3)_3$,[32] *cis*-$PtCl_2(PPh_3)_2$,[33] *cis*-$PtCl_2(PMe_2Ph)_2$,[21] *trans*-$Pt(H)Cl(PPh_3)_2$,[33] *trans*-$PtI(Me)(PPh_3)_2$,[34] $RhCl(PPh_3)_3$,[35] and *trans*-$IrCl(CO)(PPh_3)_2$ [36] were prepared according to published procedures.

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$PtCl(Ph)(PPh_3)_2$ was prepared from $Pt(Ph)_2(PPh_3)_2$ and HCl (1 : 1).

1,1-Bis(trifluoromethyl)methyleneamidolithium [13] was freshly prepared immediately before use by distilling an excess of 1,1-bis(trifluoromethyl)methyleneamine (b.p. *ca.* 16°) into a frozen solution of methyl-lithium in diethyl ether at −196° and then allowing the stirred reaction mixture to warm slowly to 6°; the excess was removed under reduced pressure. Particular care was taken in the handling of this compound.[13,17]

Reactions of 1,1-*Bis(trifluoromethyl)methyleneamidolithium (The Lithium Chloride Elimination Route to Complexes).*—(a) *With* cis-*dichlorobis(triphenylphosphine)platinum*(II). The platinum complex (0·556 g, 0·70 mmol), as a slurry in benzene (50 ml), was slowly added to the lithium reagent (1·40 mmol) in diethyl ether (2 ml) at 0°. After stirring for 3 h at 20°, the reaction mixture was filtered and the solid extracted with chloroform. The extracts were evaporated to dryness to give cis-*chloro*[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(triphenylphosphine)platinum*(II) (0·511 g).

(b) *With* cis-*dichlorobis(dimethylphenylphosphine)platinum*(II). The complex (1·009 g, 1·86 mmol) in benzene (50 ml) was added during ½ h to a solution of the lithium reagent (4·0 mmol) in diethyl ether (6 ml) at 0°. Upon warming to 20°, a white solid and a yellow solution were formed. The reaction mixture was then stirred (4 h) and filtered. The filtrate was concentrated to *ca.* 10 ml under reduced pressure, whereafter n-hexane was added. Recrystallisation ($CHCl_3$–n-C_6H_{14}) of the precipitated yellow powder afforded yellow needles of cis-*bis*[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(dimethylphenylphosphine)platinum*(II) (0·851 g).

In another experiment, the platinum complex (0·520 g, 1·00 mmol) and the lithium reagent (1·0 mmol) in benzene (40 ml) were stirred for *ca.* 1 h at 10° and then for a further 4 h at 20°. The solution was filtered and solvent was removed *in vacuo*. The residue was redissolved in diethyl ether (*ca.* 10 ml) and addition of n-hexane gave the white, amorphous cis-*chloro*[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(dimethylphenylphosphine)platinum*(II) (*ca.* 15%). Upon cooling to −30°, the filtrate gave yellow crystals of *cis*-bis[1,1-bis(trifluoromethyl)methyleneamido]bis(dimethylphenylphosphine)platinum(II) (0·250 g, 0·31 mmol).

(c) *With* trans-*hydrido(chloro)bis(triphenylphosphine)platinum*(II). The hydride (0·756 g, 1·0 mmol) in benzene (35 ml) was slowly added to a solution of the lithium reagent in diethyl ether (1·6 ml) at 0°. The reaction mixture was stirred at 5° for 15 min and then at 20° for a further 2 h. Filtration afforded a yellow filtrate, the volume of which was reduced to *ca.* 10 ml. n-Hexane (*ca.* 20 ml) was added to give yellow crystals of trans-*hydrido*[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(triphenylphosphine)platinum*(II) (0·585 g). The *deuterio-analogue* was similarly prepared.

(d) *With* trans-*hydrido(chloro)bis(dimethylphenylphosphine)platinum*(II). Similarly, this platinum hydride (0·150 g, 0·3 mmol) in benzene (10 ml) and the lithium reagent (0·3 mmol) afforded yellow crystals of trans-*hydrido*[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(dimethylphenylphosphine)platinum*(II) (0·095 g).

(e) *With* trans-*iodo(methyl)bis(triphenylphosphine)platinum*(II). The complex (0·523 g, 0·61 mmol) in benzene (50 ml) was slowly added to the lithium compound (0·71 mmol) in diethyl ether (10 ml) at 0°. The reaction mixture was stirred for 4·5 h at 20°. Volatile materials were removed *in vacuo* and the residue was extracted with diethyl ether (15 ml). When the ethereal solution was cooled (−30°), yellow crystals of 1,1-*bis(trifluoromethyl)methyleneamido(methyl)bis(triphenylphosphine)platinum*(II) (*ca.* 15%) were obtained.

(f) *With chloro(phenyl)bis(triphenylphosphine)platinum*(II). The platinum complex (0·160 g, 0·10 mmol) in benzene (40 ml) was slowly added to the lithium reagent (0·20 mmol) in diethyl ether (10 ml) at 0°. The reaction mixture was stirred at 0° for 2 h and then for 2 h at 20°. Solvent was removed *in vacuo* and replaced with benzene (40 ml). After filtration, the bulk of the benzene was removed from the filtrate and n-hexane was added to give, upon cooling (−30°, 14 h), pale yellow crystals of 1,1-*bis(trifluoromethyl)methyleneamido(phenyl)bis(triphenylphosphine)platinum*(II) (*ca.* 55%).

(g) *With chlorotris(triphenylphosphine)rhodium*(I). The rhodium complex (0·443 g, 0·48 mmol) was added to a solution of the lithium reagent (0·7 mmol) in diethyl ether (1·1 ml) and benzene (25 ml) at 3°. The reaction mixture was stirred for ½ h at 3° and then for 2 h at 20°. Solvent was removed *in vacuo* and the residue was extracted into dichloromethane (*ca.* 15 ml). To the solution, n-hexane was added to give a yellow precipitate [0·235 g, water present (i.r.)] which was filtered off. The filtrate was cooled to −30° to give yellow crystalline 1,1-*bis(trifluoromethyl)methyleneamidotris(triphenylphosphine)rhodium*(I) (0·165 g).

(h) *With* trans-*chlorocarbonylbis(triphenylphosphine)iridium*(I). The iridium complex (0·382 g, 0·49 mmol) was added to a solution of the lithium reagent (1·0 mmol) in benzene (20 ml) at 2°. The mixture was stirred for ½ h at 2° and then for 1·5 h at 20°. Filtration and evaporation of solvent from the filtrate gave, after recrystallisation (Et_2O at −30°), yellow crystals of *trans*-[1,1-bis(trifluoromethyl)methyleneamido]carbonylbis(triphenylphosphine)iridium(I) (0·32 g).

Reactions of 1,1-*Bis(trifluoromethyl)methyleneamino(trimethyl)stannane (The Trimethyltin Chloride Elimination Route to Complexes).*—(a) *With* cis-*dichlorobis(dimethylphenylphosphine)platinum*(II). The stannane (0·5 ml, *ca.* 2·5 mmol) was added by pipette to a slurry of the platinum complex (0·568 g, 0·84 mmol) in benzene (30 ml) at 20°. The reaction mixture was heated under reflux (5 h). Solvent was removed at 20° *in vacuo* to leave a yellow oil. n-Hexane was added and the mixture was stirred to give a pale yellow powder and an almost colourless solution. Solvent was decanted from the solid, which was then washed with more n-hexane (30 ml) and dried (½ h, 0·001 mmHg) to give an almost quantitative yield of *cis*-chloro[1,1-bis(trifluoromethyl)methyleneamido]bis(dimethylphenylphosphine)platinum(II) (Found: C, 33·9; H, 3·3; N, 2·5%).

(b) *With* cis-*dichlorobis(triphenylphosphine)platinum*(II). Similarly, but using somewhat more forcing conditions (Table 1), *cis*-chloro[1,1-bis(trifluoromethyl)methyleneamido]bis(triphenylphosphine)platinum(II) (authentic spectra) was obtained.

(c) *With* trans-*chlorocarbonylbis(triphenylphosphine)iridium*(I). The stannane (0·30 ml, 1·5 mmol) was added to a slurry–solution of the iridium complex (0·434 g, 0·56 mmol) in benzene (15 ml). The reaction mixture was stirred at 20° for 12 h to give a clear orange solution, which was concentrated to *ca.* 3 ml, and n-hexane was added. Yellow crystals of *trans*-[1,1-bis(trifluoromethyl)methyleneamido]carbonylbis(triphenylphosphine)iridium(I) (0·451 g) (authentic spectra) were filtered off, washed with n-hexane (2 × 15 ml), and dried (1 h, 0·001 mmHg).

(d) *With chlorotris(triphenylphosphine)rhodium*(I). The stannane (0·20 ml, 1·0 mmol) in benzene (15 ml) was added to the rhodium complex (0·463 g, 0·5 mmol) in benzene (15 ml). A clear solution was obtained within 15 min. After 1·75 h, the volume of solvent was reduced to *ca.* 5 ml. Addition of n-hexane (25 ml) yielded the yellow amorphous 1,1-bis(trifluoromethyl)methyleneamidotris(triphenylphosphine)rhodium(I) (0·500 g) (Found: C, 63·1; H, 4·2; N, 1·4%).

Platinum Alkylideneamides and Related Compounds by the Oxidative Addition Route.—(*a*) 1,1-Bis(trifluoromethyl)methyleneamine (0·375 g, 2·2 mmol) was distilled *in vacuo* into a frozen (−196°) solution of tris(triphenylphosphine)platinum(0) (1·00 g, 1·0 mmol) in benzene (20 ml). Using a condenser at 0° to recycle the free amine, the stirred reaction mixture was allowed to warm to 20° and was then stirred for 4 h. Volatiles were removed *in vacuo* and the residue was washed with diethyl ether (*ca.* 40 ml) to give white crystals of 1,1-bis(trifluoromethyl)methyleneaminebis(triphenylphosphine)platinum(0) [18] (0·696 g).

(*b*) No reaction was observed between 1,1-bis(trifluoromethyl)methyleneamine and tetrakis(diphenylmethylphosphine)platinum(0) under similar conditions.

(*c*) 1,1-Bis(trifluoromethyl)methyleneamino(trimethyl)stannane (0·30 ml, 1·50 mmol) was added to a stirred solution of stilbenebis(triphenylphosphine)platinum(0) (0·297 g, 0·33 mmol) in benzene (15 ml). The yellow colour of the solution was partially discharged. The reaction mixture was stirred (1 h) and the volume of solvent was reduced to *ca.* 3 ml. n-Hexane was added to give the pale yellow 1,1-*bis(trifluoromethyl)methyleneamido(trimethylstannyl)bis(triphenylphosphine)platinum*(II) (0·32 g).

(*d*) 1,1-Bis(trifluoromethyl)methyleneamino(trimethyl)stannane (0·20 ml, 1·0 mmol) was added, by pipette, to a stirred solution of the platinum complex of (*c*) (0·246 g, 0·25 mmol) in deuteriobenzene (5 ml, 95% [$^2H_6$]benzene). The reaction mixture was stirred for 1 h at 40° and most of the solvent was removed *in vacuo*. n-Hexane was added to give the yellow 1,1-bis(trifluoromethyl)methyleneamido(trimethylstannyl)bis(triphenylphosphine)platinum(II) (80%), which was washed with n-hexane (3 × 5 ml) and dried (1 h, 0·001 mmHg).

1,1-Bis(trifluoromethyl)methyleneamino(trimethyl)stannane (0·20 ml, 1·0 mmol) was added, by pipette, to a stirred solution of tris(triphenylphosphine)platinum(0) (0·981 g, 1·0 mmol) in benzene (50 ml) at 20°. The reaction mixture was stirred for *ca.* 2 h at 40°. Most (*ca.* 40 ml) of the benzene was removed at 20° *in vacuo*, n-hexane (30 ml) was added to give a yellow powder, which was recrystallised from benzene–n-hexane and identified as 1,1-*bis(trifluoromethyl)methyleneaminetris(triphenylphosphine)platinum*(0) (0·92 g, 80%). This surprising result was reproducible; however, we attribute it to adventitious hydrolysis of the sensitive stannane. Thus, the reaction is believed to be between $Pt(PPh_3)_3$ (a slight excess) and $(CF_3)_2C{:}NH$. Evidence for this is the lack of participation of C_6D_6 in the above reaction, and the following experiment.

A deep yellow colour developed instantly when triphenylphosphine was added to a benzene solution of 1,1-bis(trifluoromethyl)methyleneaminebis(triphenylphosphine)platinum(0). The yellow solid was identical (spectra) with $Pt[(CF_3)_2CNH](PPh_3)_3$, prepared above.

Reactions of Transition Metal Alkylideneamides with Hydrogen Chloride.—Hydrogen chloride (1·2 mmol) in diethyl ether (0·5 ml) was added to a stirred solution of 1,1-bis(trifluoromethyl)methyleneamidocarbonylbis(triphenylphosphine)iridium(I) (0·444 g, 0·49 mmol) in benzene (10 ml). The colour was instantly discharged and a white precipitate formed. The solid was washed with n-hexane (15 ml), dried (1 h, 0·05 mmHg), and identified as $IrHCl_2(CO)(PPh_3)_2$ [37] (0·41 g, 99%) (Found: C, 55·5; H, 4·1. Calc. for $C_{37}H_{31}Cl_2IrOP_2$: C, 54·4; H, 3·8%), ν(IrH) 2237; ν(CO) 2022; ν(IrCl) 311, 260 cm^{-1}.

Hydrogen chloride [0·46(5) mmol] in diethyl ether [0·19 ml] was added to a solution of chloro[1,1-bis(trifluoromethyl)methyleneamido]bis(dimethylphenylphosphine)platinum(II) (0·313 g, 0·46 mmol) in benzene (30 ml) at 5°. The reaction mixture was stirred for 3 h at 20°. Most of the benzene was removed *in vacuo*. Addition of n-hexane (30 ml) gave a white solid, which was filtered off, washed with n-hexane (2 × 20 ml), dried, and identified as *cis*-dichlorobis(dimethylphenylphosphine)platinum(II) (*ca.* 100%) (Found: C, 35·6; H, 4·4. Calc. for $C_{16}H_{22}Cl_2P_2Pt$: C, 35·4; H, 4·1%), ν(PtCl) 312, 290 cm^{-1}.

Lack of Reaction between cis-*Chloro*[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(dimethylphenylphosphine)platinum*(II) *and Di-isopropylamine.*—Di-isopropylamine (1 ml, a large excess) was added to the platinum compound (0·542 g, 0·50 mmol) in benzene (20 ml), which was recovered essentially unchanged after being heated for 5 h under reflux.

Isomerisation and Related Reactions.—(a) *Isomerisation of* trans-*hydrido(or deuterido)*[1,1-*bis(trifluoromethyl)methyleneamido*]*bis(triphenylphosphine)platinum*(II). The *trans*-hydride (0·274 g, 0·31 mmol) and triphenylphosphine (0·0812 g, 0·31 mmol) were heated under reflux in benzene (10 ml) for 1 h. The colour of the solution became deep yellow. The volume of benzene was reduced to *ca.* 4 ml. Addition of diethyl ether (15 ml) gave (on cooling to −30°) pale yellow crystals. Recrystallisation (CH_2Cl_2–n-C_6H_{14}) afforded white crystals of $Pt[(CF_3)_2CNH](PPh_3)_2$ (0·140 g, 50%) (authentic i.r. spectrum). [It is curious that the product is not (II) (see Scheme); a similar comment applies to the reaction of $Pt(PPh_3)_3 + (CF_3)_2C{:}NH$ (*vide supra*).]

Similarly, the deuterio-platinum complex (0·259 g, 0·29 mmol) and triphenylphosphine (0·0768 g, 0·29 mmol) in benzene (10 ml), after heating under reflux (2 h), gave $Pt[(CF_3)_2CND](PPh_3)_2$ (authentic i.r. spectrum).

When *trans*-hydrido[1,1-bis(trifluoromethyl)methyleneamido]bis(triphenylphosphine)platinum(II) (0·178 g) and benzene (25 ml) were heated under reflux for 1·5 h in the absence of added triphenylphosphine, the starting platinum complex was recovered unchanged from the reaction mixture. In other experiments with diethyl ether as solvent, there was no isomerisation during 1 h, with or without added triphenylphosphine.

(b) *Reaction of* 1,1-*bis(trifluoromethyl)methyleneaminebis(triphenylphosphine)platinum*(II) *with deuterium oxide.* The platinum complex (*ca.* 50 mg) was stirred with a mixture of deuterium oxide (*ca.* 1 ml) and deuteriochloroform (2 ml) in the presence of a trace of deuterium chloride. After 20 min, volatiles were removed *in vacuo* to afford the white solid *N*-deuterio-isotopomer, which was warmed at 50° *in vacuo* to remove final traces of moisture.

(c) *Attempted isomerisations.* I.r. spectra indicated no significant reaction when a solution of 1,1-bis(trifluoromethyl)methyleneamido(methyl)bis(triphenylphosphine)-platinum(II) (0·045 g, *ca.* 0·05 mmol) and triphenylphosphine (0·013 g, *ca.* 0·05 mmol) in benzene (20 ml) was heated under reflux for 3 h.

A solution of 1,1-bis(trifluoromethyl)methyleneamido-(phenyl)bis(triphenylphosphine)platinum(II) and an excess of triphenylphosphine in benzene (5 ml) was heated under reflux (3 h). n-Hexane was then added to the reaction mixture to give a pale yellow powder, which was identified (i.r.) as unchanged starting platinum complex.

A solution of 1,1-bis(trifluoromethyl)methyleneamidotris-(triphenylphosphine)rhodium(I) (1·052 g, *ca.* 1·0 mmol) in benzene (50 ml) was heated under reflux (3 h). The reaction mixture was allowed to cool to room temperature and most (*ca.* 90%) of the benzene was removed *in vacuo*. n-Hexane (40 ml) was added to give a tan precipitate and an orange-yellow solution. The precipitate was filtered off and dried (1 h, 0·001 mmHg) [Found: C, 62·5; H, 4·8; N, 1·2%) i.r. revealed no significant bands due to ν(CN) or ν(NH)].

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