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Oxidative additions to bis(trifluoromethyl)platinum(II) complexes with *N*-donor ligands

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Abstract

Reaction of *cis*-$Pt(CF_3)_2L_2$ (L = pyridine (py); L_2 = 2,2′-bipyridyl (bipy), *N,N,N′,N′*-tetramethylethylenediamine (tmen)) with halogens, X_2, in dry CH_2Cl_2 gave initially the isomer of $Pt(CF_3)_2X_2L_2$ in which the halogen has added *trans* across the original square plane. The initial products, $Pt(CF_3)_2X_2(bipy)$ (X = Cl, Br), slowly isomerize under light to the isomer with the two X-ligands *cis*, apparently to relieve steric pressure.

Cis-$Pt(CF_3)_2L_2$ with L = py, 1/2(bipy) (but not that with L = 1/2(tmen)) reacted slowly with alkyl halides, RX (MeI, $PhCH_2Br$, CF_3I), in acetone under light to give $Pt(CF_3)_2RXL_2$. Only the isomer of $Pt(CF_3)_2MeI(bipy)$ with methyl *trans* to iodide was observed, but for the pyridine analogue two isomeric products were in equilibrium. $Pt(CF_3)_2MeI(py)_2$ also slowly lost MeI in acetone; addition of NaI or py to the solution accelerated the reaction. $Pt(CF_3)_2(bipy)$ with $PhCH_2Br$ gave only the isomer of $Pt(CF_3)_2$-$(CH_2Ph)Br(bipy)$ in which benzyl bromide had added *trans* across the square plane, but with $Pt(CF_3)_2py_2$ only the isomer of $Pt(CF_3)_2$-$(CH_2Ph)Brpy_2$ with benzyl *cis* to bromide was observed. Subsequent reaction in the presence of excess $PhCH_2Br$ gave, among other products, $[PhCH_2NC_5H_5]$-$[Pt(CF_3)_2Brpy]$. *Fac*-$Pt(CF_3)_3IL_2$ was the only significant product from the reactions involving CF_3I.

Aspects of ^{19}F, ^{13}C and ^{195}Pt NMR spectra, and IR spectra, are discussed.

Introduction

There is an extensive literature on the chemistry of di- and tri-methylplatinum(IV) complexes, dating back to the preparation of $[PtMe_3Cl]_4$ in 1907 [1], but much less is known of analogous platinum(IV) complexes with other alkyl groups. For example, the only other trialkylplatinum(IV) compound reported with all three alkyl groups the same is $[PtEt_3Cl]_4$ (prepared from $PtCl_4$ and Et_2Hg) [2]. The chemistry of triethylplatinum(IV) compounds has not been developed, probably because of the view that replacement of methyl by ethyl would cause only minor variations in

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behaviour. However, significant differences would be expected with an alkyl group very different from methyl. Such a group is the trifluoromethyl group.

It has long been recognized that perfluoroalkyl transition metal complexes in general have very different properties from corresponding alkyl complexes. For example, they have enhanced thermal stability [3] and metal–carbon bond lengths are very short [4]. In platinum(II) complexes, perfluoroalkyl groups have a high NMR *trans* influence, comparable to that of methyl [5,6] but a much lower structural *trans* influence on a Pt–Cl bond [7]. Replacement of methyl groups bound to platinum(II) by trifluoromethyl groups leads to deactivation of the metal centre toward oxidative addition reactions [8]. The most effective explanation of this difference in properties remains that of Hall and Fenske [9], who analysed the bonding in $MeMn(CO)_5$ and $(CF_3)Mn(CO)_5$. They concluded that:

(a) both CH_3 and CF_3 form strong covalent bonds to transition metals (giving a high *trans* influence);

(b) the effect of this electron transfer to the metal, combined with the electronegativity of the fluorine atoms, gives the trifluoromethyl carbon atom a positive potential, which affects the electrons on a neighbouring atom (i.e. the metal) (inhibiting oxidative addition to the metal);

(c) the C–M bond has much greater carbon *s*-character in the trifluoromethyl complex (giving short metal–carbon bonds).

A potential route to trifluoromethyl complexes of platinum(IV) involves oxidative additions to trifluoromethylplatinum(II) compounds, but, as noted above, trifluoromethyl groups tend to deactivate platinum(II) toward these reactions. Thus, although the powerful oxidant X_2 will oxidize *cis*-$Pt(CF_3)_2L_2$ (L = EtNC, 1/2(bipy), PMe_2Ph) to $Pt(CF_3)_2X_2L_2$ (X_2 = halogen) [10], no reaction has been observed with the weaker oxidants MeI and CF_3I [8].

The most reactive dimethylplatinum(II) complexes towards oxidative addition appear to be *cis*-$PtMe_2py_2$ [11–13], $PtMe_2$(bipy) [14], and $PtMe_2$(phen) [14,15]. Thus in the present work, we examined the reactivity toward oxidative addition of *cis*-$Pt(CF_3)_2py_2$ (**1**) and $Pt(CF_3)_2$(bipy) (**2**). $Pt(CF_3)_2$(tmen) (**3**) might be expected to be less reactive because of steric hindrance by the *N*-methyl groups. Its reactions were included for comparison with those of **1** and **2**.

In the study we used oxidative addition reagents with a range of oxidizing powers, from halogens, through the less reactive reagents MeI, CF_3I, and $PhCH_2Br$, to the weak reagent PhBr. Clark and Manzer [10] have previously shown that $Pt(CF_3)_2$(bipy) (**2**) reacts with iodine to give $Pt(CF_3)_2I_2$(bipy).

A preliminary account of some of this work has been published [11].

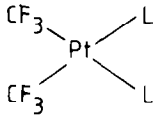
Results and discussion

Analytical data for new compounds are given in Table 1, ^{19}F and other NMR data for the trifluoromethyl groups in Table 2, and ^1H and ^{13}C NMR data in Tables 3 (pyridine complexes) and 4 (bipy complexes).

Reactions of $Pt(CF_3)_2L_2$ with halogens

At room temperature, complexes **1**, **2** and **3** in dry dichloromethane * reacted

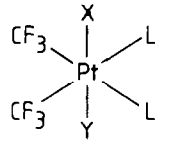
* With **1** or **3**, the reaction with Cl_2 in moist dichloromethane gave an additional species in solution whose chemistry is under investigation.



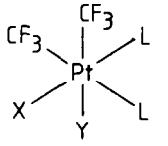
L = py (1)

L = ½(bipy) (2)

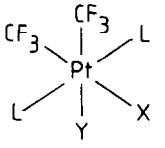
L = ½(tmen) (3)



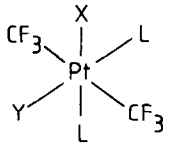
Isomer a



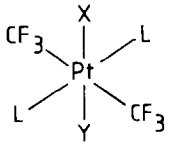
Isomer b



Isomer c



Isomer d



Isomer e

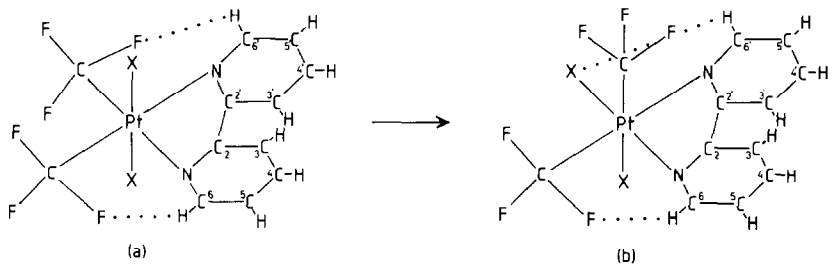
X	Y	L = py	L_2 = bipy	L_2 = tmen
Cl	Cl	**4**	**5**	**6**
Br	Br	**7**	**8**	**9**
I	I	**10**	**11**	**12**
CH_3	I	**13**	**14**	
$C_6H_5CH_2$	Br	**15**	**16**	

immediately with a slight excess of Br_2 or I_2, or with Cl_2 bubbled through the solution. The geometry of the platinum(IV) product was established by ^{19}F NMR spectroscopy. In each case the spectrum showed one singlet with satellites, corresponding to equivalent trifluoromethyl groups coupling to ^{195}Pt ($I = 1/2$) in those molecules (34% abundance) which contained that isotope of platinum. Isomer b, in which the trifluoromethyl groups are non-equivalent can therefore be ruled out as the initial product of reaction, since it is extremely unlikely that both chemical shifts and Pt–CF_3 coupling constants for the two species would accidentally coincide. Isomers d and e can also be ruled out, since mutually *trans* trifluoromethyl groups would be expected to lead to a very low Pt–CF_3 coupling constant (cf. 289 Hz in isomer c with L = PMe_2Ph, X = Y = I [10]), very much lower than the range of

$^2J(Pt-CF_3)$ observed for our compounds, 377–456 Hz (Table 2). These values are significantly less than those for $^2J(Pt-CF_3)$ in the platinum(II) starting materials *cis*-$Pt(CF_3)_2L_2$ (741–794 Hz), as commonly found when platinum(II) complexes are oxidized to platinum(IV), with the ligands *trans* to CF_3 unchanged [5,10]. Isomer c (and isomer e) could not exist for the chelating ligands. Since the NMR parameters for the compounds with the three different *N*-donor ligands are quite similar, it is unlikely that a different isomer forms for the pyridine complexes. This leaves isomer a as the initial product of all of the oxidative addition reactions of *cis*-$Pt(CF_3)_2L_2$ with halogens. This is consistent with what is known about the initial product of the vast majority of oxidative addition reactions to platinum(II) – that the addition takes place *trans* across the original square plane [8,16–18].

Solutions of $Pt(CF_3)_2X_2L_2$ (isomer a) in acetone were allowed to stand for prolonged periods in the dark, and under normal laboratory lighting (fluorescent tubes). ^{19}F NMR was used to monitor the solutions. Over a two week period in the light, the bipyridyl complexes $Pt(CF_3)_2X_2(bipy)$ (X = Cl, **5a**, X = Br, **8a**) were converted completely into a second isomer, whose structure could be determined from the ^{19}F spectrum. This spectrum showed two 1/3/3/1 quartets of equal intensity each flanked by satellite quartets. The two trifluoromethyl groups were therefore non-equivalent, with a small coupling (4–5 Hz) between the two sets of fluorine nuclei. The only isomer possible for $Pt(CF_3)_2X_2(bipy)$ with non-equivalent CF_3 groups is isomer b. The two values of $^2J(Pt-CF_3)$ are so similar that an unequivocal assignment of the two ^{19}F signals to particular trifluoromethyl groups is not possible. In *fac*-$Pt(CF_3)_3X(bipy)$ (X = Br, **21**; X = Cl, **22**) in which the splitting pattern makes assignment definite (see below), it is noted that the chemical shift for the trifluoromethyl group *trans* to halide is more negative and has a lower $Pt-CF_3$ coupling constant than the trifluoromethyl groups *trans* to bipyridyl (Table 2). On this basis, the tentative assignments given in Table 2 for **5b** and **8b** were made.

None of the other complexes $Pt(CF_3)_2X_2L_2$ showed any tendency to isomerize, although $Pt(CF_3)_2I_2py_2$ (**10a**) in acetone in the light slowly underwent elimination of I_2 to regenerate *cis*-$Pt(CF_3)_2py_2$ (**1**). In isomer a of the bipyridyl complexes there is considerable steric pressure in the plane C_2PtN_2 in which the bipy ligand is constrained to lie, in particular between the trifluoromethyl groups and H(6), H(6′) (Fig. 1a). The proximity of trifluoromethyl groups to C(6), C(6′) is evidenced by the "through space" $^{19}F-^{13}C$ coupling constants to these carbon nuclei discussed below. For the smaller halides, Cl and Br, this steric pressure may be partly relieved by the isomerization reaction, which replaces CF_3 in the plane of bipyridyl with X (Fig. 1b), but for the bulkier iodide ligand this change would not be favourable, so isomerization does not occur. By this reasoning, steric pressure would be further relieved for X = Cl, Br by a further isomerization to isomer d, in which both of the trifluoromethyl ligands would be removed from the plane of the bipyridyl ligand. However, this would cause the high *trans* influence CF_3 groups to be mutually *trans*, and this is much less favoured electronically than isomers in which CF_3 is *trans* to ligands with a weaker *trans* influence, bipy and X [8]. This isomerization therefore does not occur. The reductive elimination of I_2 from $Pt(CF_3)_2I_2py_2$ (**10a**) is probably also assisted by steric pressure. The organic ligands will interact more with the iodide ligands than in the bipyridyl case, because the pyridine molecules are not constrained to the C_2PtN_2 plane.



(a) (b)

X = Cl 5a X = Cl 5b

X = Br 8a X = Br 8b

Fig. 1. Steric interactions in isomers of $Pt(CF_3)_2X_2(bipy)$.

These isomerization reactions probably proceed by rearrangement of five-coordinate complexes $Pt(CF_3)_2X(bipy)^+$ formed by ionization of one of the halide ligands. As with many other platinum(IV) complexes [19–21], light absorption assists in the labilization of ligands which are normally inert.

Reactions of $Pt(CF_3)_2L_2$ with methyl iodide

$Pt(CF_3)_2(bipy)$ (**2**) in acetone with a large excess of MeI (50 mol equivalents) was converted almost completely during 24 h under normal laboratory lighting into a platinum(IV) product $Pt(CF_3)_2MeI(bipy)$, as shown by the ^{19}F NMR spectrum of the reaction solution. One singlet with satellites was observed, which allowed the structure of the product to be assigned as **14a**. This product was isolated from solution, and gave satisfactory analyses (Table 1).

The ^1H-decoupled ^{13}C spectrum of **14a** showed a septet with satellites for the methyl carbon, from coupling (4.9 Hz) of this nucleus with the six equivalent ^{19}F nuclei. Its ^1H spectrum in $(CD_3)_2CO$ showed a septet (from a small F–H coupling, 0.5 Hz) with satellites.

With *cis*-$Pt(CF_3)_2py_2$ (**1**) under similar reaction conditions the reaction with MeI produced a mixture of isomers of $Pt(CF_3)_2MeIpy_2$. The major isomer (80% of total) gave a singlet with satellites in the ^{19}F spectrum, and so was formulated as **13a**. The minor isomer showed two quartets with satellites arising from non-equivalent CF_3 groups with F–F coupling, and so was formulated as **13b**. By comparison with the data for **13a** and for *fac*-$Pt(CF_3)_3Ipy_2$ (**19**, see below) the CF_3 group with the higher shielding and lower Pt–CF_3 coupling constant was assigned as that *trans* to iodide, as shown in Table 2. There was no further change in the spectrum of this solution with time (in the presence of excess methyl iodide).

An attempt was made to separate the isomers **13a** and **13b** by passing their solution in CH_2Cl_2 down a Florisil column. Each fraction was evaporated to dryness in a rotary evaporator, then redissolved in acetone. From the ^{19}F NMR spectra of these fractions it became evident that passage down the column was causing almost total conversion of **13a** into **13b**, since the spectra showed peaks due to the latter isomer, with only weak peaks from **13a**. When a solution of **13b** was allowed to stand in pure acetone, it was converted entirely into **13a** (along with reductive elimination of MeI, see below).

The isomers **13a** and **13b** thus appear to be in fairly delicate balance. The equilibrium between them appears to be influenced by solvent, so that the presence

Table 1

Analytical data

Compound	Colour	Yield (%)	Analysis (Found (calc) (%))				
			C	H	N	F [a]	Other [a]
cis-$Pt(CF_3)_2py_2$ (**1**)	White	89	29.3 (29.3)	2.2 (2.1)	5.8 (5.7)	23.3 (23.2)	
$Pt(CF_3)_2$(bipy) (**2**)	Pale yellow	76	29.5 (29.5)	1.6 (1.7)	5.8 (5.7)		
$Pt(CF_3)_2$(tmen) (**3**)	White	82	21.4 (21.4)	3.6 (3.6)	6.3 (6.2)		
$Pt(CF_3)_2Cl_2py_2$ (**4a**)	Yellow	52	25.7 (25.6)	1.9 (1.8)	4.9 (5.0)	20.6 (20.3)	
$Pt(CF_3)_2Cl_2$(bipy) (**5a**)	White	87	25.8 (25.7)	1.5 (1.4)	4.9 (5.0)	20.1 (20.4)	
(**5b**)	White		26.2 (25.7)	1.6 (1.4)	4.8 (5.0)		
$Pt(CF_3)_2Cl_2$(tmen) (**6a**)	Yellow	69	18.4 (18.5)	3.2 (3.1)	5.3 (5.4)	22.1 (21.9)	
$Pt(CF_3)_2Br_2py_2$ (**7a**)	Yellow	82	22.1 (22.1)	1.8 (1.6)	4.2 (4.3)	17.5 (17.5)	Br 24.3 (24.5)
$Pt(CF_3)_2Br_2$(bipy) (**8a**)	Dark yellow	92	22.0 (22.2)	1.5 (1.2)	4.4 (4.3)	17.7 (17.6)	Br 25.5 (24.6)
(**8a** + **8b**)	Dark yellow		22.4 (22.2)	1.3 (1.2)	4.3 (4.3)		
$Pt(CF_3)_2Br_2$(tmen) (**9a**)	Yellow	89	15.9 (15.8)	2.7 (2.7)	4.7 (4.6)	19.1 (18.7)	Br 26.7 (26.2)
$Pt(CF_3)_2I_2py_2$ (**10a**)	Dark purple	71	19.1 (19.3)	1.3 (1.4)	3.7 (3.8)	15.6 (15.3)	
$Pt(CF_3)_2I_2$(bipy) (**11a**)	Red-brown	89	19.2 (19.4)	1.2 (1.1)	3.8 (3.8)	15.7 (15.3)	
$Pt(CF_3)_2I_2$(tmen) (**12a**)	Black	82	13.5 (13.7)	2.4 (2.3)	4.0 (4.0)	16.3 (16.2)	I 36.3 (36.1)
$Pt(CF_3)_2MeIpy_2$ (**13a** + **13b**)	White	47	24.9 (24.7)	2.2 (2.1)	4.4 (4.4)	18.0 (18.0)	
$Pt(CF_3)_2MeI$(bipy) (**14a**)	Orange	78	24.9 (24.7)	1.8 (1.8)	4.4 (4.4)	18.3 (18.1)	
$Pt(CF_3)_2(CH_2Ph)Br$(bipy) (**16a**)	White	15	33.9 (34.6)	2.2 (2.3)	4.5 (4.2)		
fac-$Pt(CF_3)_3Ipy_2$ (**19**)	Pale yellow	74	22.8 (22.7)	1.3 (1.5)	4.3 (4.1)	25.2 (24.9)	I 18.0 (18.5)
fac-$Pt(CF_3)_3I$(bipy) (**20**)	Orange	57	22.6 (22.8)	1.1 (1.2)	4.1 (4.1)	24.6 25.0)	
fac-$Pt(CF_3)_3Br$(bipy) (**21**)	White	52	24.6 (24.5)	1.4 (1.3)	4.8 (4.4)		
fac-$Pt(CF_3)_3Cl$(bipy) (**22**)	White	50	26.5 (26.3)	1.6 (1.4)	5.1 (4.7)		

[a] Where measured.

of MeI mixed with acetone in the initial reaction mixture shifts the equilibrium toward **13b** to the extent that significant proportions of this isomer are observed in this solution.

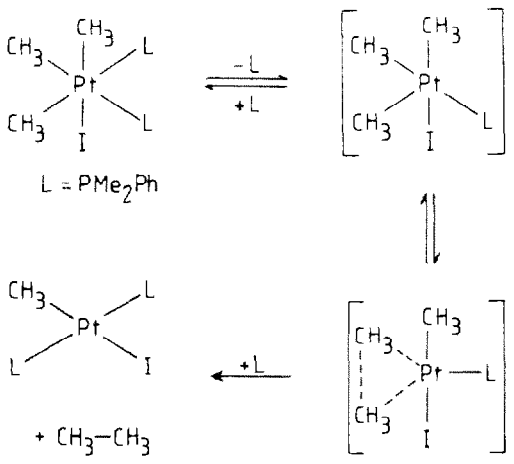
The slow reactions of **1** and **2** with methyl iodide contrast with the instantaneous reactions with halogens discussed above, and with the very rapid reactions of *cis*-$PtMe_2L_2$ with MeI [12]. Methyl iodide is less reactive as an oxidative addition reagent than the halogens, and, as expected (see Introduction) the complexes with trifluoromethyl groups are less reactive towards oxidative addition than those with methyl groups. Repetition of these reactions under conditions kept as similar as possible gave varying yields of the platinum(IV) products. This, coupled with the sensitivity of the reactions to exposure to light, suggests that generation of free radicals is involved in the mechanism of the oxidative addition reaction. The radical scavenger duroquinone was added to a solution of **2** and MeI in acetone, with the expectation that the reaction would be slowed relative to a "control" reaction without duroquinone. The ^{19}F spectrum of the reaction mixture after 24 h, however, showed a number of sets of peaks which were never observed in the absence of duroquinone, which must therefore influence the course of the reaction in a more profound way than by scavenging radicals. Addition of benzoyl peroxide as a radical initiator caused only a slight increase in rate.

Under conditions in which reaction of **1** or **2** with MeI proceeded to completion, $Pt(CF_3)_2$(tmen) (**3**) did not react at all with MeI. The steric hindrance provided by the *N*-methyl groups combines with the deactivating effect of the CF_3 groups to inhibit reaction.

When an acetone solution of $Pt(CF_3)_2MeIpy_2$ (**13a**) was allowed to stand (exposed to laboratory lighting), slow loss of MeI occurred to regenerate the platinum(II) complex **1**. After 14 d only 19% of the original Pt^{IV} complex remained. Although this solution contained no detectable amounts of **13b**, it is, of course, possible that the reductive elimination proceeded via this isomer, in which the methyl group is *cis* to iodide. When a solution of **13b** in acetone was kept at room temperature, isomerization to **13a** occurred too quickly to allow observation of whether reductive elimination of MeI was faster from one isomer than the other. When a solution of $Pt(CF_3)_2MeI$(bipy) (**14a**) in acetone was exposed to light, MeI was again lost, but much more slowly than from **13a**. After one month, 62% of the original Pt^{IV} complex remained.

Analogous trimethylplatinum(IV) complexes, *fac*-$PtMe_3IL_2$, where L is a nitrogen-donor ligand, do not undergo reductive elimination reactions under comparable conditions [12]. Where L has a higher *trans* effect (e.g. where L is a tertiary phosphine), reductive elimination of ethane occurs more readily (e.g. on heating) [22–24]. While details of the mechanism of reductive elimination vary from complex to complex [22], a step common to most of the proposed mechanisms is the initial loss of one ligand to form a five-coordinate intermediate from which reductive elimination occurs. Re-association of the ligand previously lost gives the platinum(II) product. (e.g. reductive elimination of C_2H_6 from *fac*-$PtMe_3I(PMe_2Ph)_2$, Scheme 1 [23]). A mechanism has been proposed for the reductive elimination of iodobenzene from $PtPh_2I_2(PEt_3)_2$, in which the first step is dissociation of iodide [25].

In an attempt to determine whether a similar mechanism might apply to the reductive elimination of MeI from $Pt(CF_3)_2MeIpy_2$ (**13a**), 3–4 mol equivalents of NaI or pyridine were added to an acetone solution of **13a**, and the course of the reaction was compared (by ^{19}F NMR spectroscopy) with that in a solution without these additives. To our surprise, reductive elimination of MeI occurred more rapidly in the solution containing added ligands than in the solution containing only **13a**.



Scheme 1

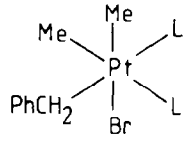
Addition of other potential ligands such as bipy, chloride, or bromide has a similar effect. The reductive elimination reaction from **13a** therefore appears to occur by an associative mechanism, rather than the dissociative mechanism mentioned above.

Steric interactions in the platinum(IV) complex will be relieved by reductive elimination. That steric factors can be important in some reactions, is illustrated by the much greater stability of *fac*-$PtMe_3I(Ph_2PCH_2CH_2PPh_2)$ [26] than of *fac*-$PtMe_3I(PPh_3)_2$ [23], which instantaneously decomposes by reductive elimination of MeI (unlike most trimethylplatinum(IV) complexes which lose ethane). The much slower elimination of MeI from $Pt(CF_3)_2MeI(bipy)$ (**14a**) than from **13a** may be related to lower steric interactions involving iodide, because the bipyridyl ligand is constrained into the PtN_2 plane.

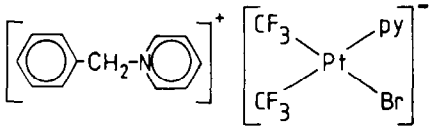
Reactions of $Pt(CF_3)_2L_2$ with benzyl bromide

As with methyl iodide, benzyl bromide in excess reacted with $Pt(CF_3)_2L_2$ where L = py (**1**) or 1/2(bipy) (**2**) but not when L = 1/2(tmen) (**3**).

When an acetone solution of **1** and benzyl bromide (50 mol equivalents) was kept at room temperature, peaks due to **1** slowly decreased as new peaks (quartets with satellites), that could be assigned to isomer b of $Pt(CF_3)_2(CH_2Ph)Brpy_2$ (i.e., structure **15b**) increased. No peaks appeared that could be due to isomer **15a**, which would be formed if benzyl bromide added *trans* across the original square plane. There is no firm basis for assigning the signals to particular trifluoromethyl groups in **15b**. The benzyl protons, as expected from the symmetry of this isomer showed an AB pattern (with additional peaks from platinum coupling). The ^{13}C spectrum showed a quartet of quartets, with the different coupling constants to the ^{19}F nuclei of the non-equivalent trifluoromethyl groups only slightly different. If the reaction between **1** and benzyl bromide was carried out in the dark, complete conversion into **15b** occurred within 11 days. With longer standing, further reaction occurred, to give a variety of products (discussed below). When the reaction was carried out under laboratory lighting, the oxidative addition reaction proceeded more quickly, but so also did subsequent reactions. To obtain a solution containing only **15b**, it was therefore preferable to carry out the reaction in the dark.



(17)



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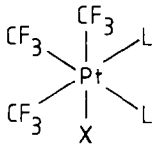
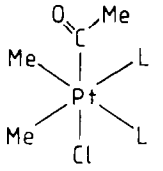


X	L	
I	py	**19**
I	½(bipy)	**20**
Br	½(bipy)	**21**
Cl	½(bipy)	**22**



(23)

$Pt(CF_3)_2$(bipy) (**2**) slowly reacted with excess benzyl bromide in acetone in the light, but, in contrast with the reaction of **1**, only isomer a was formed. Complete reaction of **2** had occurred within 28 days, to give $Pt(CF_3)_2(CH_2Ph)Br$(bipy) (**16a**) together with some $Pt(CF_3)_2Br_2$(bipy) (**8b**) presumably formed as a by-product from radical reactions. As expected for this isomer, the methylene protons gave a singlet with satellites. The methylene C atom gave a septet from coupling to ^{19}F.

It is clear from the above that the thermodynamically preferred isomer is different when L = 1/2(bipy) and L = py. The reactions are so slow that it is very likely that in one of these cases the isomer that is initially formed rearranges to the preferred isomer. There is no way of determining which isomer was initially formed. However, it should be noted that the reactions of *cis*-$PtMe_2L_2$ with benzyl bromide, which are rapid, give exclusively the isomer **17** in which benzyl is *cis* to bromide (L = PMe_2Ph [23], py [13]).

As mentioned above, additional reactions occurred when the reaction solution which produced $Pt(CF_3)_2(CH_2Ph)Brpy_2$ (**15b**) was kept at room temperature, especially when the solution (containing excess benzyl bromide) was exposed to laboratory lighting. These reactions were not analysed in detail, but one major product was identified as a salt with benzylpyridinium as the cation and a platinum(II) complex as the anion, **18**. The ^{19}F NMR spectrum of this species showed two quartets with satellites, indicating that two non-equivalent trifluoromethyl groups were present. The Pt–CF_3 coupling constants, 776 and 870 Hz, corresponded to a platinum(II) complex (cf. 794 Hz in $Pt(CF_3)_2py_2$). From the magnitude of these coupling constants, and the limited range of ligands possible in this system, the complex was formulated as *cis*-$Pt(CF_3)_2pyBr^-$. The ^{13}C NMR spectrum showed, as expected, three peaks corresponding to bound pyridine, with

Pt–C couplings resolved for C_β (cf. ^{13}C spectrum of *cis*-$Pt(CF_3)_2py_2$ (**1**)). The ^{13}C NMR spectrum also showed a set of peaks, with no platinum coupling, very similar to those reported for benzylpyridinium chloride [27]. The ^1H NMR spectrum in $(CD_3)_2CO$, while complex, showed the characteristic peaks of benzylpyridinium ions, including a singlet from the methylene protons at 5.93 ppm [28–30]. Since free pyridine did react with benzyl bromide during two weeks in acetone to give a precipitate of $[PhCH_2py]Br$, it is possible that the benzylpyridinium cation could be formed by reaction of pyridine dissociated from **15b** with an excess of benzyl bromide. Subsequent reactions of the complex "$Pt(CF_3)_2(CH_2Ph)Brpy$" would then have to produce the anion *cis*-$Pt(CF_3)_2pyBr^-$. Alternatively, $PhCH_2py^+$ could be eliminated in an intramolecular reaction from **15b**, to give $[PhCH_2py][Pt(CF_3)_2Brpy]$ (**18**) directly.

Reactions of $Pt(CF_3)_2L_2$ with trifluoromethyl iodide

$Pt(CF_3)_2L_2$ with L = py (**1**) or 1/2(bipy) (**2**) (but not that with L = 1/2(tmen) (**3**)) reacted slowly in acetone with an excess of CF_3I to give $Pt(CF_3)_3IL_2$; exposure to laboratory lighting was required for a significant rate. The reaction was usually carried out in a sealed Pyrex Carius tube with a 10-fold excess of CF_3I, with exposure to fluorescent lighting for one week. Under these conditions, conversion was almost complete. Exposure to direct sunlight for a similar period led to formation of many by-products. Brief exposure to a UV lamp did not accelerate the reaction if the tube was subsequently stored in the dark.

The products of the reaction, $Pt(CF_3)_3IL_2$, could be readily isolated, and analysed well for this formula. They gave characteristic ^{19}F NMR spectra (see Fig. 2), with two multiplets with satellites. The more intense multiplet was a quartet, and the less intense a septet. There were, therefore, three trifluoromethyl groups in the product, two of which were equivalent. This pattern is consistent with any of

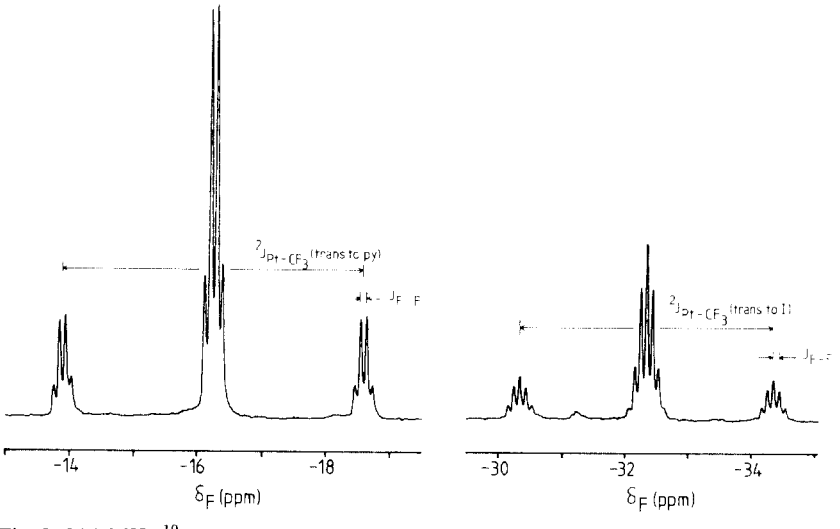


Fig. 2. 94.1 MHz ^{19}F NMR spectrum of *fac*-$Pt(CF_3)_3Ipy_2$ (**19**) in acetone.

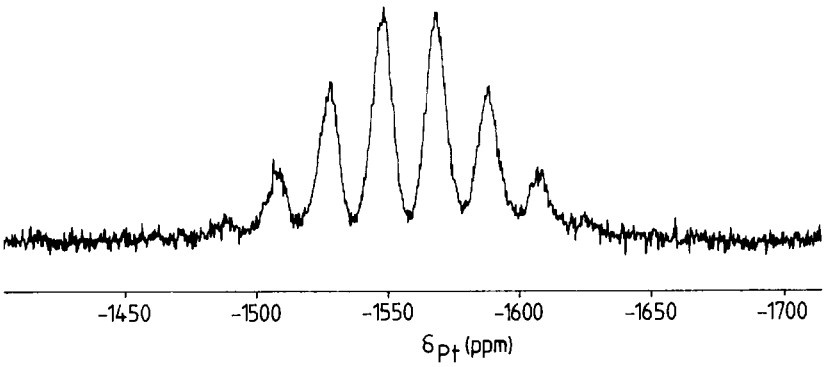


Fig. 3. ^{1}H-decoupled 21.3 MHz ^{195}Pt NMR spectrum of *fac*-$Pt(CF_3)_3Ipy_2$ (**19**) in acetone.

isomers a, c or d, with X = CF_3, Y = I in each case. Isomer c, with the ligands L mutually *trans* would not be possible for the bipyridyl case. For isomer d, the two ligands L (i.e., two different pyridine ligands, or two halves of the bipyridyl ligand) would be non-equivalent, which would affect the number of ^{13}C and ^{1}H signals observed. These spectra show no sign of this non-equivalence. For an isomer with two CF_3 groups mutually *trans*, the Pt–CF_3 coupling for the more intense multiplet would be expected to be very small (see discussion above), which is not observed. The isomer formed is therefore a, with the three CF_3 groups *facial* (i.e., structure **19** (L = py) or **20** (L = 1/2(bipy)). All trimethylplatinum(IV) complexes which have been adequately characterized have a similar *facial* arrangement of the methyl ligands, which avoids having two alkyl ligands, with their high *trans* influence, being mutually *trans*.

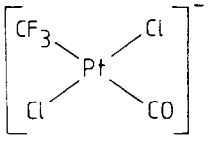
These represent the first tris(trifluoromethyl)platinum complexes, and indeed, the first transition metal complexes with more than two trifluoromethyl groups. Simple metathetical reactions, with the aid of silver salts, were used to prepare *fac*-$Pt(CF_3)_3X(bipy)$, X = Br (**21**), Cl (**22**).

The ^{1}H-decoupled ^{195}Pt spectrum of $Pt(CF_3)_3Ipy_2$ showed a multiplet at −1558.5 ppm (Fig. 3). The pattern observed can be rationalized as arising from the strongest peaks of a quartet of septets, from coupling of the platinum nucleus with the two sets of six and three ^{19}F nuclei. The ^{195}Pt spectrum of *fac*-$PtMe_3Ipy_2$ [13] was recorded for comparison. δ(Pt) was −2508.3 ppm. The trifluoromethyl groups therefore appear to have a much lower shielding effect on the Pt nucleus than methyl groups.

Reactions with other reagents

Bromobenzene is a relatively weak oxidative addition reagent, which reacts only slowly with *cis*-$PtMe_2py_2$ [12]. It did not react with any of the compounds $Pt(CF_3)_2L_2$ at room temperature, even upon prolonged standing.

Acetyl chloride is a much more powerful oxidative addition reagent, which reacts readily with *cis*-$PtMe_2L_2$ to give $PtMe_3(C(O)Me)ClL_2$ (**23**) (L = PMe_2Ph [16], py [12]). However, with *cis*-$Pt(CF_3)_2$(tmen) acetyl chloride did not give a platinum(IV) product. In solution, peaks due to *trans*-$Pt(CF_3)(CO)Cl_2^-$ (**24**) were observed in



(24)

NMR spectra, along with those due to fluoride ion (−185 ppm) (*trans*-$Pt(CF_3)(CO)Cl_2^-$ has been prepared independently by reaction of aqueous HCl with $Pt(CF_3)(CO)(tmen)^+$, which in turn was prepared by reaction of CO gas with $Pt(CF_3)(Me_2CO)(tmen)^+$ [31]). A quartet (^3J(HF) 7.3 Hz) also slowly grew at 50.07 ppm, which corresponded to CH_3COF [32] formed by reaction of CH_3COCl with HF (cf. the reported reaction between CH_3COBr and HF [33]).

Coordinated trifluoromethyl groups in some compounds are very sensitive to attack by acids, initially producing difluorocarbene complexes, which react with any water present to give a carbonyl complex and HF [34,35]. Reactions of platinum(II) trifluoromethyl complexes are being investigated, and will be described in detail elsewhere [31]. (The product of reaction of $Pt(CF_3)_2(tmen)$ with aqueous HCl in acetone is *trans*-$Pt(CF_3)(CO)Cl_2^-$ [31].)

Even when the acetyl chloride and acetone were dried as carefully as possible, there was evidently enough water present to generate sufficient HCl to attack one coordinated trifluoromethyl group, and to convert the complex into a carbonyl complex.

NMR parameters involving the trifluoromethyl groups

In methylplatinum(IV) complexes $^2J(Pt-CH_3)$ depends almost entirely on the ligand *trans* to the methyl group. *Cis* influences can, to a first approximation, be ignored [36]. This allows the $Pt-CH_3$ coupling constants to be used with some confidence in assigning structures [37]. As noted above, one-bond Pt–C coupling constants, while still most sensitive to the *trans* ligand, are much more sensitive to the *cis* ligands than the two-bond coupling [38,39]. It will be seen from Table 2 that, if the ligand *trans* to trifluoromethyl remains constant, $^2J(Pt-CF_3)$ is quite sensitive to the ligand *cis* to CF_3. For example, in the series of compounds $Pt(CF_3)_2XYpy_2$ with structure a, in which CF_3 remains *trans* to pyridine, $^2J(Pt-CF_3)$ varies from 382.1 Hz when XY = Cl_2 to 476.1 Hz when XY = MeI, a change of 24.6% based on the lowest value. For the corresponding dimethylplatinum(IV) complexes with analogous structures [13], $^2J(Pt-CH_3)$ varies only from 69.8 Hz (XY = MeI) to 72.7 Hz (XY = I_2), a change of only 4.2%, while ^1J(Pt–C) varies from 504.9 Hz (XY = I_2) to 674.8 Hz (XY = MeI), 33.7%. (^{13}C data are not available for XY = CF_3I). In the limited series available, the order of $^2J(Pt-CF_3)$, $Cl_2 < Br_2 < CF_3I < I_2 <$ MeI, does not parallel that for $^2J(Pt-CH_3)$, MeI < $CF_3I < Br_2 < Cl_2 < I_2$ or ^1J(Pt–C), $I_2 < Br_2 < Cl_2 <$ MeI. Because of this dependence on *cis* as well as *trans* ligands, $^2J(Pt-CF_3)$ cannot be used in assignments as readily as $^2J(Pt-CH_3)$.

It is also evident from Table 2 that δ(F) depends markedly on the ligands both *trans* and *cis* to the trifluoromethyl group. For example, in the series $Pt(CF_3)_2XYpy_2$ with structure a, δ(F) (*trans* to pyridine) varies from −3.84 ppm for XY = I_2 to −21.82 ppm for XY = Cl_2. In *fac*-$Pt(CF_3)_3Ipy_2$, the two different types of trifluoromethyl groups have quite different chemical shifts (−16.27 ppm *trans* to pyridine, −32.32 ppm *trans* to iodide). ^{19}F chemical shifts are therefore useful in making

Table 2

NMR data for trifluoromethyl groups [a]

Compound	δ(F) [b] (ppm)	^2J(Pt–CF_3) (Hz)	Other parameters (δ (ppm); J (Hz))
cis-$Pt(CF_3)_2py_2$ (**1**)	−24.59	793.5	δ(C) 115.03(q), ^1J(Pt–C) 1898.6, ^1J(C–F) 332.0, ^3J(F–C) 2.2
$Pt(CF_3)_2$(bipy) (**2**)	−23.90	741.0	
$Pt(CF_3)_2$(tmen) (**3**)	−24.60	752.0	δ(C) 113.72(q), ^1J(Pt–C) 1934.5, ^1J(C–F) 334.0, ^3J(F–C) 3.5
$Pt(CF_3)_2Cl_2py_2$ (**4a**)	−21.82	382.1	
$Pt(CF_3)_2Cl_2$(bipy) (**5a**)	−25.49	377.2	
(**5b**)	−25.70(q) [c]	351.6	J(F–F) 4.3
	−29.56(q) [d]	381.5	
$Pt(CF_3)_2Cl_2$(tmen) (**6a**)	−23.08	378.4	
$Pt(CF_3)_2Br_2py_2$ (**7a**)	−15.12	404.0	
$Pt(CF_3)_2Br_2$(bipy) (**8a**)	−19.60	398.0	
(**8b**)	−18.77(q) [c]	365.9	J(F–F) 4.9
	−27.77(q) [d]	393.8	
$Pt(CF_3)_2Br_2$(tmen) (**9a**)	−14.93	400.4	
$Pt(CF_3)_2I_2py_2$ (**10a**)	−3.84	450.4	
$Pt(CF_3)_2I_2$(bipy) (**11a**)	−9.87	440.7	δ(C) 93.64, ^1J(Pt–C) 1279.6, ^1J(C–F) 338.8
$Pt(CF_3)_2I_2$(tmen) (**12a**)	−0.65	455.3	
$Pt(CF_3)_2MeIpy_2$ (**13a**)	−20.07	476.1	
(**13b**)	−34.71(q) [c]	441.9	J(F–F) 6.1
	−17.98(q) [d]	473.6	
$Pt(CF_3)_2MeI$(bipy) (**14a**)	−23.30	465.1	
$Pt(CF_3)_2(CH_2Ph)Brpy_2$ (**15b**)	−19.64(q)	460.8	J(F–F) 5.5
	−26.73(q)	485.2	
$Pt(CF_3)_2(CH_2Ph)Br$(bipy) (**16a**)	−27.04	441.9	
$[PhCH_2py][Pt(CF_3)_2Brpy]$ (**18**)	−17.30(q) [c]	775.7	J(F–F) 4.3
	−21.84(q) [d]	869.8	
fac-$Pt(CF_3)_3Ipy_2$ (**19**)	−16.27(q) [d]	438.2	J(F–F) 8.5
	−32.32(se) [c]	373.5	
fac-$Pt(CF_3)_3I$(bipy) (**20**)	−20.88(q) [d]	432.1	J(F–F) 4.9, δ(C) *trans* to bipy: 96.64, ^1J(Pt–C) 1362.9, ^1J(C–F) 341.9, δ(C) *trans* to I: 96.68, ^1J(Pt–C) 1283.2, ^1J(C–F) 360.3 Hz
	−34.13(se) [c]	402.8	
fac-$Pt(CF_3)_3Br$(bipy) (**21**)	−20.97(q) [d]	430.9	J(F–F) 4.9
	−33.94(se) [c]	405.3	
fac-$Pt(CF_3)_3Cl$(bipy) (**22**)	−20.94(q) [d]	430.9	J(F–F) 4.9
	−33.96(se) [c]	404.1	

[a] In acetone. [b] A singlet is observed (with satellites) unless otherwise indicated by one of the following symbols: q = quartet, se = septet. [c] *trans* to halogen. [d] *trans* to L.

assignments only if data are available for closely related compounds of known structure.

Because there is no Nuclear Overhauser Effect to enhance signal sensitivity, and because C–F coupling causes the signal intensity to be distributed over a number of peaks, satisfactory ^{13}C NMR spectra of the trifluoromethyl C-atoms were obtained

Table 3

^{1}H and ^{13}C NMR data for pyridine complexes

Compound	NMR data (δ (ppm)) [a]						Other peaks (δ (ppm); J (Hz))
	Pyridine peaks						
	C_α	H_α	C_β	H_β	C_γ	H_γ	
cis-$Pt(CF_3)_2py_2$ (**1**)	152.19(13.7)	8.82(24.9)	126.84(26.4)	7.55	139.98(7.8)	7.97	
$Pt(CF_3)_2Cl_2py_2$ (**4a**)	151.42	8.88(14.2)	127.00(14.1)	7.72	141.93	8.23	
$Pt(CF_3)_2Br_2py_2$ (**7a**)	153.73	8.97(16.4)	126.95(15.6)	7.70	141.84	8.25	
$Pt(CF_3)_2I_2py_2$ (**10a**)	157.24	9.26(17.2)	126.75(16.6)	7.68	141.69	8.26	
$Pt(CF_3)_2Mepy_2$ (**13a**)	154.68	8.91(15.4)	126.86(16.1)	7.64	141.20	8.21	Pt–CH_3: δ(H) 2.22 (61.0), J(F–H) 0.7 δ(C) 21.44 (565.6) J(F–C) 5.1
(**13b**)	[b]	8.77(16.7) [c] 9.04(10.3) [d]	[b]	7.67	[b]	8.03	Pt–CH_3: δ(H) 2.21 (69.8) J(F–H) not resolved
$Pt(CF_3)_2(CH_2Ph)Brpy_2$ (**15b**)	155.08 [g]	[f]	123.29(16.9) [c] 126.34(11.7) [e]	[f]	138.15 [g]	[f]	Pt–CH_2–: ^{1}H AB pattern δ_A 4.86(105.0) δ_B 4.30(69.0), J(AB) 8.5. δ(C) 32.17 (542.5) (q–q) J(C–F) 4.7. Phenyl C(1) 130.62(18.3) C(2,6) 128.51(11.0) C(3,4,5) 128.3, 130.1
$[PhCH_2py][Pt(CF_3)_2Brpy]$ (**18**)	152.65 [h] 145.16 [i]	[f] [f]	124.70(24.9) [h] 133.87 [i]	[f] [f]	138.21 [h] 146.49 [i]	[f] [f]	CH_2: δ(H) 5.93, δ(C) 65.77. Phenyl 129.1–130.0

[a] Coupling constants to ^{195}Pt in parentheses where they are resolved. [b] ^{13}C peaks from this isomer obscured by other peaks. [c] Pyridine *trans* to CF_3. [d] Pyridine *trans* to Me. [e] Pyridine *trans* to benzyl. [f] ^{1}H peaks not unequivocally assigned. Spectrum complex. [g] Peaks from non-equivalent pyridine ligands coincident. [h] Pyridine coordinated to platinum. [i] Pyridine of benzyl pyridinium cation.

only in a few favourable cases, when the sample was available in sufficient quantity and solubility was high enough. The data, the first obtained for Pt–CF_3 complexes, are listed in Table 2. For the limited range of complexes studied δ(C) has higher values for the platinum(II) complexes (113.7–115 ppm) than for the platinum(IV) complexes (93.6–96.7 ppm). There was some variation in ^1J(C–F), for example, 341.9 Hz for trifluoromethyl *trans* to bipyridyl and 360.3 Hz *trans* to iodide in *fac*-$Pt(CF_3)_3I$(bipy) (**20**). For the platinum(II) complexes coupling to the F nuclei of the adjacent trifluoromethyl group was resolved (2–4 Hz), but not for the platinum(IV) complexes.

The Pt–C coupling constants are very much larger than those for the corresponding methyl complexes. For *cis*-$Pt(CF_3)_2py_2$ (**1**) ^1J(Pt–C) is 1898.6 Hz, compared with 688.5 Hz for $PtMe_2py_2$ [12]. For the platinum(IV) complexes, there is the expected reduction in ^1J(Pt–C) [40], for example, to 1279.6 Hz for $Pt(CF_3)_2I_2$(bipy) (**11a**), but the coupling is still much larger than for $PtMe_2I_2py_2$, 504.9 Hz [13]. The Fermi contact contribution to one-bond Pt–X coupling constants is considered to be dominant, with the degree of *s*-character in the bonding orbitals of Pt and X an important variable [40,41]. The large Pt–C (CF_3) coupling constants are consistent with a much higher contribution from the C 2*s* orbital to the Pt–C bond in the trifluoromethyl compounds compared with the methyl compounds, as proposed by Hall and Fenske [11].

The limited data available do not allow a detailed comparison of the variations in ^1J(Pt–C) and ^2J(Pt–CF_3), but the coupling constants do follow the same order.

NMR parameters for pyridine ligands

These data are given in Table 3. In pyridine complexes, the multiplet due to H_γ is readily assigned since it has the lowest intensity. H_α gives a doublet from coupling to H_β, broadened by long range coupling to H_γ, with satellites from platinum coupling. In the ^{13}C spectrum of *cis*-$Pt(CF_3)_2py_2$, C_γ is also readily assigned on the basis of its low intensity, to a peak at 140 ppm. A peak at 126.8 ppm showed much larger platinum coupling (26.4 Hz) than a peak at 152.2 ppm (13.7 Hz). We therefore initially assigned the peak at 126.8 ppm to C_α (a similar assignment was made for *cis*-$PtMe_2py_2$ on the same basis [12]). However, this assignment is the opposite to that proposed by Chow and Martin for some pyridine complexes of platinum(II) [42]. Selective decoupling experiments showed that H_α was indeed bound to the carbon atom resonating at 152.2 ppm, which is therefore assigned to C_α. Corresponding assignments must also be made for the platinum(IV) compounds, although platinum coupling is resolved only for C_β (Table 3).

There is little change in the NMR parameters for the compounds $Pt(CF_3)_2XYpy_2$ (isomer a) in which pyridine remains *trans* to trifluoromethyl. For those compounds with the alternative structure (isomer b) (**13b, 15b**), the two pyridine ligands are non-equivalent, but distinct peaks are resolved only for C_β or H_α. The nucleus with the lower coupling constant to ^{195}Pt has been assigned to the pyridine ligand *trans* to the non-fluorinated alkyl (methyl in **13b**, benzyl in **15b**).

In contrast to the bipyridyl complexes (see below), no fluorine coupling was observed to C_α in any of the complexes.

NMR parameters for bipyridyl ligands

^{13}C data are given in Table 4. Assignments were based on those of Erickson et al. [43] for bipyridyl complexes of platinum(II). Platinum coupling to all of these

(*Continued on p. 416*)

Table 4

^{13}C and selected ^{1}H NMR data for 2,2′-bipyridyl complexes [a]

Compound	Ligand *trans* to ring	C(2,2′)	C(3,3′)	C(4,4′)	C(5,5′)	C(6,6′)	H(6,6′)	Other peaks [b]
$Pt(CF_3)_2$(bipy) (**2**)	CF_3	157.18(16.1)	124.75(11.7)	141.52(< 2)	128.40(22.0)	152.89(39.6) (se 2.9)	9.15(20.6)	
$Pt(CF_3)_2Cl_2$(bipy) (**5a**)	CF_3	155.43(8.0)	126.35(10.3)	143.00(< 2)	129.44(13.5)	151.70(16.7) (se 3.2)	9.21(11.0)	
(**5b**)	CF_3	158.81(7.7)	128.63(10.9)	146.17(< 2)	132.22(13.5)	151.54(13.5) (s)	9.57(12.2)	
	Cl	157.51(21.2)	129.60(22.4)	146.83(7.1)	133.25(31.4)	154.69(18.6) (q 5.1)	9.26(32.7)	
$Pt(CF_3)_2Br_2$(bipy) (**8a**)	CF_3	155.51(8.8)	126.30(10.3)	142.83(< 2)	129.48(14.7)	152.51(17.3) (q 4.5)	9.24(11.3)	
(**8b**)	CF_3	156.08(9.0)	125.96(10.9)	143.08(< 2)	129.39(15.4)	150.30(16.0) (s)	9.88(12.9)	
	Br	154.91(19.0)	126.80(21.2)	143.86(7.1)	130.23(30.1)	151.70(17.9) (q 5.8)	9.25(28.1)	
$Pt(CF_3)_2I_2$(bipy) (**11a**)	CF_3	156.16(9.4)	126.30(10.7)	142.70(< 2)	129.32(15.6)	153.19(19.8) (m)	9.29(12.5)	

$Pt(CF_3)_2MeI(bipy)$ (**14a**)	CF_3	155.64(9.5)	126.14(11.0)	142.12(< 2)	129.00(16.2)	152.28(17.7) (m)	9.21(12.3)	CH_3: C 14.18 (523.07) (se 4.9) H 1.61 (64.6) (se 0.5)
$Pt(CF_3)_2(CH_2Ph)Br(bipy)$ (**16a**)	CF_3	155.60(5.1)	126.47(12.5)	141.56(< 2)	129.63(14.7)	151.44(17.6) (m)	9.11(12.8)	CH_2: C 31.36 (504.7) (se 4.0) ^{1}H 3.91 (81.2) (s) Ph: C(1) 141.75 (43.2) H(1) 6.82 C(2,6) 128.39 (16.9) C(3,5) 128.66 (11.7) H(3) 6.62 C(4) 126.47 (12.5) H(4) 6.40
$Pt(CF_3)_3I(bipy)$ (**20**)	CF_3	155.80(9.5)	126.13(9.8)	143.05(< 2)	129.33(15.6)	155.48(18.3) (se 3.7)	9.27(13.1)	

[a] Chemical shifts in ppm, couplings to ^{195}Pt (Hz) in parentheses. [b] s = singlet, q = quartet, se = septet, m = complex multiplet. Splitting within the quartet or septet patterns is included with the symbol in the parenthesis.

carbon nuclei was resolved, except in some cases, for C(4,4′). For those complexes for which the two rings of the bipyridyl ligand are non-equivalent (**5b, 8b**) separate signals were observed for the two rings. Peaks were assigned to the ring *trans* to trifluoromethyl on the basis that Pt–C coupling constants would be smaller than for the ring *trans* to halide, and similar to the values in compounds with structure a, in which both rings of the bipyridyl ligand are *trans* to CF_3.

^1H data are given only for H(6,6′). These protons gave a doublet (from coupling with H(5,5′), $J \sim 5.8$ Hz) with satellites. The Pt–H coupling constants were determined more easily when H(5,5′) was decoupled. Separate signals were observed for H(6) and H(6′) when the rings were non-equivalent (isomer b), and assigned on a similar basis to that used for ^{13}C.

The ^{13}C resonances for the bipyridyl ligands all showed a singlet with satellites (when resolved), except for C(6) or C(6′) which frequently showed splittings which could only arise through coupling with ^{19}F nuclei. In the spectra of the complexes $Pt(CF_3)_2X_2$(bipy) with structure b, **5b** (X = Cl) and **8b** (X = Br), the carbon atom labelled C(6) in Fig. 1(b), in the ring *trans* to X, showed a quartet (with satellites) which would arise from coupling with the ^{19}F nuclei of one trifluoromethyl group. This ring is *cis* to the CF_3 group bound in the PtN_2 plane, and C(6) will be adjacent to this group. C(6′) showed no splitting, nor did C(2) or C(2′). It is unlikely that the CF_3 group bound perpendicular to the PtN_2 plane is the single group coupling to C(6), as there seems no good reason why C(6′) should not then show similar coupling.

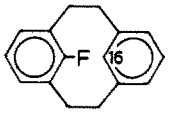
For $Pt(CF_3)_2$(bipy) and for the isomers with structure a, for which the trifluoromethyl groups are chemically equivalent and the two rings of the bipyridyl ligand are the same, splitting was always observed for C(6,6′) but the pattern observed varied from a quartet (e.g., $Pt(CF_3)_2Br_2$(bipy) (**8a**), Fig. 4(a)) to a septet (e.g., $Pt(CF_3)_2Cl_2$(bipy) (**5a**) Fig. 4(c)), or a rather complex multiplet (e.g. $Pt(CF_3)_2$-MeI(bipy) (**14a**), Fig. 4(b)) (in each case with additional peaks from platinum coupling). These variations can be explained qualitatively in terms of the relative magnitudes of J(F–C) and J(F–F). F–F coupling is usually observed in the ^{19}F spectrum when the bound trifluoromethyl groups are non-equivalent, but the coupling will still be present, though not observed in the ^{19}F spectrum, when the CF_3 groups are equivalent. When the spectrum of C(6) is under examination, the two CF_3 groups in isomer a will be magnetically non-equivalent, so that the ^{13}C spectrum of C(6) is the X part of a $A_3A'_3X$ spectrum, whose appearance depends only on the relative magnitudes of $J_{AA'}$, J_{AX}, and $J_{A'X}$. If C(6) couples with the fluorine nuclei of only one CF_3 group (the group *cis* to C(6)), then $J_{A'X} = 0$. If $J_{AA'}$ (i.e. J(F–F)) $\ll J_{AX}$, then C(6) will give only a simple quartet. If $J_{AA'} \gg J_{AX}$, then X will become "virtually coupled" [44] to the second CF_3 group, and the signal will become a septet with splitting $1/2J_{AX}$. If $J_{AA'} \approx J_{AX}$, a more complex multiplet would be expected. Since the splitting in a septet signal (as in **5a**) is close to half that in a quartet signal (as in **8a**) it appears that the major variable is J(FF), which probably depends on the extent to which the CF_3 groups interact with each other sterically.

No coupling to ^{19}F nuclei was observed for H(6,6′).

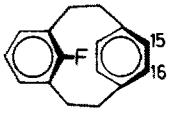
If the F–C coupling were operating through bonds, one might expect the C-atom in the ring *trans* to CF_3 in structure b to couple, rather than the C-atom in the ring *cis* to CF_3. As well, C(2,2′), might be expected to show similar coupling. As

Fig. 4. ^{1}H-decoupled 100.1 MHz ^{13}C spectrum of C(6,6′) for complexes $Pt(CF_3)_2XY(bipy)$ with structure (a); (a) $Pt(CF_3)_2Br_2(bipy)$ (**8a**); (b) $Pt(CF_3)_2MeI(bipy)$ (**14a**); (c) $Pt(CF_3)_2Cl_2(bipy)$ (**5a**).

mentioned above, a CF_3 group in the PtN_2 plane would be expected to interact sterically with C(6)-H *cis* to itself. We therefore propose that the coupling is "through space" in origin. Similar "through space" C–F coupling has frequently been postulated in organic molecules in which fluorine is forced close to a carbon atom [45–49]. For example, in the monofluoro[2.2]cyclophanes **25** and **26**, ^{19}F



(25)



(26)

couples to C(16) and C(15,16) respectively, with no coupling to the protons bound to these carbon atoms [46]. It was suggested that this interaction was predominantly $2p$–$2p$ in nature.

IR spectra

Infrared data in the literature for trifluoromethyl complexes with transition metals have been restricted to compounds with only one trifluoromethyl group. Here, two strong bands have been attributed to C–F stretching, a symmetric ν(C–F) band at higher frequency, and a lower frequency band (often split) from

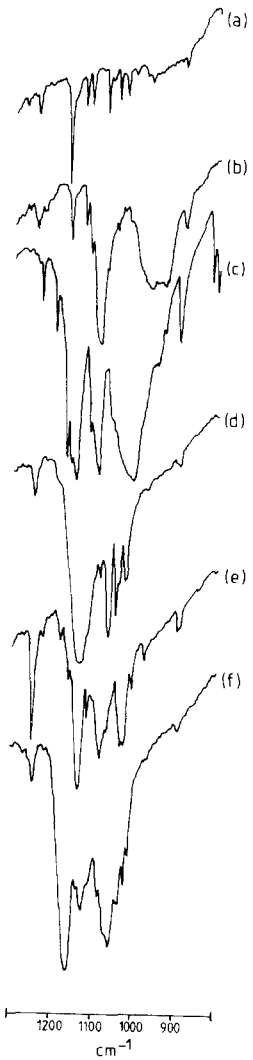


Fig. 5. IR spectrum in the ν(C–F) region of bipyridyl complexes: (a) $PtCl_2$(bipy); (b) $Pt(CF_3)(CH_3)$(bipy); (c) $Pt(CF_3)_2$(bipy) (**2**); (d) $Pt(CF_3)Cl_2$(bipy) (**5a**); (e) $Pt(CF_3)MeI$(bipy) (**14a**); (f) $Pt(CF_3)_3I$(bipy) (**20**).

degenerate asymmetric modes [5,50,51]. A typical spectrum of this kind is observed for $Pt(CF_3)(CH_3)(bipy)$ (Fig. 5(b)). The preparation of this complex is described elsewhere [31]. Complexes with two or more trifluoromethyl groups showed more complex spectra, some of which are illustrated in Fig. 5. These patterns are characteristic of the type of compound. For example, the compounds $Pt(CF_3)_2L_2$ (L = py (**1**), L_2 = tmen (**3**)) show patterns similar to that for $Pt(CF_3)_2(bipy)$ (**2**) (Fig. 5(c)) except for weaker peaks due to the organic ligands. The complexes $Pt(CF_3)_2X_2(bipy)$ with structure a, X = Br (**8a**), I (**11a**) show patterns similar to that for X = Cl (**5a**) (Fig. 5(d)). The spectrum of $Pt(CF_3)_2(CH_2Ph)Br(bipy)$ (**16a**) in this region is like that of $Pt(CF_3)_2MeI(bipy)$ (**14a**) (Fig. 5(e)), and the spectra of $Pt(CF_3)_3X(bipy)$ differ only slightly from that for X = I (**20**) (Fig. 5(f)) when X = Cl (**22**), Br (**21**). The different patterns probably arise primarily from coupling between the C–F stretching modes of different trifluoromethyl groups. The IR pattern can therefore be used with some confidence to give an indication of the nature of a compound if spectra for related compounds are available for comparison.

Experimental

Instrumentation and general methods

100 MHz ^1H, 94.2 MHz ^{19}F, 25.05 MHz ^{13}C, and 21.36 MHz ^{195}Pt NMR spectra were recorded on a JEOL JNM FX-100 spectrometer with a 10 mm tunable probe. 400 MHz ^1H and 100.4 MHz ^{13}C spectra were obtained on a JEOL JNM GX-400 spectrometer, with a 5 mm dual $^1H/^{13}C$ probe. Chemical shifts (positive to lower shielding) are relative to internal tetramethylsilane (TMS) for ^1H and ^{13}C, to internal $CFCl_3$ for ^{19}F, and to external Na_2PtCl_6/H_2O for ^{195}Pt. Unless otherwise stated, all spectra were recorded for solutions in $(CD_3)_2CO$ or (for some ^{19}F and ^{195}Pt spectra) $(CH_3)_2CO$.

IR spectra were recorded with Nujol mulls on a Perkin–Elmer 283B spectrometer.

C, H, and N microanalyses were performed by the microanalytical service in this Department, or by the Australian Microanalytical Service, AMDEL, Melbourne, who also carried out the F analyses.

Starting materials

Trifluoromethyl iodide was supplied by Fluorochem Ltd. Published methods were used to prepare $PtCl_2(NBD)$ [52] and hence $PtMe_2(NBD)$ [12] (NBD = norbornadiene). $Pt(CF_3)_2(NBD)$ was prepared by the reaction of $PtMe_2(NBD)$ with excess CF_3I, as previously described for the cyclooctadiene (COD) analogue [10]. $Pt(CF_3)_2L_2$ (L = py (**1**), 1/2(bipy) (**2**), or 1/2(tmen) (**3**)) were prepared by a method similar to that previously used to prepare **2** and **3** from $Pt(CF_3)_2(COD)$ [10]:

To a solution of 1 g $Pt(CF_3)_2(NBD)$ in 10 ml chloroform was added slightly more than two molar equivalents of ligand (for L = py) or one molar equivalent for the chelating ligands. The solution was heated under reflux for 15 min then the volume was reduced to 1 ml. The white solid which deposited was filtered off, washed with cyclohexane, and dried under vacuum. The yield was 75–90%.

Platinum(IV) complexes

One representative procedure is given for each oxidative addition reagent used, as the other complexes in the series were prepared by similar methods. All the

compounds isolated are listed in Table 1, with analytical data. All were stable in air indefinitely, except for $Pt(CF_3)_2Cl_2(tmen)$ (**6a**) and $Pt(CF_3)_2MeIpy_2$ (**17**), which darkened significantly after several days' standing.

*Reaction of cis-$Pt(CF_3)_2py_2$ (**1**) with chlorine*

Compound **1** (0.10 g, 0.20 mmol) was suspended in 5 ml dry CH_2Cl_2 (distilled from calcium hydride). Chlorine gas (dried by bubbling through conc. H_2SO_4) was bubbled through the suspension for 1 min, during which the solid dissolved. The solution volume was reduced to 1 ml under reduced pressure, and 8 ml cyclohexane was added to precipitate a colourless solid, which was filtered off, washed with 3 ml cyclohexane, then 3 ml ether, and dried under vacuum. Yield of $Pt(CF_3)_2Cl_2py_2$ (**4a**) was 0.06 g (52%).

*Reaction of **1** with bromine*

Compound **1** (0.10 g, 0.20 mmol) was suspended in 3 ml CH_2Cl_2, and the mixture was stirred during the addition of 25 μl bromine (0.50 mmol). Stirring was continued for 1 h. The mixture, which now contained some suspended yellow solid, was reduced to dryness in a rotary evaporator. The solid residue was washed with 3 ml ether, and dried under vacuum. Yield of the yellow solid, $Pt(CF_3)_2Br_2py_2$ (**7a**) was 0.11 g (82%).

*Reaction of **1** with iodine*

Compound **1** (0.10 g, 0.20 mmol) was suspended in 5 ml CH_2Cl_2, with stirring. A solution of 0.064 g iodine (0.25 mmol) in 5 ml CH_2Cl_2 was added slowly. Some precipitate formed. Stirring was continued for 1 h, then the volume of CH_2Cl_2 was reduced to 0.5 ml under reduced pressure. Cyclohexane (3 ml) was added. The dark purple solid was filtered off, washed twice with 3 ml cyclohexane, and dried under vacuum. Yield of $Pt(CF_3)_2I_2py_2$ (**10a**) was 0.086 g (71%).

*Reaction of **1** with iodomethane*

Compound **1** (0.20 g, 0.40 mmol) was dissolved in 5 ml distilled acetone and 1.27 ml MeI (2.0 mmol) was added. The solution was stirred for two days under laboratory lighting (fluorescent tubes), after which the ^{19}F NMR spectrum of the solution showed that there had been almost complete conversion into a mixture of isomers of $Pt(CF_3)_2MeIpy_2$ (**13a** and **13b**). Removal of solvent gave an orange oil which solidified on addition of ether. The solid was redissolved in CH_2Cl_2 and the solution was passed down a short Florisil column. The eluted solution was concentrated nearly to dryness under reduced pressure, and cyclohexane was added to precipitate the product, which was washed with ether and dried under vacuum. Yield of $Pt(CF_3)_2MeIpy_2$ (**13a** and **13b**) was 0.12 g (47%).

*Reaction of **2** and **1** with benzyl bromide*

$Pt(CF_3)_2(bipy)$ (**2**) (0.05 g, 0.10 mmol) was dissolved in 5 ml distilled acetone and 1 ml benzyl bromide (8.4 mmol) was added. The solution was stirred at room temperature for one month with protection from light. The volume of the solution was reduced to 1 ml, and an excess of ether was added to precipitate a white solid, which was filtered off, washed twice with 3 ml ether, and vacuum dried. Yield of $Pt(CF_3)_2(CH_2Ph)Br(bipy)$ (**16a**) was 0.01 g (15%).

When the reaction solution from *cis*-$Pt(CF_3)_2py_2$ (**1**) and benzyl bromide was evaporated, an orange oil was obtained which contained approximately 20% free benzyl bromide. Attempts to remove this by washing with ether or cyclohexane were unsuccessful. Attempts to purify the sample by chromatography on Florisil resulted in decomposition.

*Reaction of **1** with trifluoromethyl iodide*

Compound **1** (0.50 g, 1.0 mmol) was dissolved in 5 ml distilled acetone in a 30 ml thick-walled Carius tube. The solution was degassed and frozen under vacuum, then 10 mmol CF_3I was condensed into the tube, which was sealed. The tube was allowed to warm, and exposed to (fluorescent) laboratory light at room temperature for 7 d, then opened. The solution was evaporated to dryness under reduced pressure. The solid residue was dissolved in CH_2Cl_2 and the solution passed down a short Florisil column. The volume of the eluted solution was reduced to 1 ml under reduced pressure, and 10 ml cyclohexane was added to precipitate a white solid, which was filtered off, washed with cyclohexane, and dried under vacuum. Yield of *fac*-$Pt(CF_3)_3Ipy_2$ (**19**) was 0.52 g (74%).

*Preparation of $Pt(CF_3)_3Br(bipy)$ (**21**)*

Compound **20** (0.031 g, 0.045 mmol) was dissolved in 1 ml acetone. A solution of 0.009 g $AgClO_4$ (0.044 mmol) in 1 ml acetone was added. The solution was protected from the light and stirred for 16 h. The AgI which formed was filtered off and an excess of LiBr (0.010 g, 0.12 mmol) was added. The solution was stirred until it became clear, then evaporated to dryness under reduced pressure. The solid was washed with distilled water (2×3 ml) to remove the excess LiBr, then with ether (2×1 ml), and finally dried under vacuum. Yield of $Pt(CF_3)_3Br(bipy)$ (**23**) was 0.015 g (52%).

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