Synthesis of Hydridotrifluoromethyl Complexes of Platinum(II). A Spectroscopic Investigation of the *trans* and *cis* Influence of Ligands in Hydridoplatinum(II) Compounds

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The starting complex *trans*-$[PtH(CF_3)(PPh_3)_2]$ is prepared from *trans*-$[PtCl(CF_3)(PPh_3)_2]$ by treatment of the derived labile solvento cationic species *trans*-$[Pt(CF_3)(PPh_3)_2(solv)]BF_4$ (solv = acetone or CH_2Cl_2) with $NaBH_4$ in EtOH at 0 °C. The hydridotrifluoromethyl complexes *trans*-$[PtH(CF_3)L_2]$ [L = $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2Ph)Ph_2$, $P(CH_2Ph)_2Ph$, $P(CH_2Ph)_3$, $PEtPh_2$, $P(C_6H_{11})_3$, or $P(C_6H_4Me\text{-}4)_3$] are obtained by reaction of *trans*-$[PtH(CF_3)(PPh_3)_2]$ with 2 equivalents of phosphine, L, in n-heptane at room temperature. Similar exchange reactions between *trans*-$[PtH(CF_3)(PPh_3)_2]$ and equivalent amounts of diphosphine, L–L = *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2PMe_2$, or $Ph_2PCH_2CH_2CH_2PPh_2$, lead to the formation of the corresponding $[PtH(CF_3)(L\text{–}L)]$ compounds. The hydridotrifluoromethyl complexes with L–L = *cis*-$Ph_2PCH{=}CHPPh_2$ and $Ph_2PCH_2CH_2PPh_2$ can be prepared also by reaction of the parent chloro derivatives $[PtCl(CF_3)(L\text{–}L)]$ with $NaBH_4$ in EtOH at room temperature. The mixed isocyanide–phosphine complexes $[PtH(CF_3)(PPh_3)(CNR)]$ [R = 2,6-$Me_2C_6H_3$, 4-$MeOC_6H_4$, or Bu^t] are obtained by reaction of *trans*-$[PtH(CF_3)(PPh_3)_2]$ with a three-fold excess of RNC in n-heptane at room temperature. All the hydridotrifluoromethyl complexes are air-stable in the solid state and in solution. They were characterized by elemental analyses and i.r., ^1H, ^{19}F, and ^{31}P n.m.r. spectra. The data obtained for ν(PtH) and ^1J(PtH) in *trans*-$[PtH(CF_3)(PPh_3)_2]$ have been used to compare the *trans* influence of CF_3^- with other σ carbon donors, R, in *trans*-$[PtH(R)(PPh_3)_2]$ derivatives. The n.m.r.-based *trans* influence order is $CF_3^- > C_6H_5^- > C_6H_9^- > CH_2CH_2CN^- > CH_2CH_2CH_2CN^- > CH_3^- > CH_2CN^- > Cl^-$, whereas the i.r.-based *trans* influence order is $C_6H_9^- > CH_2CH_2CH_2CN^- > C_6H_5^- \approx CH_3^- > CF_3^- > Cl^-$. The opposite position of CF_3^- in the two series of *trans* influence has been explained by the different mechanism operating on ^1J(PtH) and ν(PtH). The first depends predominantly on the *s* character of the platinum hybrid orbital used in the Pt–H bond, while the second is sensitive also to electrostatic effects induced by the electronegative fluorine atoms. The ^1J(PtP) data for the same series of complexes gives the following order of *cis* influence: $Cl^- > CH_2CN^- > CF_3^- \approx CH_3^- \approx C_6H_5^- \approx CH_2CH_2CN^- > CH_2CH_2CH_2CN^-$. From the spectra of *trans*-$[PtH(X)L_2]$ (X = CF_3 or Cl), the effects of replacing two PPh_3 ligands in *trans*-$[PtH(CF_3)(PPh_3)_2]$ by L on ν(PtH) and ^1J(PtH) were measured. With the assumption that the *cis* effects are additive, the i.r. and n.m.r. parameters were correlated with the electronic χ and steric θ parameters of the phosphine ligands.

Following the two initial reports on the synthesis of *trans*-$[PtH(CH_2SiMe_3)(PEt_3)_2]$[1] and *trans*-$[PtH\{C(CN)_3\}(PPh_3)_2]$,[2] there has been a growing number of papers dealing with the preparation of compounds of the type $[PtH(R)L_2]$, containing both hydride and σ-carbon bonded ligands. These metal species are of special interest since they can be regarded as models of more highly reactive intermediates which are involved in catalytic processes such as the hydrogenation of olefins[3] and the activation of the C–H bond.[4]

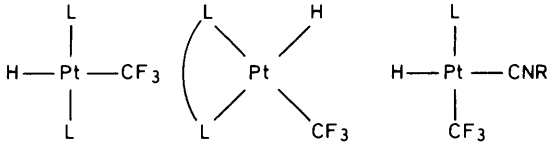
The systematic investigation that we have undertaken recently has been based on the synthesis, spectroscopic, and structural properties, and reactivity of a wide series of stable hydridocyanoalkyl complexes of Pt^{II}, of the type *trans*-$[PtH(R^X)(PPh_3)_2]$ [$R^X = (CH_2)_nCN$, n = 1—3],[5a–g] $[PtH(R^X)(L\text{–}L)]$ [$R^X = (CH_2)_nCN$, n = 1—3; $CH_2C_6H_4CN$-*o*; L–L = diphosphine or diarsine],[5b,c,f] and $[PtH(CH_2CN)(PPh_3)(CNR)]$.[5h] The unusual thermal stability of these complexes, either of *trans* and *cis* geometry, has been explained by the enhanced Pt–C(R^X) bond strength due to the presence of the electron-withdrawing cyano groups in the alkyl chain. For comparison purposes, hydrido-alkyl and -aryl complexes of Pt^{II}, of the type *cis*-$[PtH(R^H)(PPh_3)_2]$ (R^H = Me, Et, $CH_2CH{=}CH_2$, or Ph)[6] and $[PtH(R^H)(L\text{–}L)]$ (R^H = Me, L–L = diphosphine),[7] undergo facile intramolecular elimination of H–R^H even at temperatures as low as −25 °C, whereas their *trans* counterparts *trans*-$[PtH(R^H)L_2]$ [R^H = Me, Ph, or C_6H_9(cyclohexenyl); L = unidentate tertiary phosphine][7–11] show a remarkably higher thermal stability.

In our continuing search for structure–reactivity correlations for hydrido–organoplatinum(II) derivatives containing electronegatively substituted alkyl groups, of general formula $[PtH(R^X)L_2]$, we have been led to investigate the ability of fluoroalkyls to stabilize platinum(II) metal complexes containing the hydride ligand.

The metal–carbon σ bond in perfluoroalkyl complexes of transition metals is much more thermally stable and more resistant to chemical attack than that of alkyl derivatives.[12,13] The stabilizing effect of the fluoroalkyl–transition metal σ bond allowed us to isolate quite rare hydroxo-,[14] methoxo-,[14] hydroperoxo-,[15a,b] and alkylperoxo-[15b,c] trifluoromethylplatinum(II) derivatives. More recently, the selective catalytic epoxidation of terminal olefins with diluted H_2O_2 has been found to proceed with the highest efficiency with trifluoromethylplatinum(II) complexes.[16] Thus, it appears that fluoro-

alkyls play an important role in the stabilization of unusual transition-metal species. However, there are only a few reports of hydridoplatinum(II) complexes containing σ-C-bonded fluorocarbon groups. Since our preliminary communication[17] on the synthesis of *trans*-$[PtH(CF_3)(PPh_3)_2]$ and $[PtH(CF_3)(Ph_2PCH{=}CHPPh_2)]$, the preparations of some hydridofluoroaryl complexes of Pt^{II}, *e.g.* *trans*-$[PtH(R^F)L_2]$ [$R^F = C_6F_5$; L = $P(C_6H_{11})_3$ or PEt_3; R^F = 1,3,5-$C_6H_2F_3$ or 1,3-$C_6H_3F_2$; L = $P(C_6H_{11})_3$] have been reported.[18] More recently, we described the preparation and kinetic study of 1,1-reductive elimination of CH_3CF_3 from *cis*-$[PtH(CH_2CF_3)(PPh_3)_2]$.[19]

We now report the synthesis of a wide class of hydridotrifluoromethyl complexes of Pt^{II} with general structures shown in (**A**)—(**C**), having Pt–H and Pt–C bonds either in a *trans* [type (**A**)] or *cis* [type (**B**) and (**C**)] arrangement.



For (**A**): L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2Ph)Ph_2$, $P(CH_2Ph)_2Ph$, $P(CH_2Ph)_3$, $PEtPh_2$, $P(C_6H_4Me\text{-}4)_3$, or $P(C_6H_{11})_3$.

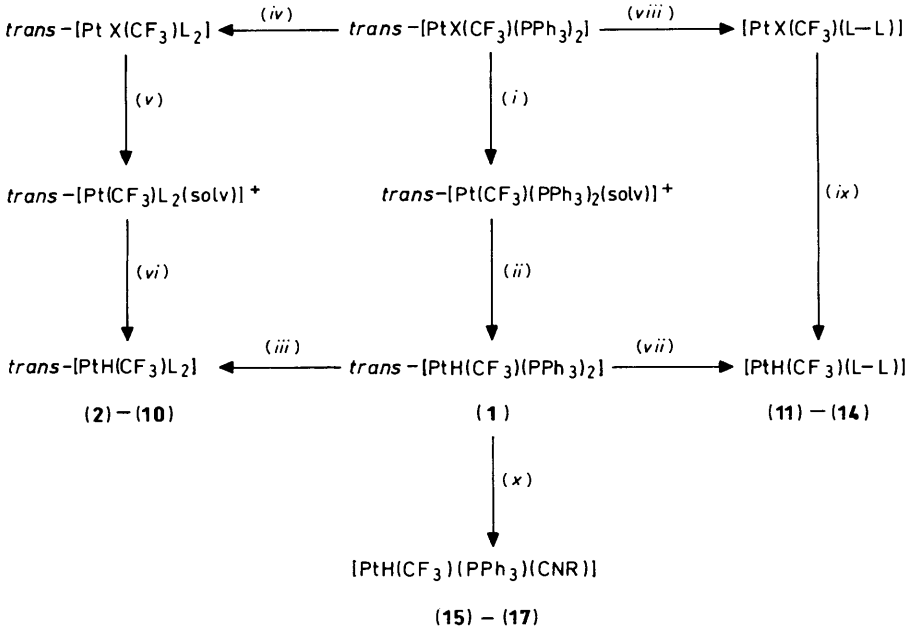
For (**B**): L–L = *cis*-$Ph_2PCH{=}CHPPh_2$ (vdpp), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), or $Me_2PCH_2CH_2PMe_2$ (dmpe).

For (**C**): L = PPh_3; RNC = 2,6-$Me_2C_6H_3NC$, *p*-$MeOC_6H_4NC$, or Bu^tNC.

The results of this study also focus on the following aspects: (*i*) stability of $[PtH(CF_3)L_2]$ complexes (L_2 = two monophosphines or a diphosphine) towards reductive elimination of H–CF_3; (*ii*) the *trans* and *cis* influence of CF_3^- in comparison with other σ-carbon donor groups in *trans*-$[PtH(R)(PPh_3)_2]$ compounds, and (*iii*) the *cis* influence of phosphine ligands, L, in hydrido complexes *trans*-$[PtH(X)L_2]$ (X = CF_3 or Cl) based on ^{195}Pt–^1H coupling constants and Pt–H stretching frequencies.

Results

Synthesis of Hydridotrifluoromethyl Complexes of Platinum(II). —The sequence of reactions leading to the formation of hydridotrifluoromethyl complexes of Pt^{II} is summarized in the Scheme. Treatment of *trans*-$[PtX(CF_3)(PPh_3)_2]$ (X = Cl or Br)[14] with an equivalent amount of $AgBF_4$ in CH_2Cl_2–$(CH_3)_2CO$ gives the cationic intermediate *trans*-$[Pt(CF_3)(PPh_3)_2(solv)]BF_4$, which reacts with a slight molar excess of $NaBH_4$ in EtOH at 0 °C to produce *trans*-$[PtH(CF_3)(PPh_3)_2]$ (**1**) in 71% isolated yield. Attempts to prepare (**1**) by treating the halogeno-derivatives *trans*-$[PtX(CF_3)(PPh_3)_2]$ (X = Cl or Br) with $NaBH_4$ in EtOH, as reported for the preparation of *trans*-$[PtH(CH_2CN)(PPh_3)_2]$,[5b] were unsuccessful. Reactions of *trans*-$[Pt(CF_3)(PPh_3)_2(solv)]^+$ with NaOH and NaOMe in MeOH at room temperature afford the corresponding Pt–OH and Pt–OMe derivatives, respectively, as previously reported.[14] Reaction of the solvento cationic complex with a three-fold excess of NaOH in MeOH at 65 °C gave, after 20 min, a 70% yield of *trans*-$[Pt(OMe)(CF_3)(PPh_3)_2]$ [i.r. and ^1H n.m.r. as reported;[14] ^{19}F n.m.r. (CD_2Cl_2), δ (CF_3) −9.61 p.p.m. (t), $^3J(FP)$ 15.0, $^2J(FPt)$ 574; $^{31}P\text{-}\{^1H\}$ n.m.r. (CD_2Cl_2), δ(P) 22.3 p.p.m. (q), $^3J(PF)$ 15.0, $^1J(PPt)$ 3 269 Hz]. Prolonged heating (1 h) of the methoxo complex in the presence of NaOH forms a deep brown solution that decomposes without yielding any well defined compound. On the other hand, we have observed (see



Scheme. Synthesis of hydridotrifluoromethyl complexes of Pt^{II}. (*i*) +$AgBF_4$, −AgX; X = Cl or Br; CH_2Cl_2–acetone; (*ii*) +$NaBH_4$, EtOH, 0 °C; (*iii*) +2 L, −2 PPh_3, n-heptane, r.t., L = $PMePh_2$ (**2**), PMe_2Ph (**3**), PMe_3 (**4**), $P(CH_2Ph)Ph_2$ (**5**), $P(CH_2Ph)_2Ph$ (**6**), $P(CH_2Ph)_3$ (**7**), $PEtPh_2$ (**8**), $P(C_6H_{11})_3$ (**9**), or $P(C_6H_4Me\text{-}4)_3$ (**10**); (*iv*) +2 L, −2 PPh_3, n-heptane; L = $PMePh_2$, PMe_2Ph, or PMe_3; (*v*) X = Cl or Br; +$AgBF_4$, −AgX, EtOH; L = $PMePh_2$ or PMe_2Ph; (*vi*) +$NaBH_4$, EtOH, 0 °C; (*vii*) +L–L, −2 PPh_3, n-heptane, r.t.; L–L = *cis*-$Ph_2PCH{=}CHPPh_2$ (**11**), $Ph_2PCH_2CH_2PPh_2$ (**12**), $Me_2PCH_2CH_2PMe_2$ (**13**), or $Ph_2P(CH_2)_3PPh_2$ (**14**); (*viii*) +L–L, −2 PPh_3, benzene, r.t.; L–L = *cis*-$Ph_2PCH{=}CHPPh_2$ or $Ph_2PCH_2CH_2PPh_2$; (*ix*) +$NaBH_4$, EtOH; (*x*) +RNC, −PPh_3, n-heptane, r.t.; RNC = 2,6-$Me_2C_6H_4NC$ (**15**), 4-$MeOC_6H_4NC$ (**16**), or Bu^tNC (**17**)

Table 1. Selected i.r. and analytical data for hydridotrifluoromethyl complexes of platinum(II)[a]

Compound	ν(PtH)/cm^{-1}		ν(CF)/cm^{-1} (Nujol)		Analysis (%)		M.p./°C
	Nujol	CH_2Cl_2	sym	deg	C	H	(decomp.)
(1) *trans*-[PtH(CF_3)(PPh_3)$_2$]	2 073m	2 069m	1 086vs	998s, 979vs, 964s	56.20 (56.30)	3.90 (3.95)	187—189
(2) *trans*-[PtH(CF_3)($PMePh_2$)$_2$]	2 050s	2 040m	1 079vs, 1 068vs	988vs, 977vs, 967vs	48.40 (48.75)	4.10 (4.10)	105—107
(3) *trans*-[PtH(CF_3)(PMe_2Ph)$_2$]	2 025s	2 020m	1 079vs, 1 068vs	968vs, 951vs, 943s	37.75 (37.70)	4.50 (4.30)	113—114
(4) *trans*-[PtH(CF_3)(PMe_3)$_2$]	2 017s	2 018m	1 078vs	980—940vs,br[b]	20.40 (20.15)	4.80 (4.60)	122—124
(5) *trans*-[PtH(CF_3){$P(CH_2Ph)Ph_2$}$_2$]	2 066s	2 071m	1 077vs, 1 068sh	975vs, 953vs	57.45 (57.30)	4.45 (4.55)	180—181
(6) *trans*-[PtH(CF_3){$P(CH_2Ph)_2Ph$}$_2$]	2 086m	2 058m,br	1 074vs	962vs, 940vs	58.35 (58.20)	4.55 (4.65)	118
(7) *trans*-[PtH(CF_3){$P(CH_2Ph)_3$}$_2$]	2 102m	2 054m,br	1 082vs	978vs, 951vs	59.30 (59.10)	4.75 (4.95)	140—142
(8) *trans*-[PtH(CF_3)($PEtPh_2$)$_2$]	2 065s	2 052m	1 079vs, 1 068vs	970—940vs,br[b]	50.40 (50.20)	4.25 (4.50)	124—126
(9) *trans*-[PtH(CF_3){$P(C_6H_{11})_3$}$_2$]	2 015s	2 062m,br	1 070vs	959vs, 951 (sh)	53.50 (53.80)	8.00 (8.15)	185—188
(10) *trans*-[PtH(CF_3){$P(C_6H_4Me\text{-}4)_3$}$_2$]	2 073m	2 068m	1 082vs	980vs, 968s, 960s	58.85 (59.10)	4.90 (4.95)	195—200
(11) [PtH(CF_3)($Ph_2PCH{=}CHPPh_2$)]	2 030s	*c*	1 090vs	985vs, 968s, 962s	49.20 (49.00)	3.60 (3.50)	225—228
(12) [PtH(CF_3)($Ph_2PCH_2CH_2PPh_2$)]	2 030s	*c*	1 090vs	982vs, 975sh, 965vs	48.70 (48.90)	3.75 (3.80)	224—227
(13) [PtH(CF_3)($Me_2PCH_2CH_2PMe_2$)]	1 995s,br	1 998m	1 090vs	964vs,br, 945vs,br	20.00 (20.25)	4.25 (4.15)	138—140
(14) [PtH(CF_3)($Ph_2PCH_2CH_2CH_2PPh_2$)]	2 042m	2 061m	1 092vs	983vs, 970vs	49.40 (49.65)	3.85 (4.00)	206
(15) [PtH(CF_3)(PPh_3)($CNC_6H_3Me_2$-2,6)][d]	*c*	*c*	1 100vs[b]	1 000vs, 990vs[b]	51.20 (51.05)	3.70 (3.80)[e]	150—152
(16) [PtH(CF_3)(PPh_3)(CNC_6H_4OMe-4)][f]	2 093w	*g*	1 100vs[b]	1 000—975vs,br[b]	49.30 (49.10)	3.70 (3.50)[h]	133—135
(17) [PtH(CF_3)(PPh_3)(CNBu^t)][i]	2 098w	2 102w	1 097vs[b]	987vs,br, 975 (sh)	45.55 (47.20)	4.20 (4.15)[j]	160—162

[a] Abbreviations: m = medium, s = strong, vs = very strong, w = weak, (sh) = shoulder, br = broad. For analyses calculated values are in parentheses. [b] Partially overlapped with phosphine absorptions. [c] Absorption not observed. [d] ν(C≡N) 2 195vs (Nujol) and 2 180vs cm^{-1} (CH_2Cl_2). [e] N 2.35 (2.15). [f] ν(C≡N) 2 193vs (Nujol) and 2 195vs cm^{-1} (CH_2Cl_2). [g] Too insoluble. [h] N 2.45 (2.10)%. [i] ν(C≡N) 2 208vs (Nujol) and 2 210vs cm^{-1} (CH_2Cl_2). [j] N 2.50 (2.30)%.

Table 2. Proton, ^{19}F, and ^{31}P n.m.r. spectral data for *trans*-[PtH(CF_3)L_2] complexes[a]

Compound	^1H					^{19}F				^{31}P-{^1H}		
	δ(H)	^1J(PtH)	^2J(HP)	^3J(HF)	δ(other)	δ(CF_3)	^2J(PtF)	^3J(FH)	^3J(PF)	δ(P)	^1J(PtP)	^3J(PF)
(1)	−8.23 (qt)	544	18.5	28.0		−16.8 (dt)	448	28.0	10.0	29.6 (q)	3 118	10.0
(2)	−8.23 (qt)	588	19.3	28.5	2.19 (t)[b]	−16.2 (dt)	455	28.5	10.1	9.6 (q)	2 966	10.1
(3)	−8.31 (qt)	626	21.2	28.3	1.93 (t)[c]	−16.5 (dt)	462	28.3	11.0	−6.8 (q)	2 821	11.0
(4)	−8.45 (qt)	657	22.1	28.3	1.58 (t)[d]	−17.5 (dt)	466	28.3	11.7	−17.9 (q)	2 653	11.7
(5)	−8.89 (qt)	565	17.3	28.8	4.08 (t)[e]	−16.2 (dt)	421	28.8	8.8	24.6 (q)	3 091	8.8
(6)	−9.24 (qt)	583	17.9	29.6	3.75 (t)[f]	−14.7 (dt)	430	29.3	8.4	20.6 (q)	3 071	8.4
(7)	−9.70 (qt)	585	18.3	29.4	3.24 (t)[g]	−15.0 (dt)	432	29.4	7.4	17.4 (q)	2 980	7.4
(8)	−8.53 (qt)	575	18.4	28.6	1.18—2.69 (m)[h]	−15.9 (dt)	450	28.6	9.7	25.1 (q)	2 989	9.7
(9)	−10.48 (qt)	569	17.6	28.5	1.05—2.27 (m)[i]	−12.5 (dt)	471	28.5	7.2	38.5 (q)	2 858	7.2
(10)	−8.50 (qt)	556	18.4	27.7	2.28 (s)[j]	−16.3 (dt)	443	27.7	9.6	27.0 (q)	3 053	9.6

[a] Spectra recorded in CD_2Cl_2; proton chemical shifts reported from $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as +5.32 p.p.m.; fluorine chemical shifts referenced to internal $CFCl_3$; phosphorus chemical shifts referenced to external 85% H_3PO_4; δ in p.p.m., *J* in Hz; s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet. [b] P–CH_3; ^2J(HP) + ^4J(HP) = 6.6, ^3J(PtH) = 33.4 Hz. [c] P–CH_3; ^2J(HP) + ^4J(HP) = 6.7, ^3J(PtH) = 35.3 Hz. [d] P–CH_3; ^2J(HP) + ^4J(HP) = 7.1, ^3J(PtH) = 33.8 Hz. [e] P–CH_2; ^2J(HP) + ^4J(HP) = 7.6, ^3J(PtH) = 35.4 Hz. [f] P–CH_2; ^2J(HP) + ^4J(HP) = 7.3, ^3J(PtH) = 30.6 Hz. [g] P–CH_3; ^2J(HP) + ^4J(HP) = 7.0, ^3J(PtH) = 31.0 Hz. [h] P–CH_2CH_3. [i] P–C_6H_{11}. [j] CH_3.

Experimental section) that the analogous reaction of *trans*-[PtMe(PPh_3)$_2$(solv)]$^+$ with a four-fold excess of NaOH in MeOH at 50—60 °C for 1 h gave the hydrido derivative *trans*-[PtH(Me)(PPh_3)$_2$] in 58% crystallization yield [equation (1)]. It is worthwhile to note that *trans*-[Pt(OMe)Me(PPh_3)$_2$] has been reported to decompose upon heating in MeOH to give impure *trans*-[PtH(Me)(PPh_3)$_2$].[9]

$$\textit{trans}\text{-}[PtCl(Me)(PPh_3)_2] \xrightarrow[CH_2Cl_2\text{–acetone}]{+AgBF_4,\ -AgCl} \textit{trans}\text{-}[PtMe(PPh_3)_2(solv)]^+ \xrightarrow[50\text{–}60\ ^\circ C]{NaOH,\ MeOH} \textit{trans}\text{-}[PtH(Me)(PPh_3)_2] \quad (1)$$

The two co-ordinated PPh_3 ligands in (**1**) are readily displaced in n-heptane at room temperature by reaction with 2 equivalents of more basic unidentate tertiary phosphines, L [L = $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2Ph)Ph_2$, $P(CH_2Ph)_2Ph$, $P(CH_2Ph)_3$, $PEtPh_2$, $P(C_6H_{11})_3$, or $P(C_6H_4Me\text{-}4)_3$] to form the corresponding *trans*-[PtH(CF_3)L_2] complexes, (**2**)—(**10**), in 25—89% yield [reaction (*iii*)]. The *trans* geometry of these complexes has been fully established by their i.r. (Table 1) and n.m.r. (Table 2) spectra.

Complexes (**2**) and (**3**) could be obtained also by the sequence of reactions (*iv*)—(*vi*) of the Scheme, starting from *trans*-[PtX(CF_3)L_2] (X = halide; L = $PMePh_2$[14] or PMe_2Ph[15c]) and proceeding as described for (**1**). By this route complexes (**2**) and (**3**) were obtained in 46 and 29% yield, respectively.

The reactions shown in the Scheme appear to be influenced by the bulkiness and nucleophilicity of the entering ligands. Thus, no phosphine exchange occurs between *trans*-[PtH(CF_3)(PPh_3)$_2$] and either the bulky PBu^t_3 ligand or arsines such as $AsMePh_2$ and $AsMe_2Ph$; the starting material being recovered unchanged after stirring for several days in n-heptane at room temperature.

Except for the (*p*-tolyl)phosphine derivative (**10**), all the *trans*-hydridotrifluoromethyl complexes prepared are very soluble in

Table 3. Proton, ^{19}F, and ^{31}P n.m.r. spectral data[a] for complexes of the type $[PtH(CF_3)(L\text{–}L)]$ and $[PtH(CF_3)(PPh_3)(CNR)]$

Compound	^1H δ(H)	^1J(PtH)	^2J(HP)	^3J(HF)	δ(other)	^{19}F δ(CF_3)	^2J(PtF)	^3J(FH)	^3J(FP)	$^{31}P\text{-}\{^1H\}$ δ(P)	^1J(PtP)	^3J(PF)
(**11**)	−2.42 (dqnt)[b]	1 260	194 (*trans*) 14.7 (*cis*)	14.7		−10.5 (dt)	767	14.7	57.8 (*trans*) 14.7 (*cis*)	*c*		
(**12**)	−2.56 (dqnt)[b]	1 233	188.7 (*trans*) 14.8 (*cis*)	14.8	2.2—2.5 (m)[d]	−10.6 (dt)	757	14.8	57.4 (*trans*) 14.8 (*cis*)	*c*		
(**13**)	−2.67 (ddq)	1 173	187 (*trans*) 18.2 (*cis*)	14.1	1.2—2.0 (m)[e]	−12.1 (dt)	729	14.1	61.0 (*trans*) *14.1* (*cis*)	19.3 (q)[f] 33.5 (q)[g]	1 874 1 700	61.0 14.1
(**14**)	−3.82 (dqnt)[b]	1 175	181 (*trans*) 16.3 (*cis*)	16.3	2.2—2.5 (m)[h]	−11.6 (ddd)	757	16.3	55.5 (*trans*) 13.5 (*cis*)	−0.75 (dq)[f,i] 2.97 (dq)[g,i]	1 980 1 790	55.5 13.5
(**15**)	−5.86 (dq)	1 110	20.5	14.6	2.03 (s)[j]	−12.0 (dd)	802	14.6	57.5	21.4 (q)	2 056	57.5
(**16**)	−5.77 (dq)	1 118	20.0	14.6	3.71 (s)[k]	−12.5 (dd)	813	14.5	58.0	23.3 (q)	2 056	58.0
(**17**)	−6.37 (dq)	1 106	20.0	14.6	1.20 (s)[l]	−13.0 (dd)	799	14.6	57.9	23.4 (q)	2 073	57.9

[a] Spectra recorded in CD_2Cl_2; experimental conditions as in footnote *a* of Table 2; s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, m = unresolved multiplet. [b] The accidental equality of $^2J(HP_{cis})$ with ^3J(HF) gives rise to a doublet of quintets instead of the theoretical doublet of double quartets (see text). [c] Too insoluble for ^{31}P n.m.r. measurements. [d] P–CH_2. [e] P–CH_2 + P–CH_3 protons. [f] P *trans* to CF_3. [g] P *trans* to H. [h] P–CH_2 + –CH_2– protons. [i] ^2J(PP) = 21.3 Hz. [j] CH_3. [k] OCH_3. [l] CH_3.

chlorinated solvents, aromatic hydrocarbons, and, to various extents, in Et_2O and saturated hydrocarbons. They are all white, air-stable, crystalline compounds which can be handled for months in the solid state at room temperature, except for the PMe_3 derivative, (**4**), which is better stored at −15 °C. No decomposition is observed in solution for at least several hours at room temperature.

Compounds of the general formula $[PtH(CF_3)(L\text{–}L)]$ (**11**)—(**14**), having a chelate diphosphine ligand, could be synthesized by reactions (*vii*) or (*viii*) and (*ix*) of the Scheme in good yield (*ca.* 70—88%) by both routes. As noted for the reactions of arsine ligands with *trans*-$[PtH(CF_3)(PPh_3)_2]$, no PPh_3 exchange occurs between (**1**) and a diarsine such as *o*-phenylenebis(dimethylarsine) on stirring for several days in n-heptane at room temperature (r.t). The vdpp and dppe derivatives (**11**) and (**12**), respectively, are only sparingly soluble in most common organic solvents and are indefinitely stable in air. The parent dmpe and dppp compounds (**13**) and (**14**), respectively, are soluble in chlorinated and aromatic hydrocarbons and insoluble in hexanes.

The diphosphine complexes (**11**)—(**14**) do not undergo reductive elimination of H–CF_3 at room temperature. The dmpe derivative, (**13**), slowly reacts with CD_2Cl_2 solvent [equation (2)] affording, in a few days (*ca.* 50% conversion), the chloro derivative $[PtCl(CF_3)(dmpe)]$, by comparison with an authentic sample obtained by reaction of dmpe with *trans*-$[PtCl(CF_3)(PPh_3)_2]$. I.r. (Nujol mull, cm^{-1}): ν(PtCl) 279w. N.m.r. (CD_2Cl_2): ^{19}F, δ(CF_3) −25.5 (dd), $^3J(FP_{trans})$ 58.2, $^3J(FP_{cis})$ 10.0, ^2J(FPt) 566; $^{31}P\text{-}\{^1H\}$, δ(P) (*trans* to CF_3) 29.0 (dq) [^3J(PF) 58.2, ^2J(PP) 3.7, ^1J(PPt) 1 825]; and (*cis* to CF_3) 23.1 p.p.m. (dq) [^3J(PF) 10.0, ^2J(PP) 3.7, ^1J(PPt) 3 745 Hz].

$$[PtH(CF_3)(dmpe)] \xrightarrow[\text{r.t., 4 d}]{+CD_2Cl_2,\ -CHD_2Cl} [PtCl(CF_3)(dmpe)] \quad (2)$$

The selectivity of the Pt–H cleavage, coupled with the basicity of the metal centre derived by the presence of the electron-donating dmpe ligand, suggests that the reaction may proceed through an oxidative addition–reductive elimination process of the solvent, as proposed for the Pt–H cleavage by halogens and alkyl halides in some hydridocyanoalkyl complexes.[5c]

I.r. and n.m.r. spectroscopic data for complexes (**11**)—(**14**) are listed in Tables 1 and 3, respectively.

Mixed isocyanide–phosphine complexes of the type $[PtH(CF_3)(PPh_3)(CNR)]$ (**15**)—(**17**) were obtained in 66—72% yield by reaction of an excess of isocyanide RNC with *trans*-$[PtH(CF_3)(PPh_3)_2]$ in n-heptane at room temperature [reaction (*x*)]. On the basis of ^1H, ^{19}F, and ^{31}P n.m.r. spectra (Table 3) and i.r. analysis (Table 1), they have all been assigned a structure in which a CF_3 group is *trans* to PPh_3 and *cis* to the hydride ligand. Compounds (**15**)—(**17**) are all white, crystalline compounds, stable in air, soluble in polar solvents, and insoluble in hexanes.

Characterization of the Complexes.—The hydridotrifluoromethylplatinum(II) complexes (**1**)—(**17**) have been characterized by their elemental analyses (Table 1), i.r. (Table 1), ^1H, ^{19}F, and ^{31}P n.m.r. spectra (Tables 2 and 3).

I.r. spectra. The *trans* complexes (**1**)—(**10**) and the diphosphine derivatives (**11**)—(**14**) show ν(PtH) as a medium to strong absorption (Nujol mull) in the range 2 015—2 102 and 1 995—2 042 cm^{-1}, respectively. The 1,2-bis(dimethylphosphino)ethane complex (**13**) has the lowest value of ν(PtH), as expected for the higher *trans* influence of alkylphosphine compared to arylphosphine homologues.[20] The mixed isocyanide–phosphine complexes, (**16**) and (**17**), display ν(PtH) as a weak absorption, which is not detected for (**15**). The behaviour shown by (**15**)—(**17**) parallels that found for other hydrido–isocyanide complexes of Pt^{II}, such as $[PtH(CH_2CN)(PPh_3)(CNR)]$[5h] and *trans*-$[PtH(CNR)L_2]^+$ (L = phosphine, R = alkyl, aryl).[21]

All the hydridotrifluoromethyl complexes of Pt^{II} reported here show strong absorptions due to C–F stretchings in the range 940—1 100 cm^{-1} in Nujol mull (Table 1). The highest-

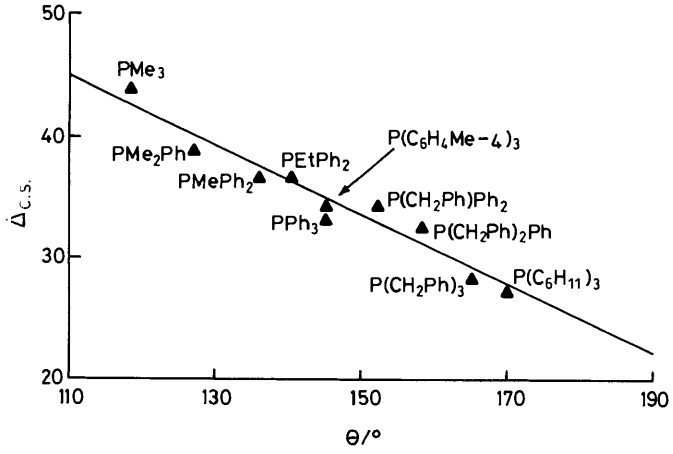


Figure 1. Plot of the co-ordination chemical shift ($\Delta_{c.s.}$) *vs.* the cone angle, θ, of phosphines, L, in complexes *trans*-[PtH(CF_3)L_2] (**1**)—(**10**)

frequency band (*ca.* 1 090 cm^{-1}) is attributed to the symmetric stretching, while the lower absorption (1 000—945 cm^{-1}), which may be split into three peaks, is assigned to the degenerate stretching mode.[22] For perfluoroalkyl complexes, the carbon–fluorine bonds α to the transition metal show reduced C–F stretching frequencies[23] and increased bond lengths[24] compared to aliphatic compounds. This phenomenon has been interpreted as the weakening of the α-C–F bond in transition-metal complexes. Accordingly, this bond has been found to be susceptible to electrophilic attack.[25] Although frequency comparisons between trifluoromethyl complexes are difficult due to the complex splitting of the lower-frequency band, we note that the C–F stretching frequencies in *trans*-platinum(II)–hydridotrifluoromethyl complexes generally shift by *ca.* 5—20 cm^{-1} to lower frequencies with respect to the parent *trans*-halogeno derivatives. This feature, which is presumably related to the stronger σ-donor ability of the hydride ligand compared to halides, also reflects the higher chemical reactivity of the C–F bonds in *trans*-[PtH(CF_3)L_2] complexes compared to their *trans*-halogeno counterparts to electrophilic attack to yield carbene derivatives.[26]

N.m.r. spectra. In their ^{1}H n.m.r. spectra (Table 2), the *trans* complexes (**1**)—(**10**) display a quartet of triplets (flanked by ^{195}Pt satellites) for the hydride resonance arising from coupling with three equivalent fluorine atoms and two equivalent phosphorus nuclei. All the *trans* complexes have chemical shifts (δ −8.2 to −10.5) and ^1J(PtH) (544—657 Hz) values consistent with the hydride ligand *trans* to a strong σ-carbon donor group.[5b,f,9]

The ^{19}F n.m.r. spectra (Table 2) show the expected multiplicity (doublet of triplets for the central CF_3 resonance) confirming the *trans* arrangement of the phosphines. The ^{19}F chemical shifts of the CF_3 group (δ −12.5 to −17.5) fall upfield, by *ca.* 6 p.p.m., with respect to the corresponding *trans*-halogeno derivatives.[14,15b,22] Also, the ^2J(PtF) values for (**1**)—(**10**) are lower by *ca.* 300 Hz than those of the parent *trans*-[PtX(CF_3)L_2] (X = halide) complexes,[14,15b,22] indicating a stronger *trans* influence of the hydride ligand.

The ^{31}P n.m.r. spectra of (**1**)—(**10**) exhibit a central quartet (flanked by ^{195}Pt satellites) for the mutually *trans* phosphine ligands due to coupling with three equivalent fluorine atoms. The ^{31}P chemical shifts and ^1J(PtP) coupling constants depend markedly on the nature of the co-ordinated phosphine ligand. A plot of the co-ordination chemical shifts $\Delta_{c.s.}$ [$\Delta_{c.s.}$ = $\delta(P_{complex}) - \delta(P_{free\ ligand})$] *vs.* the cone angle θ of the phosphine gives the straight line shown in Figure 1. Larger $\Delta_{c.s.}$ values observed for less sterically demanding phosphines are a common feature for phosphine–metal complexes and have been interpreted[27,28] as the opening of the C–P–C angles upon co-ordination, which is larger for phosphines bearing less bulky substituents.

Table 4. Selected i.r.[a] and n.m.r.[b] data for *trans*-[PtH(R)(PPh_3)$_2$] complexes

R	δ(H)	^1J(PtH)/ Hz	ν(PtH)/ cm^{-1}	δ(P)	^1J(PtP)/ Hz	Ref.
Me	−3.77	656	1 968	37.18	3 114	9
$CH_2CH_2CH_2CN$	−4.51	636	1 955[c]	35.1	3 160	5*f*
C_6H_9[d]	−4.65	608	1 920	*e*	*e*	11
CH_2CH_2CN	−5.07	633	2 019[f]	34.4	3 121	5*f*
Ph	−5.71	600	1 966	31.0	3 120	9
CH_2CN	−7.32	746	2 041	32.2	3 034	5*b*
CF_3	−8.34	544	2 069	29.6	3 118	This work

[a] In CH_2Cl_2 unless otherwise stated. [b] In CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [c] This work. [d] N.m.r. data in C_6D_6. [e] Not reported. [f] Nujol mull.

All the other hydridotrifluoromethyl complexes (**11**)—(**17**) have a *cis* arrangement of the hydride and trifluoromethyl ligands on the basis of their n.m.r. spectra (Table 3). The ^{1}H n.m.r. spectra of the diphosphine complexes (**11**)—(**14**) show the expected doublet of double quartets of the hydride resonance for compound (**13**) only, while for (**11**), (**12**), and (**14**) the signal appears as a doublet of quintets owing to accidental equality of $^2J(HP_{cis})$ with ^3J(HF). The ^{19}F n.m.r. spectrum of (**14**) displays the expected multiplicity for the CF_3 resonance (doublet of double doublets), whereas for (**11**)—(**13**) the central signal appears as a doublet of triplets due to the equality of ^3J(HF) with $^3J(FP_{cis})$. The ^{31}P n.m.r. spectra of (**11**) and (**12**) could not be obtained owing to the low solubility of these compounds. The ^{31}P n.m.r. spectrum of (**13**) shows two quartets (flanked by ^{195}Pt satellites) centred at δ 19.3 [^3J(PF) 61] and 33.5 [^3J(PF) 14.1 Hz] attributable to the phosphorus nuclei *trans* and *cis* to the CF_3 group, respectively. Compound (**14**) shows an additional splitting of the ^{31}P resonances due to phosphorus–phosphorus mutual coupling of 21.3 Hz.

The isocyanide–phosphine complexes (**15**)—(**17**) give rise to ^{1}H, ^{19}F, and ^{31}P n.m.r. spectra (Table 3) in agreement with a configuration in which CF_3 is *cis* to H and *trans* to PPh_3 [structure (**C**) in the Introduction]. In fact, ^3J(HF) and ^3J(FP) values are of comparable magnitude with those found for ^3J(HF) and $^3J(FP_{trans})$ in the diphosphine complexes (**11**)—(**14**), in which a CF_3 group is again *cis* to hydride and *trans* to a phosphorus ligand. The structure of complexes (**15**)—(**17**) is analogous to that found for the products of the reaction of *trans*-[PtH(CH_2CN)(PPh_3)$_2$] with excess of RNC ligands. Similar reactions between *trans*-[PtH($CH_2CH_2CH_2CN$)(PPh_3)$_2$] and isocyanides lead instead to the formation of platinum(0) species.[5h]

Discussion

trans *Influence of Trifluoromethyl and Other σ-Carbon Donor Ligands.*—There appears to be some controversy about the *trans* influence estimate of CF_3^- relative to CH_3^-, and other σ-carbon donors, on the basis of structural[29] and spectroscopic (i.r.,[29b] n.m.r.,[22,30] and ^{129}I Mössbauer[31]) determinations in platinum(II) complexes. From these studies it was observed that the n.m.r. *trans* influences of CF_3^- and CH_3^- are high and not very different, whereas the *trans* influence of CF_3^- is considerably smaller than that of CH_3^- on the basis of i.r. and

Table 5. Selected i.r., ^1H, and ^{31}P n.m.r. data for *trans*-[PtH(Cl)L_2] complexes

Compound	I.r./cm^{-1}		^1H N.m.r.[c]				^{31}P-{^1H} N.m.r.[c]	
	ν(PtH)[a]	ν(PtCl)[b]	δ(H)	^1J(PtH)	^2J(HP)	δ(other)	δ(P)	^1J(PtP)
trans-[PtH(Cl)(PPh_3)$_2$]	2 234	275	−16.13 (t)	1 192	13.5		38.57 (s)	3 012
trans-[PtH(Cl)($PMePh_2$)$_2$]	2 217	276	−16.45 (t)	1 257	13.8	2.21 (t)[d]	11.78 (s)	2 890
trans-[PtH(Cl)(PMe_2Ph)$_2$]	2 207	283	−16.83 (t)	1 309	15.6	1.86 (t)[e]	−2.96 (s)	2 742
trans-[PtH(Cl)(PMe_3)$_2$]	2 201	269	−17.14 (t)	1 351	16.7	1.52 (t)[f]	−13.93 (s)	2 597
trans-[PtH(Cl){$P(CH_2Ph)Ph_2$}$_2$]	2 236	282	−16.80 (t)	1 245	11.8	4.11 (t)[g]	27.55 (s)	3 044
trans-[PtH(Cl){$P(CH_2Ph)_2Ph$}$_2$]	2 238	267	−17.47 (t)	1 257	10.8	3.78 (t),[h] 3.74 (t)[h]	28.90 (s)	3 087
trans-[PtH(Cl){$P(CH_2Ph)_3$}$_2$]	2 234	275	−17.62 (t)	1 279	11.9	3.31 (t)[i]	23.92 (s)	2 965
trans-[PtH(Cl){$P(C_6H_{11})_3$}$_2$]	2 216	273	−18.73 (t)	1 279	12.7	1.04—2.20[j]	38.68 (s)	2 803

[a] In CH_2Cl_2 solution. [b] Nujol mull. [c] Spectra recorded in CD_2Cl_2; *J* in Hz; t = triplet, s = singlet; ^1H n.m.r. spectra are referenced to internal $SiMe_4$ and ^{31}P n.m.r. spectra to external 85% H_3PO_4. [d] P–Me: ^2J(HP) + ^4J(HP) = 6.8, ^3J(HPt) = 31.8 Hz. [e] P–Me: ^2J(HP) + ^4J(HP) = 6.9, ^3J(HPt) = 34.7 Hz. [f] P–Me: ^2J(HP) + ^4J(HP) = 7.1, ^3J(HPt) = 33.7 Hz. [g] P–CH_2: ^2J(HP) + ^4J(HP) = 8.0, ^3J(HPt) = 32.3 Hz. [h] The two benzyl groups display two overlapping triplets: ^2J(HP) + ^4J(HP) = 7.1, ^3J(HPt) = 27.9 and 33.0 Hz, respectively. [i] P–CH_2: ^2J(HP) + ^4J(HP) = 7.2, ^3J(HPt) = 31.8 Hz. [j] P–C_6H_{11}, unresolved multiplet.

Mössbauer data. Structural investigations of the σ-donor abilities of CF_3^- and CH_3^- based on Pt–C[29b] and Pt–P[29c] bond distances gave contrasting results. The *trans* influence estimate for σ-C-bonded groups in hydridoplatinum(II) complexes of the type *trans*-[PtH(R)L_2] must be derived from a spectroscopic investigation alone, since *X*-ray diffraction measurements do not provide reliable information on the Pt–H bond lengths.[5d,e,32]

As has been previously reported,[20] the spectroscopic parameters which can be used for this purpose are ^1J(PtH), ^1J(PtP), ν(PtH), and, to a lesser extent, δ(H). A comparison of selected i.r. and n.m.r. data for the series of complexes *trans*-[PtH(R)(PPh_3)$_2$] is given in Table 4. Based on ^1J(PtH) values the CF_3 ligand has the highest *trans* influence among the R groups. The higher *trans* influence of CF_3^- relative to CH_3^- and H^- results also from ^1J(PtH) data for the series of complexes *trans*-[PtH(R){$(C_6H_{11})_3$}$_2$], *e.g.* R = CF_3^- (569) > CH_3^- (648)[8] > H^- (794 Hz).[33] However, the Pt–P coupling constants for phosphorus *trans* to hydride and trifluoromethyl ligands (Table 3) indicate that the ^1J(PtP)-based n.m.r. *trans* influence of hydride is slightly larger than that of CF_3^-.

The Pt–H stretching frequency in *trans*-[PtH(X)L_2] complexes is very dependent on the ligand X, usually decreasing with increasing *trans* influence of X.[20] In *trans*-[PtH(CF_3)L_2] derivatives (Table 1), the Pt–H stretchings display values which are *ca.* 160—200 cm^{-1} lower than those observed for *trans*-[PtH(Cl)L_2] derivatives (Table 5), as expected for the higher *trans* influence of σ-C-donors relative to halides.[20] Conversely, *trans*-[PtH(CF_3)(PPh_3)$_2$] shows ν(PtH) at 2 069 cm^{-1} (CH_2Cl_2), about 100 cm^{-1} higher in frequency than those found in the homologous hydridoplatinum(II) derivatives *trans*-[PtH(R)(PPh_3)$_2$] (R = Me or Ph, Table 4) in the same solvent. Thus, for *trans*-[PtH(R)(PPh_3)$_2$] complexes the order of *trans* influence based on ν(PtH) data is: $C_6H_9^-$ > $CH_2CH_2CH_2CN^-$ > $C_6H_5^-$ ≈ CH_3^- > CF_3^- > Cl^-. The lower *trans* influence of CF_3^- relative to CH_3^- has also been observed in the chloro derivatives *trans*-[PtCl(R)($PMePh_2$)$_2$] (R = Me, CF_3, or C_2F_5) on the basis of 'Pt–Cl' (i.r. and structural) data.[29b] These findings, which apparently contradict the aforementioned n.m.r. *trans* influence, may be tentatively explained by the different electronic mechanism operating on ^1J(PtH) and ν(PtH) parameters. Thus, ^1J(PtH) depends predominantly on the *s* character of the platinum hybrid orbital used in the Pt–H bond (α^2_{Pt}), while ν(PtH) is also sensitive to electrostatic effects induced by the electronegative fluorine atoms.[20,29b,30a]

Unlike ν(PtH) and ^1J(PtH), which indicate variations in the Pt–H bond itself, δ(H) reflects primarily variations at the platinum atom with changes in the ligand *trans* to hydride. It has been found for *trans*-[PtH(X)L_2] complexes that there is an inverse linear correlation between δ(H) and δ(Pt).[34] For hydride *trans* to X in a series of complexes *trans*-[PtH(X)L_2] (X = Cl, Br, or I) the order of increasing shielding is I < Br < Cl.[35] Table 4 reports δ(H) for a series of *trans*-[PtH(R)(PPh_3)$_2$] complexes. As can be seen, increasing electronegativity of the R group causes δ(H) to move to higher field, as noted previously for hydrido derivatives of Pt^{II}.[10,20,36] This trend appears to reflect an increase of the polarization of the Pt–R σ bond on going from methyl to trifluoromethyl, through cyanoalkyl and aryl groups. Thus, in the bond resonances M–R ⟷ M^+R^-, electron-withdrawing substituents on R make the ionic contribution more effective compared to the unsubstituted counterparts. The values of δ(H) (Table 4) are in the range −3.77 to −8.34 and, qualitatively, they are consistent with the higher *trans* influence of R groups compared to halides, *e.g.* δ(H) of *trans*-[PtH(Cl)(PPh_3)$_2$] is −16.13 (Table 5).

cis *Influence of Ligands.*—The *cis* influence of various anionic and neutral ligands appears to be a recognized phenomenon in square-planar platinum(II) complexes, even if it has been investigated less by experimental[10,30,37] and theoretical[38] techniques, compared to the corresponding *trans* influence.[20,37a] Plausible reasons are, either, the generally observed reduction in magnitude of the *cis vs. trans* influence and the more complex mechanism of its transmission, *i.e.* the relative importance of the σ and π contribution for *cis* mutual interactions.

Trifluoromethyl and other σ *carbon donor ligands.* The ^1J(PtP) data for *trans*-[PtH(R)(PPh_3)$_2$] complexes (Table 4) and *trans*-[PtH(Cl)(PPh_3)$_2$] (Table 5) can be used to estimate the *cis* influence of ligands, R. The observed *cis* influence order is: Cl^- > CH_2CN^- > CH_3^- ≈ CF_3^- ≈ $C_6H_5^-$ ≈ $CH_2CH_2CN^-$ > $CH_2CH_2CH_2CN^-$. The σ-donor ligands that exert a relatively small *trans* influence (*e.g.* Cl^- and CH_2CN^-) display a large *cis* influence. A similar trend has been also found in several $[Pt(ttp)X]^+$ complexes (ttp = chelating triphosphine ligand; X = various anionic and neutral ligands) on the basis of ^1J(PtP) data.[37b] However, the above ^1J(PtP)-based *cis* influence order is not supported by structural data on *trans*-[PtH(CH_2CN)(PPh_3)$_2$][5e] and *trans*-[PtH(CF_3)(PPh_3)$_2$] [data obtained from low-temperature (180 K) *X*-ray structural determination],[39] which both display Pt–P bond distances of 2.274 Å. On the other hand, the larger *cis* influence of CF_3^- compared to CH_3^- has been observed in certain platinum(II) complexes on the basis of structural[29b,c] and ^1J(PtP) data.[30b]

Phosphine ligands. For the study of the *cis* influence of a

Table 6. Multiple regression analysis for the fit of ^1J(PtH) *vs.* (both) χ and θ of the phosphine ligands, L, according to equation (3)[a,b]

trans-[PtH(Cl)L_2]	*trans*-[PtH(CF_3)L_2]
L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(CH_2Ph)Ph_2$, or $P(CH_2Ph)_2Ph$	L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $PEtPh_2$, $P(C_6H_4Me\text{-}4)_3$, $P(CH_2Ph)Ph_2$, or $P(CH_2Ph)_2Ph$
r = 0.975	r = 0.960
a = −33 ± 7	a = −21 ± 6
b = 0.1 ± 0.8	b = −0.4 ± 0.6
c = 1 632 ± 65	c = 890 ± 56

[a] r = Multiple correlation coefficient. [b] Error limits are standard errors of estimate.

number of phosphine ligands in complexes of the type *cis*-[$PtCl_2(PBu^n_3)L$],[40] the following *cis* influence series is deduced from ^1J(PtP) data: L = $P(OPh)_3$ > $P(OMe)_3$ > PPh_3 > PMe_2Ph > PBu^n_3, PEt_3. It should be noted that this order is opposite to that generally found for the corresponding *trans* influence of these ligands.[20]

Our series of complexes *trans*-[PtH(CF_3)L_2] (**1**)—(**10**) (Tables 1 and 2) and the parent hydridochloro derivatives *trans*-[PtH(Cl)L_2] (Table 5) provide an opportunity to investigate the *cis* influence of phosphine ligands, L, by studying changes in spectroscopic parameters such as n.m.r. coupling constants, *e.g.* ^1J(PtH), ^2J(PtF), ^2J(HP), and ^3J(FP), and the Pt–H stretching frequency, all reflecting variations in the Pt–H and Pt–CF_3 bonding situation. It is assumed that the effects of replacing two phosphine ligands are additive. Thus, it is expected that the resulting spectral variations will be magnified in these systems as a consequence of the combined *cis* interaction of both ligands on the Pt–H and Pt–CF_3 bonds. A similar approach was anticipated by Clark and co-workers[20] in the observation of ^1J(PtH) variations in some hydridoplatinum(II) compounds of the type *trans*-[PtH(NO_3)L_2] (L = PMe_2Ph or PEt_3) and *trans*-[PtH(PPh_3)L_2]$^+$ (L = PEt_3 or $AsEt_3$). For the two series of compounds the smallest values of ^1J(PtH) were given by PMe_2Ph and $AsEt_3$, respectively. Recently, the determination of *trans* and *cis* influences of various anionic and neutral ligands, Z, in diamineplatinum(II) complexes *cis*-[$Pt(^{15}NH_3)_2Z_2$]$^{m+}$ based on ^{15}N n.m.r. parameters has been reported.[37i]

As for *trans*-[PtH(CF_3)L_2] (**1**)—(**10**) derivatives, inspection of Table 2 shows that progressive substitution of a phenyl group of the co-ordinated PPh_3 ligands in (**1**) by a methyl group (*i.e.*, a better electron-releasing substituent), as in derivatives (**2**)—(**4**), makes ^1J(PtH) increase up to 113 Hz for (**4**) and, consistently, also ^2J(PtF), ^2J(HP), and ^3J(FP) along the same series of complexes. Analogously, the parallel replacement of a phenyl by a benzyl group as in compounds (**5**)—(**7**) causes, again, a smaller but regular increase in ^1J(PtH) with a maximum shift of 41 Hz for (**7**).

Similar trends in ^1J(PtH) are observed in the homologous phenyl, methyl, and benzyl substituents in the parent *trans*-[PtH(Cl)L_2] complexes (Table 5) with maximum shifts of +159 Hz for *trans*-[PtH(Cl)(PMe_3)$_2$] and +87 Hz for *trans*-[PtH(Cl){$P(CH_2Ph)_3$}$_2$], respectively, when starting from *trans*-[PtH(Cl)(PPh_3)$_2$]. Similarly, ^2J(HP) increases from 13.5 to 16.7 Hz on going from the PPh_3 to the PMe_3 derivative through $PMePh_2$ and PMe_2Ph compounds. However, there is no regular trend in ^2J(HP) values in the benzylphosphine series.

Since the above-reported spectroscopic variations appear to be related to changes in the electronic properties of the phosphine ligands, L, we thought it worthwhile to correlate the

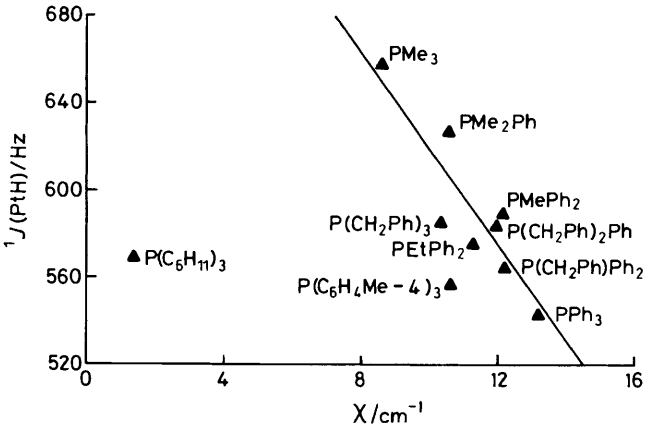


Figure 2. Plot of the electronic parameter, χ, of phosphines, L, *vs.* ^1J(PtH) in complexes *trans*-[PtH(CF_3)L_2] (**1**)—(**10**)

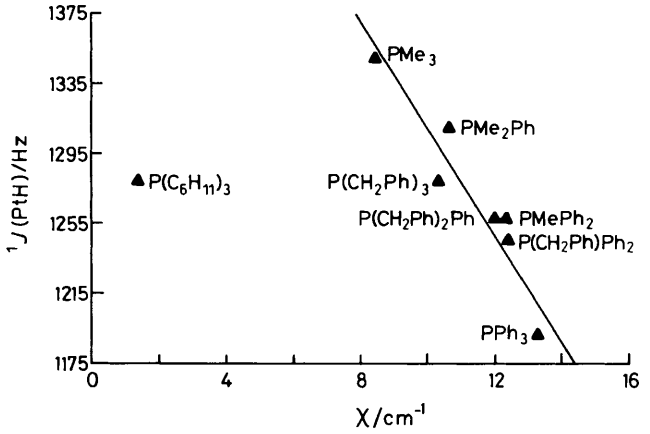


Figure 3. Plot of the electronic parameter, χ, of phosphines, L, *vs.* ^1J(PtH) in complexes *trans*-[PtH(Cl)L_2] (Table 5)

electronic parameter χ[41] with ^1J(PtH) of *trans*-[PtH(X)L_2] (X = CF_3 or Cl) complexes. These plots are shown in Figures 2 (X = CF_3) and 3 (X = Cl). While the correlation of ^1J(PtH) with χ for X = CF_3 is just acceptable if $P(C_6H_{11})_3$ and $P(C_6H_4Me\text{-}4)_3$ are not included in the plot (Figure 2, r = −0.900), such correlation is fairly good for X = Cl, if $P(C_6H_{11})_3$ is again not considered (Figure 3, r = −0.958). The decrease of ^1J(PtH) with decreasing donor ability of the *cis*-phosphine ligands might indicate a corresponding decrease in the electron density of the *s*-valence orbital of the Pt nucleus, to the extent that the coupling is determined by the Fermi contact term.[20] It appears that unusually bulky phosphines such as $P(C_6H_{11})_3$ behave anomalously with respect to this linear correlation which is expected to hold when significant but slight changes in χ are considered within a closely resembling series of ligands.

As steric factors appear to be of paramount importance in determining the ^1J(PtH) values in these complexes, we have also correlated such values with the steric parameter θ as shown in Figure 4 (X = CF_3) and Figure 5 (X = Cl). As can be seen, in both cases the phosphine ligands can be grouped into two distinct sets, each yielding a rather good linear correlation. Thus, in Figure 4, r = −0.994 for L = PMe_3, PMe_2Ph, $PMePh_2$, $P(C_6H_4Me\text{-}4)_3$, and PPh_3; r = −0.995 in Figure 5 for L = PMe_3, PMe_2Ph, $PMePh_2$, and PPh_3. On the other hand, in Figure 4, r = 0.951 for L = PPh_3, $P(CH_2Ph)Ph_2$, $P(CH_2Ph)_2Ph$, and $P(CH_2Ph)_3$ [$P(C_6H_{11})_3$ not included];

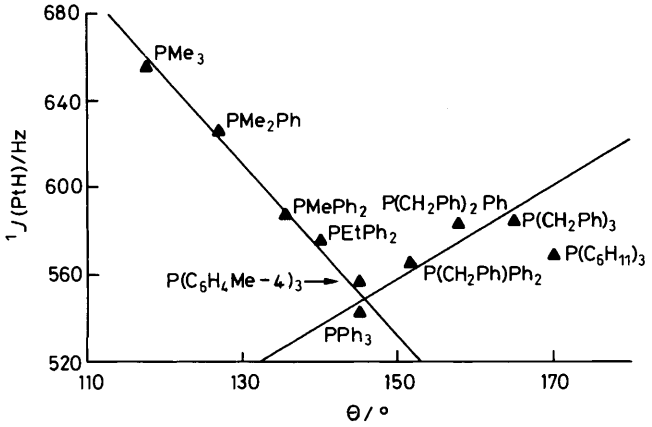


Figure 4. Plot of the cone angle, θ, of phosphines, L, *vs.* ^1J(PtH) in complexes *trans*-[PtH(CF_3)L_2] (**1**)—(**10**)

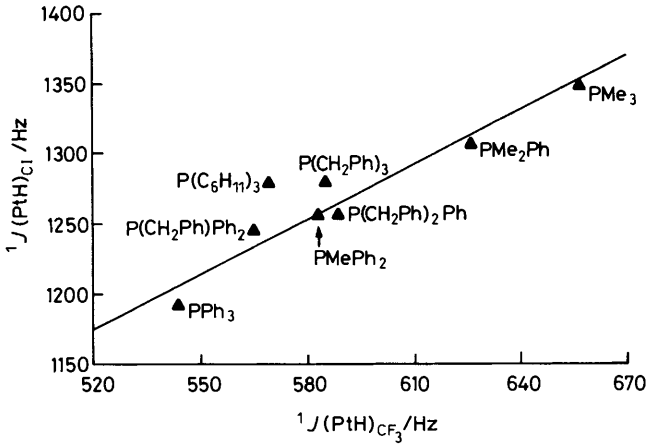


Figure 6. Plot of ^1J(PtH) for *trans*-[PtH(Cl)L_2] (Table 5) *vs.* ^1J(PtH) for *trans*-[PtH(CF_3)L_2] (**1**)—(**10**) complexes

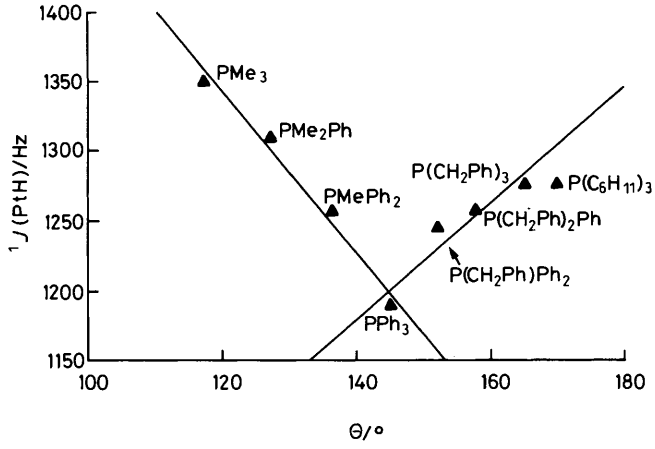


Figure 5. Plot of the cone angle, θ, of phosphines, L, *vs.* ^1J(PtH) in complexes *trans*-[PtH(Cl)L_2] (Table 5)

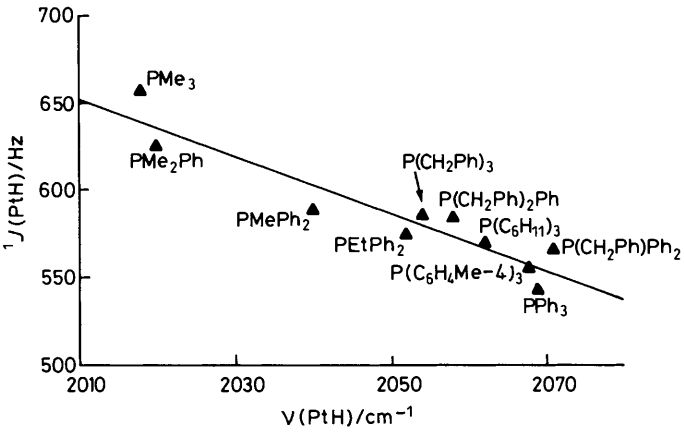


Figure 7. Plot of ^1J(PtH) *vs.* ν(PtH) in complexes *trans*-[PtH(CF_3)L_2] (**1**)—(**10**)

in Figure 5, $r = 0.959$ for L = PPh_3, $P(CH_2Ph)Ph_2$, $P(CH_2Ph)_2Ph$, and $P(CH_2Ph)_3$ [$P(C_6H_{11})_3$ not included]. Apparently, the presence of the bulky benzyl substituents causes sufficient distortion of bond angles to reverse the effect of changes in the ligand cone angle on ^1J(PtH) parameters. The $P(C_6H_{11})_3$ ligand now seems to be 'less anomalous' than in the ^1J(PtH) *vs.* χ correlations. As expected, a plot of ^1J(PtH) for *trans*-[PtH(Cl)L_2] *vs.* ^1J(PtH) for *trans*-[PtH(CF_3)L_2] is fairly linear [Figure 6, $r = 0.974$, $P(C_6H_{11})_3$ not included], indicating that the substituent effect on ^1J(PtH) occurs in a consistent manner throughout the two series.

Both electronic and steric effects can be better taken into account by multilinear correlations of ^1J(PtH) with both χ and θ parameters,[42] according to the model given in equation (3). The results of multiple linear-regression analyses are shown in Table 6.

$$^1J(\mathrm{PtH}) = a\chi + b\theta + c \qquad (3)$$

Figure 7 shows that in the series of hydridotrifluoromethyl complexes *trans*-[PtH(CF_3)L_2] (**1**)—(**10**), there is an inverse linear correlation ($r = -0.943$) between ^1J(PtH) and ν(PtH) (measured in CH_2Cl_2 solution, Table 1). These data provide evidence that for these complexes the n.m.r. and i.r. *cis* influences are opposite in effect, *i.e.* electron-donating substituents in the phosphine ligand (*e.g.* PMe_3) appear to strengthen or weaken the *cis* Pt–H bond depending on whether the n.m.r. coupling constant or the i.r. stretching frequency are taken into account.

A similar behaviour is observed for the hydridochloro derivatives *trans*-[PtH(Cl)L_2] (Table 5) for which high values of ^1J(PtH) are associated with low values of ν(PtH). For such complexes, however, there is no regular trend between values of ν(PtCl) (measured in the solid state) and changes of phosphine ligands. The relationship, if any, could be masked by solid-state effects.

There appear to be no reports on the *cis* influence of ligands in platinum(II) complexes based on i.r. data. It has been observed, however, that for complexes of the type *trans*-[PtCl(X)L_2] the platinum–chlorine bond length and the associated stretching frequency are frequently used as a measure of the *trans* influence of a ligand X.[20] These parameters are inversely correlated so that ligands of high *trans* influence give rise to low values of ν(PtCl) and high values of Pt–Cl distances. If the i.r. structural data were to hold also for the *cis* influence of phosphine ligands in the series of hydrido complexes *trans*-[PtH(X)L_2] (X = CF_3 or Cl), it would be concluded that trialkylphosphines have a higher *cis* influence compared to triarylphosphines, since they give lower values of ν(PtH). This would also mean that, based on i.r. data, trialkylphosphines are ligands of both high *trans* and *cis* influence.

Conclusions

The hydridotrifluoromethyl complex *trans*-[PtH(CF_3)(PPh_3)$_2$] is stable towards nucleophilic attack of a wide series of unidentate phosphine, chelating diphosphine, and isocyanide ligands. In no case is elimination of H–CF_3 observed, the replacement of one or both triphenylphosphines being the only reaction. Also, *trans*-[PtH(Ph)(PEt_3)$_2$] does not readily eliminate benzene when in the presence of PEt_3.[9] On the other hand, *trans*-[PtH($CH_2CH_2CH_2CN$)(PPh_3)$_2$] is observed to undergo rapid elimination of cyanopropane by reaction with various phosphorus ligands,[5c] whereas *trans*-[PtH(CH_2CN)(PPh_3)$_2$] is unaffected by these reagents.[5c] Although there are no data on the reactivity of *trans*-[PtH(Me)(PPh_3)$_2$], it is likely that the resistance of *trans*-[PtH(R)L_2] complexes to decomposition when treated with phosphine ligands is higher for carbon donors bearing electron-withdrawing substituents in the alkyl chain, than for unsubstituted alkyl ligands.

Hydridoplatinum(II) complexes of the type *trans*-[PtH(X)L_2] appear to be a good model for studying the *trans* influence of a ligand X and the *cis* influence of ligands L by observing changes in spectroscopic parameters such as the Pt–H stretching frequency and ^{195}Pt–^{1}H coupling constant. We have observed that ν(PtH) and ^1J(PtH) vary in an opposite manner in these complexes, thus leading to opposite results in the determination of either the *trans* influence of CF_3 relative to other σ-carbon donors and the *cis* influence of phosphine ligands. Possible reasons may be attributed to the different contribution of electrostatic, electronic, and steric effects on the metal–ligand bond.

Experimental

General Procedures and Materials.—All reactions were carried out under an atmosphere of dry nitrogen or argon. n-Heptane was distilled under nitrogen from sodium and degassed before use by a series of freeze–pump–thaw cycles. Diethyl ether was distilled under nitrogen from sodium diphenyl ketyl and degassed as above. All other solvents were of reagent-grade purity and dried over molecular sieves without further purification. I.r. spectra were recorded on a Perkin-Elmer 983 spectrophotometer calibrated against polystyrene film. The ν(PtH) absorptions in CH_2Cl_2 solution were generally of medium intensity and sometimes broad. The reproducibility of $\nu_{max.}$ was estimated to be not better than ±2 cm^{-1}. Proton, ^{19}F, and ^{31}P n.m.r. spectra were obtained on a Varian FT-80A spectrometer. The reproducibility for ^1J(PtH), ^2J(PtF), and ^1J(PtP) was *ca.* ±4 Hz. In all the n.m.r. spectra negative chemical shifts are upfield from the reference used. Multiple regression analysis of n.m.r. data was carried out on a Tektronix 4052 computer system. Melting points were taken on a hot-plate apparatus and are uncorrected. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padova. All the phosphines and arsines were purchased from Strem Chemicals and used without further purification.

Preparation of Halogenotrifluoromethyl Complexes trans-[PtCl(CF_3)L_2] (L = $PMePh_2$, PMe_2Ph, *or* PMe_3).—The general procedure followed in the synthesis of complexes of the type *trans*-[PtCl(CF_3)L_2] (L = $PMePh_2$, PMe_2Ph, or PMe_3) involved stirring, at room temperature for *ca.* 24 h, a suspension of *trans*-[PtCl(CF_3)(PPh_3)$_2$][14] (*ca.* 2.0 mmol) in n-heptane (50 cm^3) with excess of L (*ca.* 5.0 mmol) as previously described for the preparation of *trans*-[PtBr(CF_3)($PMePh_2$)$_2$].[14] The white solids formed were filtered off and recrystallized from CH_2Cl_2–MeOH. The yields were up to 80%, except for the PMe_3 derivative which was *ca.* 40%. The compounds with $PMePh_2$ and PMe_2Ph as ligands showed the same analytical and spectroscopic properties as the same complexes previously reported using other synthetic routes.[22,29b] Analytical and spectroscopic data for *trans*-[PtCl(CF_3)(PMe_3)$_2$] are as follows (Found: C, 18.35; H, 3.85; Cl, 8.00. Calc. for $C_7H_{18}ClF_3P_2Pt$: C, 18.60; H, 4,00; Cl, 7.85%). M.p. 205—207 °C. I.r. (Nujol mull, cm^{-1}): ν(PtCl) 308m, ν_{sym}(CF) 1 090vs, ν_{deg}(CF) 980vs and 965vs. N.m.r. (CD_2Cl_2): ^{1}H, δ(PMe) 1.54 (t) [^2J(HP) + ^4J(HP) 7.6, ^3J(HPt) 27.9]. ^{19}F δ(CF_3) −10.8 p.p.m. (t) [^2J(PtF) 788, ^3J(PF) 18.6]; ^{31}P-{^{1}H} δ(P) −9.7 p.p.m. (q) [^1J(PtP) 2 681, ^3J(PF) 18.6 Hz].

Preparation of Hydridotrifluoromethyl Complexes.—trans-[PtH(CF_3)(PPh_3)$_2$] (**1**).—To a vigorously stirred suspension of *trans*-[PtCl(CF_3)(PPh_3)$_2$][14] (4.80 g, 5.72 mmol) in CH_2Cl_2 (120 cm^3), a solution of $AgBF_4$ (1.13 g, 5.80 mmol) in acetone (6 cm^3) was added. The resulting mixture was stirred for 2 h at room temperature. The white precipitate of AgCl was filtered off and the filtrate concentrated under reduced pressure to *ca.* 20 cm^3. Dropwise addition of Et_2O gave the cationic solvento intermediate *trans*-[Pt(CF_3)(PPh_3)$_2$(solv)]BF_4 [n.m.r.: ^{19}F(CD_2Cl_2), δ(CF_3) −8.1 (t), ^3J(FP) 20.0, ^2J(FPt) 775]; ^{31}P-{^{1}H}, δ(P) 25.0 p.p.m. (q) [^3J(PF) 20.0, ^1J(PPt) 3 015 Hz] as a white solid (92% yield). It was removed by filtration and then suspended in absolute ethanol (100 cm^3) and cooled in an ice–water bath. The salt $NaBH_4$ (0.23 g, 6.0 mmol) dissolved in EtOH (50 cm^3) was slowly added over *ca.* 3 h. The white-cream precipitate formed was filtered off, washed with MeOH (2 × 20 cm^3), and sucked dry. This solid was recrystallized by evaporation under reduced pressure of a CH_2Cl_2–MeOH (1:3, v/v) solution to give white needles of complex (**1**) (3.2 g, 71%).

trans-[PtH(CF_3)($PMePh_2$)$_2$] (**2**). *Method A.* A stirred solution of *trans*-[PtCl(CF_3)($PMePh_2$)$_2$] (1.03 g, 1.47 mmol) in CH_2Cl_2 (50 cm^3) was treated with a solution of $AgBF_4$ (0.20 g, 1.49 mmol) in MeOH (3 cm^3). The mixture was stirred for 10 min, then filtered and evaporated to dryness. Absolute EtOH (60 cm^3) was added and the solution cooled to 0 °C in an ice–water bath. A solution of $NaBH_4$ (0.06 g, 1.58 mmol) in EtOH (20 cm^3) was added dropwise over *ca.* 1 h. A yellow solution formed and water (15 cm^3) was slowly added. A cream solid precipitated. The mixture was left to stand overnight at −15 °C. The pale cream solid was filtered off and dried under vacuum. It was dissolved in Et_2O (80 cm^3), treated with activated charcoal, and stirred for 2 h. After filtration, the solution was concentrated under reduced pressue to *ca.* 10 cm^3. Dropwise addition of n-pentane (50 cm^3) gave complex (**2**) as a white solid. Yield 0.45 g, 46%.

Method B. To a stirred suspension of complex (**1**) (0.79 g, 1.00 mmol) in n-pentane (20 cm^3), $PMePh_2$ (0.6 cm^3, 0.60 g, 3.00 mmol) was added dropwise over *ca.* 20 min. The mixture was stirred at room temperature overnight. The white solid was filtered off, washed with n-pentane (10 cm^3), and recrystallized from Et_2O–n-pentane (3:1, v/v). Yield 0.31 g (46%).

trans-[PtH(CF_3)(PMe_2Ph)$_2$] (**3**). This complex was prepared either by method A (29% yield) or method B (47% yield) as described for (**2**). Recrystallization from Et_2O–n-pentane (2:1, v/v) afforded white needles.

trans-[PtH(CF_3)(PMe_3)$_2$] (**4**). The complex was prepared by method B described for (**2**). Recrystallization from n-pentane gave white needles (25% yield).

trans-[PtH(CF_3){P(CH_2Ph)Ph_2}$_2$] (**5**). To a suspension of complex (**1**) (0.79 g, 1.00 mmol) in n-heptane (20 cm^3) at room temperature was added, in one portion, solid P(CH_2Ph)Ph_2 (0.60 g, 2.17 mmol) and the mixture was stirred overnight. Then the white solid formed was filtered off and recrystallized from C_6H_6–n-hexane (1:3, v/v). Yield 0.60 g (73%).

trans-[PtH(CF_3){P(CH_2Ph)$_2$Ph}$_2$] (**6**). This compound was prepared as outlined for complex (**5**), starting from (**1**) (0.39 g,

0.50 mmol) and $P(CH_2Ph)_2Ph$ (0.30 g, 1.03 mmol). Yield 0.30 g (71%).

trans-$[PtH(CF_3)\{P(CH_2Ph)_3\}_2]$ (**7**). The complex was prepared as described for (**5**), starting from (**1**) (0.39 g, 0.50 mmol) and $P(CH_2Ph)_3$ (0.32 g, 1.05 mmol). Recrystallization from CH_2Cl_2–n-pentane (1:3, v/v) gave white microcrystals. Yield 0.26 g (59%).

trans-$[PtH(CF_3)(PEtPh_2)_2]$ (**8**). To a stirring suspension of complex (**1**) (0.39 g, 0.50 mmol) in n-heptane (10 cm^3), $PEtPh_2$ (0.23 g, 1.07 mmol) was slowly added over a period of 10 min. The white suspension was stirred at room temperature for 1 h. The solid formed was filtered off and recrystallized from Et_2O–n-pentane (2:1, v/v). Yield 0.24 g (69%).

trans-$[PtH(CF_3)\{P(C_6H_{11})_3\}_2]$ (**9**). Stirring, at room temperature, a mixture of $P(C_6H_{11})_3$ (0.30 g, 1.07 mmol) and complex (**1**) (0.39 g, 0.50 mmol) for 6 d in n-heptane (15 cm^3) afforded compound (**9**), which was recrystallized from Et_2O–n-heptane (3:1, v/v). Yield 0.37 g (89%).

trans-$[PtH(CF_3)\{P(C_6H_4Me\text{-}4)_3\}_2]$ (**10**). This complex was obtained from (**1**) (0.39 g, 0.50 mmol) and $P(C_6H_4Me\text{-}4)_3$ (0.32 g, 1.05 mmol) in n-heptane (10 cm^3) as described for (**5**). Recrystallization from CH_2Cl_2–Et_2O (1:3, v/v) gave (**10**) as a white product. Yield 0.36 g (82%).

$[PtH(CF_3)(Ph_2PCH{=}CHPPh_2)]$ (**11**).—This compound was obtained in similar yields (*ca.* 80%) by methods A or B as outlined below for complex (**12**). It was recrystallized from CH_2Cl_2–Et_2O (1:3, v/v).

$[PtH(CF_3)(Ph_2PCH_2CH_2PPh_2)]$ (**12**). *Method A.* To a suspension of $[PtCl(CF_3)(Ph_2PCH_2CH_2PPh_2)]$ (0.80 g, 1.14 mmol) in absolute EtOH (120 cm^3) a solution of $NaBH_4$ (0.11 g, 2.90 mmol) in EtOH (50 cm^3) was added dropwise over *ca.* 3 h. After this time, water (10 cm^3) was added and the insoluble product filtered off and washed with EtOH (20 cm^3) and Et_2O (20 cm^3). Recrystallization from CH_2Cl_2–MeOH (1:3, v/v) afforded (**12**) as a white crystalline product. Yield 0.55 g (69%).

Method B. Compound (**12**) can be obtained from (**1**) (0.79 g, 1.00 mmol) and dppe (0.41 g, 1.03 mmol) in n-heptane (30 cm^3) at room temperature for 12 h. The white solid was filtered off, washed with Et_2O (3 × 5 cm^3), and recrystallized from CH_2Cl_2–MeOH (1:3, v/v). Yield 0.54 g (81%).

$[PtH(CF_3)(Me_2PCH_2CH_2PMe_2)]$ (**13**). A suspension of (**1**) (0.95 g, 1.20 mmol) in n-heptane (40 cm^3) was treated with dmpe (0.23 cm^3, 0.18 g, 1.20 mmol) at room temperature and the reaction mixture stirred for 2 h. The resulting white solid was filtered off and recrystallized from CH_2Cl_2–n-pentane (1:4, v/v). Yield 0.40 g (79%).

$[PtH(CF_3)(Ph_2PCH_2CH_2CH_2PPh_2)]$ (**14**). This compound was prepared as described in method B for (**12**), starting from (**1**) (0.39 g, 0.50 mmol) and dppp (0.18 g, 0.51 mmol). Recrystallization from CH_2Cl_2–n-pentane (1:5, v/v) gave (**14**). Yield 0.30 g (88%).

$[PtH(CF_3)(PPh_3)(CNC_6H_3Me_2\text{-}2,6)]$ (**15**). To a suspension of complex (**1**) (0.52 g, 0.65 mmol) in n-heptane (20 cm^3), solid 2,6-dimethylphenyl isocyanide (0.26 g, 1.98 mmol) was added in one portion and the reaction mixture stirred overnight at room temperature. The white product obtained was filtered off and recrystallized from C_6H_6–Et_2O–n-pentane (1:1:3, v/v). Yield 0.31 g (72%).

$[PtH(CF_3)(PPh_3)\{CNC_6H_4(OMe)\text{-}4\}]$ (**16**). This compound was prepared from (**1**) (0.39 g, 0.50 mmol) and 4-$MeOC_6H_4NC$ (0.20 g, 1.50 mmol) as described for (**15**). Yield 0.22 g (66%).

$[PtH(CF_3)(PPh_3)(CNBu^t)]$ (**17**). This complex was prepared similarly to (**15**) starting from (**1**) (0.39 g, 0.50 mmol) and Bu^tNC (0.13 g, 1.56 mmol). Yield 0.21 g (68%).

Preparation of trans-$[PtH(Cl)L_2]$ *Complexes.*—L = PPh_3. This complex was obtained by hydrazine reduction[43,44] of *cis*-$[PtCl_2(PPh_3)_2]$[45] and recrystallized from CH_2Cl_2–MeOH (1:5, v/v) as *trans*-$[PtH(Cl)(PPh_3)_2]$·MeOH.[46]

L = $PMePh_2$,[47] PMe_2Ph,[47] *or* PMe_3.[44] These complexes were prepared according to literature methods.

L = $P(CH_2Ph)Ph_2$. This complex was prepared from *cis*-$[PtCl_2\{P(CH_2Ph)Ph_2\}_2]$[48] using the same procedure as described for *trans*-$[PtH(Cl)(PMePh_2)_2]$.[47] Yield 82%; m.p. 206—209 °C (Found: C, 58.35; H, 4.60. Calc. for $C_{38}H_{35}ClP_2Pt$: C, 58.20; H, 4.50%).

L = $P(CH_2Ph)_2Ph$. A suspension of *trans*-$[PtH(Cl)(PPh_3)_2]$ (1.00 g, 1.32 mmol) and $P(CH_2Ph)_2Ph$ (1.50 g, 5.20 mmol) in n-heptane (50 cm^3) was stirred at room temperature for 15 h. The white solid obtained was filtered off, washed with n-heptane (3 × 10 cm^3), and recrystallized from CH_2Cl_2–MeOH (1:4, v/v). Yield 0.92 g, 86% m.p. 138—140 °C (Found: C, 59.45; H, 5.05. Calc. for $C_{40}H_{39}ClP_2Pt$: C, 59.15; H, 4.85%).

L = $P(CH_2Ph)_3$. This compound was prepared and recrystallized by the same procedure described above for *trans*-$[PtH(Cl)\{P(CH_2Ph)_2Ph\}_2]$ starting from *trans*-$[PtH(Cl)(PPh_3)_2]$ (0.75 g, 1.00 mmol) and $P(CH_2Ph)_3$ (1.21 g, 4.00 mmol). Yield 0.67 g (80%); m.p. 162—163 °C (decomp.).

L = $P(C_6H_{11})_3$. This derivative was prepared in 60% yield according to a published procedure,[49] treating *trans*-$[PtH(Cl)(PEt_3)_2]$[50] with excess of $P(C_6H_{11})_3$ in refluxing EtOH for 1 h. After cooling, the white precipitate was filtered off and recrystallized from CH_2Cl_2–EtOH (1:4, v/v); m.p. 235—240 °C.

Preparation of trans-$[PtH(Me)(PPh_3)_2]$.—A solution of *trans*-$[PtCl(Me)(PPh_3)_2]$ (0.77 g, 1.0 mmol) in CH_2Cl_2 (60 cm^3) was treated with a solution of $AgBF_4$ (0.20 g, 1.03 mmol) in acetone (2 cm^3) at room temperature. After 1 h the white AgCl was filtered off and the solution taken to dryness. Methanol (40 cm^3) was added to the solid residue and the suspension stirred at 0 °C in an ice–water bath. A solution of NaOH (0.16 g, 4.00 mmol) in MeOH (15 cm^3) was added in one portion and the mixture heated under N_2 at 50—60 °C for *ca.* 1 h. The white solid was filtered off and recrystallized from C_6H_6–MeOH (1:4, v/v). Yield 0.43 g (58%); m.p. 148—150 °C (decomp. with effervescence) (Found: C, 60.55; H, 4.80. Calc. for $C_{37}H_{34}P_2Pt$: C, 60.40; H, 4.65%). I.r. (Nujol mull, cm^{-1}): ν(PtH) 1 932m. N.m.r. (CD_2Cl_2): ^1H, δ(CH_3) −0.32 (t) [^2J(HPt) 52, ^3J(HP) 5.5, ^3J(HPtCH) 2.2], δ(H) −3.67 (tq) [^1J(PtH) 654, ^2J(HP) 18.2, ^1J(HPtCH) 2.2]; ^{31}P-$\{^1H\}$ δ(P) 37.08 p.p.m. (s), [^1J(PtP) 3 114 Hz].

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