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Displacement of norbornadiene (NBD) from $Pt(CF_3)_2(NBD)$ by weak donor ligands L, and reactions of *cis*-$Pt(CF_3)_2L_2$ with water and acids

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Abstract

The NBD ligand in $Pt(CF_3)_2(NBD)$ has been replaced under mild conditions by a number of neutral S-, N-, and O-donor ligands to form *cis*-$Pt(CF_3)_2L_2$ complexes (L_2 = *N,N,N′,N′*-tetramethylethylenediamine (tmen), bipyridine (bipy), ethylenediamine (en); L = pyridine (py), NH_3, dimethylsulfoxide (DMSO), CH_3CN, C_6H_5CN, *N,N*-dimethylformamide (DMF)). Reaction with DMSO produces predominantly the isomer *cis*-$Pt(CF_3)_2$(DMSO-*S*)(DMSO-*O*), with *cis*-$Pt(CF_3)_2$(DMSO-*S*)$_2$ a minor component, as a result of steric constraints. Water or methanol attacks the CF_3 groups, producing fluoride ion.

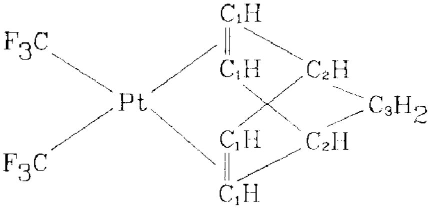
The fluorine atoms of *cis*-$Pt(CF_3)_2L_2$ (L_2 = bipy, tmen; L = py) are susceptible to electrophilic attack by H^+. Reaction with aqueous HCl or $HClO_4$ converts one CF_3 group into a coordinated CO group. With HCl, simultaneous protonation and displacement of the N-donor ligands occurred, yielding *cis*-$Pt(CF_3)(CO)Cl_2^-$. With $HClO_4$, the complexes *cis*-$Pt(CF_3)(CO)L_2^+$ are initially generated, with subsequent displacement of the tmen and py (but not bipy) ligands to form *cis*-$Pt(CF_3)(CO)(OH_2)_2^+$. The remaining CF_3 group is not attacked by H^+.

Reaction of $Pt(CF_3)_2(NBD)$ with halide ions in acetone initially produced the binuclear complexes $[(CF_3)_2Pt(\mu\text{-}X)_2Pt(CF_3)_2]^{2-}$ (X = I, Cl) containing bridging halide. With larger amounts of halide ion the expected *cis*-$Pt(CF_3)_2X_2^{2-}$ complexes were not obtained, and instead *cis*-$Pt(CF_3)(CO)X_2^-$ and fluoride ion were formed. When the complexes $[(CF_3)_2Pt(\mu\text{-}X)_2Pt(CF_3)_2]^{2-}$ were kept in the presence of NBD, *cis*-$Pt(CF_3)(CO)X_2^-$ and $Pt(CF_3)_2(NBD)$ were formed. When X = I, these two complexes then reacted together to yield *cis*-$Pt(CF_3)_2I(CO)^-$ and $Pt(CF_3)I(NBD)$.

Introduction

Complexes $PtR_2(COD)$ (COD = cycloocta-1,5-diene; R = alkyl [1–5], aryl [1–4,6,7]) have often been used as precursors of a range of PtR_2L_2 complexes. In the majority of these studies displacement of the COD ligand has been achieved only by the use of strongly coordinating ligands such as phosphines, or of harsh reaction conditions. However, when R = CF_3 the high trans effect of trifluoromethyl combined with reduced availability of Pt $d\pi$ electrons for backbonding to the olefin results in displacement of the COD ligand under milder conditions [2].

Variation of the diolefin ligand can alter the conditions needed to effect diolefin displacement [7,8]. Because of its smaller 'coordination bite' angle, NBD would be expected to bind less tightly to platinum than COD. This has been borne out by the ease of displacement of the diolefin from $Pt(CH_3)_2(NBD)$ relative to $Pt(CH_3)_2(COD)$ [8]. The compound $Pt(CF_3)_2(NBD)$ (**1**) therefore appeared to hold promise as a precursor of $Pt(CF_3)_2L_2$ complexes, where L is a weak donor ligand. This paper describes reactions of **1** with a range of ligands of varying donor strength. A preliminary account of some of this work has appeared [9].



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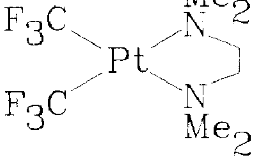
During this investigation, it became evident that the fluorine atoms in some of the products $Pt(CF_3)_2L_2$ were undergoing electrophilic attack. A study of the effect of aqueous acids on a number of $Pt(CF_3)_2L_2$ complexes was undertaken to shed further light on this reaction. In the only report to date on reaction of bis(trifluoromethyl)-transition metal complexes with dilute mineral acids, Clark and Manzer [2] concluded that $Pt(CF_3)_2(COD)$ was unreactive. By contrast, there have been several reports of acid attack on mono(trifluoromethyl)-transition metal complexes [10–12]. Reaction with H^+ initially causes abstraction of fluoride ion and the resulting difluorocarbene complex is then rapidly hydrolysed by any water present to form the carbonyl complex (eq. 1).

$$M{-}CF_3 \xrightarrow[-HF]{+H^+} M^+{=}CF_2 \xrightarrow[-2HF]{+H_2O} M^+{-}CO \qquad (1)$$

Our study has concentrated on the reactivity of $Pt(CF_3)_2(tmen)$ (**2**), $Pt(CF_3)_2(bipy)$ (**3**) and *cis*-$Pt(CF_3)_2py_2$ (**4**) with aqueous HCl and $HClO_4$.



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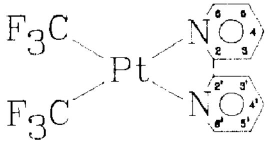

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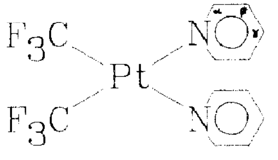

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Results and discussion

Analytical data for new compounds are given in Table 1. NMR data for new $Pt(CF_3)_2L_2$ complexes in Table 2, and NMR data for other products in Table 3.

Table 1

Analytical data

Complex		Colour	Analysis (Found (calc) (%))			
			C	H	N	F[a]
$Pt(CF_3)_2(NBD)$	**(1)**	White	25.2	2.1		26.6
			(25.4)	(1.9)		(26.8)
$Pt(CF_3)_2$(tmen)	**(2)**	White	21.4	3.6	6.3	
			(21.4)	(3.6)	(6.2)	
$Pt(CF_3)_2$(bipy)	**(3)**	Yellow	29.5	1.6	5.8	
			(29.5)	(1.7)	(5.7)	
cis-$Pt(CF_3)_2py_2$	**(4)**	White	29.3	2.2	5.8	23.3
			(29.3)	(2.1)	(5.7)	(23.2)
$Pt(CF_3)_2$(en)	**(5)**	White	12.5	1.8	7.4	28.7
			(12.2)	(2.1)	(7.1)	(29.0)
cis-$Pt(CF_3)_2(NH_3)_2$	**(6)**	White	6.9	1.8	7.5	30.7
			(6.5)	(1.7)	(7.6)	(31.1)
cis-$Pt(CF_3)_2(NCCH_3)_2$	**(9)**	White	17.3	1.4	6.6	27.5
			(17.4)	(1.5)	(6.8)	(27.5)
cis-$Pt(CF_3)_2(NCC_6H_5)_2$	**(11)**	White	35.6	1.9	5.0	21.0
			(35.6)	(1.9)	(5.2)	(21.1)
$[(n\text{-}Bu)_4N][Pt(CF_3)(CO)Cl_2]$	**(14)**	White	35.8	6.3	2.0	9.2
			(35.7)	(6.0)	(2.3)	(9.4)
$[Pt(CF_3)(CO)(tmen)]ClO_4$	**(16)**	White	19.3	3.3	5.6	11.3
			(18.9)	(3.2)	(5.5)	(11.2)
$[Pt(CF_3)(CO)(bipy)]ClO_4$	**(18)**	Yellow	26.4	1.5	5.2	10.6
			(26.3)	(1.5)	(5.1)	(10.4)
$[(n\text{-}Bu)_4N]_2[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]$	**(23)**	Yellow	30.9	5.3	1.9	16.5
			(30.8)	(5.2)	(2.0)	(16.2)
$[(n\text{-}Bu)_4N][Pt(CF_3)(CO)I_2]$	**(24)**	Yellow	27.6	4.8	1.9	7.5
			(27.4)	(4.6)	(1.8)	(7.2)
$Pt(CF_3)I(NBD)$	**(27)**	Yellow	19.5	1.6		11.5
			(19.9)	(1.7)		(11.8)
$Pt(CF_3)I$(tmen)		White	16.5	3.2	5.4	11.3
			(16.6)	(3.2)	(5.5)	(11.2)
$Pt(CF_3)I$(bipy)	**(30)**	Yellow	24.0	1.4	5.2	
			(24.2)	(1.5)	(5.1)	
trans-$Pt(CF_3)Ipy_2$		White	23.8	1.8	6.2	
			(24.1)	(1.8)	(6.4)	

[a] Where measured.

Displacement of the NBD ligand from $Pt(CF_3)_2(NBD)$ by neutral ligands

After displacement of the NBD ligand the possibility existed (for monodentate ligands) of *cis* and *trans* isomers of the $Pt(CF_3)_2L_2$ product. Using ^{19}F NMR the particular geometry could be elucidated from the magnitude of the $^{195}Pt-^{19}F$ coupling (^{195}Pt: $I = \frac{1}{2}$, 34% abundance). This coupling would be expected to be lower in magnitude for the *trans* isomer, where the two CF_3 groups (both with high NMR *trans* influence) are opposite each other, than in the *cis* arrangement where the CF_3 groups are *trans* to the ligand L, which, in these studies, possessed much lower NMR *trans* influence [2].

Compound **1** in chloroform reacted readily with *N,N,N′,N′*-tetramethylethylenediamine (tmen), bipyridine (bipy) and pyridine (py) at room temperature, yielding $Pt(CF_3)_2$(tmen) (**2**), $Pt(CF_3)_2$(bipy) (**3**) and *cis*-$Pt(CF_3)_2py_2$ (**4**) as previ-

Table 2

NMR data for $Pt(CF_3)_2L_2$ complexes

Complex [a]		Solvent	$\delta(F)$ ($^2J(Pt-F)$)	$\delta(C)$ ($J(Pt-C)$) [($J(C-F)$]		$\delta(H)$ ($J(Pt-H)$]	$\delta(Pt)$ [b]
				CF_3	Other resonances		
$Pt(CF_3)_2(NBD)$	**(1)**	$(CD_3)_2CO$	−35.1(810.6)	126.24(2024.5) [344.2]	C(1): 106.52(44.9) C(2): 53.45(36.1) C(3): 76.89(67.4)		−3971(se)
$Pt(CF_3)_2(tmen)$	**(2)**	$(CD_3)_2CO$	−24.5(758.0)	113.94(1934.5) [334.0]	$N-CH_3$: 50.51 CH_2: 63.60	$N-CH_3$: 2.82(23.7) CH_2: 2.92(22.5)	−3849(se)
$Pt(CF_3)_2(bipy)$	**(3)**	$(CD_3)_2CO$	−25.2(749.5)	[c]	C(2,2′): 157.18(16.1) C(3,3′): 124.75(11.7) C(4,4′): 141.52 C(5,5′): 128.41(22.0) C(6,6′): 152.89(39.6)	H(3,3′): 8.44 H(4,4′): 8.62 H(5,5′): 7.90 H(6,6′): 9.15(20.6)	
cis-$Pt(CF_3)_2py_2$	**(4)**	$(CD_3)_2CO$	−26.9(793.5)	115.03(1898.6) [332.0] [d]	C_α: 152.19(13.7) C_β: 126.84(26.4) C_γ: 139.98(7.8)	H_α: 8.82(26.9) H_β: 7.55 H_γ: 7.97	−3827(se)
$Pt(CF_3)_2(en)$	**(5)**	$(CD_3)_2CO$	−23.7(769.0)	120.97([c]) [330.9]	CH_2: 46.25	CH_2: 2.92(21.4) NH_2: 4.28	
cis-$Pt(CF_3)_2(NH_3)_2$	**(6)**	$(CD_3)_2CO$	−26.5(791.0)	118.63(1915.3) [329.6]			

cis-Pt(CF_3)$_2$(DMSO)$_2$	**(7)**	$CHCl_3$	−18.3 [f](881.4)			CH_3: 2.82 [h](10.7)	−3879(qq)
			−30.3 [g](788.6)			3.18 [h](11.0)	
	(8)	$CHCl_3$	−25.2(710.5)				
cis-Pt(CF_3)$_2$($NCCH_3$)$_2$	**(9)**	CH_3CN	−26.1(859.4)				
		$(CD_3)_2CO$	−26.4(864.3)	110.78([e])	CH_3: 2.51(39.0)	CH_3: 2.49(5.9)	
				[329.0] [i]	CN: 119.7(105.0)		
cis-Pt(CF_3)$_2$($NCCH_3$)	**(10)**	$(CD_3)_2CO$	−22.8 [j](947.3)				
(OC(CH_3)$_2$)			−30.0 [k](839.8)				
cis-Pt(CF_3)$_2$(NCPh)$_2$	**(11)**	PhCN	−25.2(854.5)				
		$(CD_3)_2CO$	−26.5(864.3)	111.01(2062.9)	CN: 119.07(110.0)	H(2,6): 8.04	
				[329.8] [l]	C(1): 109.80	H(3,5): 7.72	
					C(2,6):134.29		
					C(3,5):130.68		
					C(4): 136.25		
cis-Pt(CF_3)$_2$(NCPh)	**(12)**	$(CD_3)_2CO$	−22.8 [j](937.5)				
(OC(CH_3)$_2$)			−30.1 [m](844.7)				
cis-Pt(CF_3)$_2$(DMF)$_2$	**(13)**	DMF	−24.3(883.8)				−3649(se)

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[a] For ligand numbering see text figures. [b] se = septet, qq = quartet of quartets. [c] CF_3 signal not observed. [d] ^3J(C–F) = 2.2 Hz. [e] Platinum satellites not observed. [f] *trans* to *O*-bound DMSO. [g] *trans* to *S*-bound DMSO. [h] Not possible to assign to a specific DMSO group. [i] ^3J(C–F) = 4.4 Hz. [j] *trans* to $(CH_3)_2CO$. [k] *trans* to $NCCH_3$. [l] ^3J(C–F) = 4.0 Hz. [m] *trans* to NCPh.

Table 3

NMR data for the products of reaction of $Pt(CF_3)_2L_2$ complexes with aqueous acids and $Pt(CF_3)_2(NBD)$ with anionic ligands

Complex ^{a}		$\delta(F)$ ($^{2}J(Pt–F)$)	$\delta(C)$ ($J(Pt–C)$) [$J(C–F)$]			$\delta(H)$ [$J(Pt–H)$]	$\delta(Pt)$ ^{b}
			CF_3	CO	Other resonances		
cis-$Pt(CF_3)(CO)Cl_2^-$	**(14)**	−13.65(716.6)	114.66(1586.0) [336.7]	157.71(1936.7) [8.1]			−3625(q)
$Pt(CF_3)(CO)(tmen)^+$	**(16)**	−21.18(600.6)	112.04(^{c}) [336]1	158.04(1838.4) [7.4]	NCH_3: 53.27 ^{d} 51.54 ^{e} NCH_2: 61.73 ^{d} 66.48 ^{e}(13.4)	NCH_3: 3.32 ^{d}(23.8) 3.10 ^{e}(38.8) NCH_2: complex	
cis-$Pt(CF_3)(CO)(OH_2)_2^+$	**(17)**	−17.98(687.2)	^{f}	155.05(^{c}) [3.6]			
$Pt(CF_3)(CO)(bipy)^+$	**(18)**	−20.50(581.7)	^{f}	^{f}	C(2,2′): 158.86 ^{d} 158.10 ^{e} C(3,3′): 125.88 ^{e}(12.8) 126.29 ^{e}(24.9) C(4,4′): 145.61 ^{d} 144.43 ^{e} C(5,5′): 130.52 ^{e}(22.2) 130.07 ^{e}(40.3) C(6,6′): 155.11 ^{e}(48.4) 153.11 ^{e}(45.7) [4.0]	H(1,1′): 8.67 ^{d} 8.73 ^{e} H(4,4′): 8.88 ^{d} 8.93 ^{e} H(5,5′): 8.09 ^{d} 8.20 ^{e} H(6,6′): 9.26 ^{d}(21.4) 9.04 ^{e}(34.8)	

cis-$Pt(CF_3)(CO)py_2^+$	**(19)**	−21.21(643.3)	[f]	155.24(1742.3) [6.1]	C_α: 152.50 [d](10.7) 151.62 [e]([g]) C_β: 128.65 [d](20.8) 128.65 [e](42.3) C_γ: 142.67 [d](4.0) 143.65 [e](10.1)	
$Pt(CF_3)(CO)(OH_2)py^+$	**(20)**	−17.47(741.0)	[f]	[h]	C_α: 148.03(8.7) C_β: 127.46(12.1) C_γ: [i]	
$Pt(CF_3)(CO)(OH_2)py^+$	**(21)**	−21.41(600.6)				
$[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]^{2-}$	**(23)**	−17.40(900.3)	115.30(2122.8) [342.1] [j]			−4000(se)
cis-$[Pt(CF_3)(CO)I_2]^-$	**(24)**	−7.82(764.8)	122.29(1630.4) [344.2]	158.19(1834.4) [10.1]		−4293(q)
$[(CF_3)_2Pt(\mu\text{-}Cl)_2Pt(CF_3)_2]^{2-}$	**(25)**	−16.07(852.7)				
$Pt(CF_3)I(NBD)$	**(27)**	−24.62(709.2)	119.40([c]) [341.9]		C(1): 103.2 [d](30.1) C(2): 82.4 [k](136.5) C(3): 51.4(46.2) C(4): 74.1(101.2)	−3836(q)
cis-$[Pt(CF_3)_2(CO)I]^-$	**(28)**	−15.25 [k](849.6) [4.3] −26.13 [e](719.0) [4,3]	[h]	175.44([c]) [18.7] [l] [8.1] [m]		−4293(qq)

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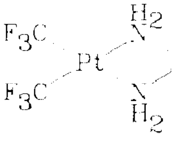
[a] All spectra recorded in acetone solution. [b] q = quartet, se = septet, qq = quartet of quartets. [c] Satellites too weak to measure coupling. [d] *trans* to CF_3. [e] *trans* to CO. [f] Not observed. [g] Coupling masked by peaks from minor products in reaction solution. [h] Not able to be assigned unequivocably. [i] Signal hidden under pyridinium peak (ca. 142.6 ppm). [j] $^3J(C\text{–}F) = 4.7$ Hz. [k] *trans* to I. [l] Coupling to *trans* CF_3 group. [m] Coupling to *cis* CF_3 group.

ously described [13]. ^{19}F NMR data for **2** and **3** (Table 2) are similar to those reported by Clark and Manzer [2] for these products obtained by displacement of the COD ligand from $Pt(CF_3)_2(COD)$. The value of $^2J(Pt-F)$ for **4**, 793.5 Hz, was comparable with the values of 758.0 and 749.5 Hz for **2** and **3** respectively (where the chelating ligand imposes a *cis* arrangement of the CF_3 groups), and **4** is therefore formulated as the *cis* isomer. The method of assignment of the ^1H and ^{13}C ligand resonances has been previously described [13].

Reaction of **1** with ethylenediamine (en) in ether immediately produced a precipitate of $Pt(CF_3)_2(en)$ (**5**). The white solid isolated was stable in dry air, but decomposed if left exposed to atmospheric moisture for longer than several days. The IR spectrum of **5** showed strong, sharp $\nu(N-H)$ bands at 3364 and 3310 cm^{-1} and sharp $\delta(HNH)$ band at 1588 cm^{-1}. The ^{19}F NMR spectrum yielded a value for $^2J(Pt-F)$ of 769.0 Hz, within the range seen above for other N-donors. The magnitude of $^3J(Pt-N-C-H)$ (21.4 Hz) obtained from the ^1H spectrum places the *trans* influence of CF_3 intermediate between methyl ($Pt(CH_3)_2(en)$: 11.2 Hz [8]) and PPh_3 ($Pt(PPh_3)_2(en)^{2+}$: 32.0 Hz [14]).



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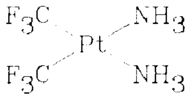

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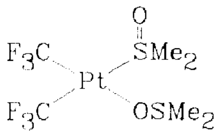

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Warming to room temperature a solution of **1** in chloroform into which a twenty molar equivalent of ammonia gas had been condensed caused a white precipitate of *cis*-$Pt(CF_3)_2(NH_3)_2$ (**6**) to form. The IR spectrum of the solid showed two $\nu(N-H)$ bands at 3384 and 3312 cm^{-1} and a broad $\delta(HNH)$ band at 1619 cm^{-1}. The Pt–F coupling, 791 Hz, was indicative of CF_3 *trans* to an N-donor as seen previously, establishing the *cis* geometry. Moisture-sensitivity, leading to decomposition, was noticed if the solid was exposed to the atmosphere for several days.

In these two reactions involving primary amines, there was no indication of any attack by the amine on the coordinated olefin.

Refluxing an ether solution of **1** with four molar equivalents of DMSO for 2 h, followed by evaporation of the ether, yielded a yellow oil. All attempts to promote crystallisation of this oil were unsuccessful. The ^{19}F NMR spectrum of the oil dissolved in chloroform (Fig. 1) consisted of two peaks of equal intensity at -18.3 ppm ($^2J(Pt-F)$ 881.4 Hz) and -30.3 ppm ($^2J(Pt\text{-}F)$ 788.6 Hz) which were considerably broader ($\Delta\nu_{1/2} = 25$ Hz) than the signals observed in ^{19}F spectra of the $Pt(CF_3)_2L_2$ complexes previously described, and a minor peak at -25.2 ppm ($^2J(Pt-F) = 710.5$ Hz) with a linewidth of more usual magnitude ($\Delta\nu_{1/2} = 3$ Hz). All of these Pt–F coupling constants were much larger than would be expected for a *trans* isomer. A small amount of **1** remained as evidenced by a peak at -33.9 ppm. The spectrum was consistent with the major product having inequivalent CF_3 groups. The broadening of the two signals was a result of unresolved F–F coupling between the two CF_3 groups. As it was unlikely that a monodentate NBD/DMSO complex (i.e. *cis*-$Pt(CF_3)_2(\eta^2\text{-NBD})(DMSO)$) would be stable in the presence of excess DMSO under reflux, this can only be explained by each of the DMSO ligands in a bis(DMSO) complex having a different coordination mode. Thus, the major species in the reaction mixture was *cis*-$Pt(CF_3)_2(DMSO\text{-}S)(DMSO\text{-}O)$ (**7**).

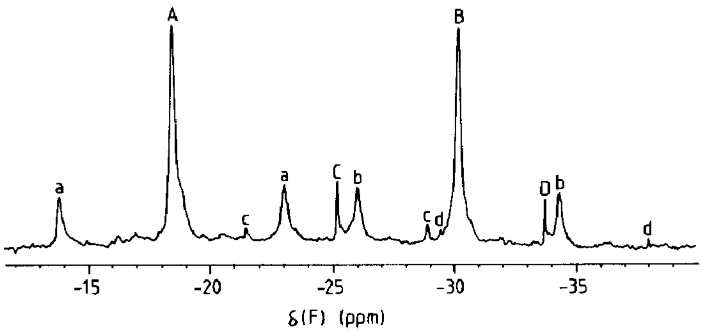


Fig. 1. 94.2 MHz ^{19}F NMR spectrum of the oil isolated from reaction of $Pt(CF_3)_2(NBD)$ (**1**) with DMSO dissolved in $CDCl_3$. *cis*-$Pt(CF_3)_2$(DMSO-*S*)(DMSO-*O*) (**7**): Aa CF_3 *trans* to DMSO-*O*; Bb CF_3 *trans* to DMSO-*S*. Cc *cis* – $Pt(CF_3)_2$(DMSO-*S*)$_2$ (**8**). Dd $Pt(CF_3)_2$NBD) (**1**).

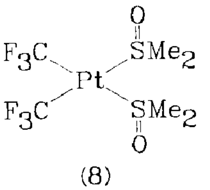
The larger of the two Pt–F coupling constants was assigned to the trifluoromethyl group *trans* to *O*-bound ligand. The ^{195}Pt signal from **7** appeared as the expected quartet of quartets at –3879 ppm. The ^{1}H NMR spectrum displayed two signals of equal intensity from the methyl protons on each DMSO ligand at 2.82 and 3.18 ppm, with platinum couplings of 10.7 and 11.0 Hz respectively.

The minor signal at – 25.2 ppm (Fig. 1) was most likely due to *cis*-$Pt(CF_3)_2$(DMSO-*S*)$_2$ (**8**). The narrow linewidth was as expected for equivalent CF_3 groups and the magnitude of the Pt–F coupling (710.5 Hz) corresponded to *S*-bound rather than *O*-bound DMSO. The ^{195}Pt shift of this complex relative to **7** would have provided further support for this formulation, but the small proportion of this complex prevented the detection of a ^{195}Pt signal.

Little reaction occurred under similar conditions if the solvent used was chloroform or benzene. Dissolution of **1** in neat DMSO and heating at 85 ° C for 30 min gave a similar mixture of **7** and **8**.

For other *cis*-$PtR_2(DMSO)_2$ complexes ($R = CH_3$ [8,15,16], aryl [16]) evidence for *S*-coordination only has been reported. It is most probable that *cis*-$Pt(CF_3)_2(DMSO)_2$ favours a mixed *S*- and *O*-coordination of the two DMSO ligands because of steric constraints. The preference for coordination of DMSO through the sulfur atom may be inferred from the lack of any evidence for a bis(DMSO-*O*) complex.

Solid **1** dissolved in CH_3CN with gentle heating, giving rise to a single peak with platinum satellites in the ^{19}F spectrum at –26.1 ppm. The Pt–F coupling of 859.4 Hz was indicative of CF_3 *trans* to a ligand with low *trans* influence and allowed identification of the product as *cis*-$Pt(CF_3)_2(NCCH_3)_2$ (**9**). Removal of the excess CH_3CN under vacuum yielded a white solid, which proved to be moisture-sensitive.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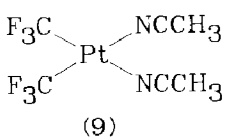
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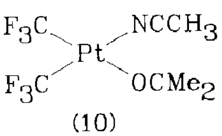
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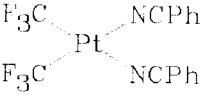
The ^{19}F spectrum of a solution of **9** in acetone yielded, in addition to the major peak at –26.4 ppm (^2J(Pt–F) = 864.3 Hz, $\Delta\nu_{1/2}$ = 5 Hz) from **9**, two minor peaks of equal intensity at -22.8 ppm (^2J(Pt–F) = 947.3 Hz, $\Delta\nu_{1/2} = 28$ Hz) and -30.0 ppm (^2J(Pt–F) = 839.8 Hz, $\Delta\nu_{1/2} = 28$ Hz). The value of 947.3 Hz for Pt–F coupling indicated that this particular CF_3 group was *trans* to a ligand with very weak *trans* influence, which in this system could only be acetone. The other ^2J(Pt–F) value of 839.8 Hz was consistent with CF_3 still *trans* to $NCCH_3$. From this it was deduced that the CH_3CN ligands in **9** were fairly weakly bound, and some displacement by acetone occurs to produce *cis*-$Pt(CF_3)_2(NCCH_3)(OCMe_2)$ (**10**). The proportion of **10** did not increase, even after a solution of **9** in acetone had stood for four months.

Heating a solution of benzonitrile to which **1** had been added, followed by addition of hexane, precipitated *cis*-$Pt(CF_3)_2(NCPh)_2$ (**11**) as a white solid. When dissolved in acetone **11** displayed similar behaviour to that observed for **9** in the same solvent, forming a significant amount of *cis*-$Pt(CF_3)_2(NCPh)(OCMe_2)$ (**12**).



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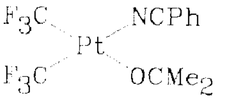

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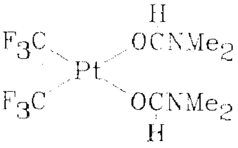


(13)

No detectable reaction occurred on prolonged heating of **1** in dry acetone. Formation of acetone adducts has been reported by Uson et al. [17] upon dissolution of the C_6F_5 complexes $[(C_6F_5)_2Pt(\mu\text{-}X)_2Pt(COD)]_n$ (X = Br, I) in acetone, where cleavage of the binuclear unit yields *cis*-$Pt(C_6F_5)_2(OCMe_2)_x$ and $PtX_2(COD)$.

With gentle heating, dissolution of **1** in DMF was achieved. The Pt–F coupling obtained from the ^{19}F spectrum was 883.8 Hz, confirming that the NBD ligand had been replaced by O-donor DMF ligands yielding *cis*-$Pt(CF_3)_2(DMF)_2$ (**13**). The ^{195}Pt signal was located at -3649 ppm, and appeared as a septet from coupling to the six equivalent fluorine nuclei. Problems associated with the complete removal of excess DMF prevented the isolation of solid **13**.

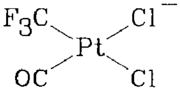
Reaction between **1** and water and methanol resulted in electrophilic attack on the CF_3 groups, as evidenced by the generation of fluoride ion (^{19}F signal at -163 ppm [18]). Extensive decomposition, leading to the deposition of a black solid, presumably platinum metal, accompanied this attack. At room temperature little reaction was observed in the reaction of **1** and water prior to noticeable decomposition (after about 1 h). At 80 °C deomposition was immediate. With dry methanol it was possible to reflux the solution for up to 2 h before decomposition of the Pt^{II} complex became apparent. At this stage the ^{19}F spectrum indicated approximately 80% conversion to a new complex giving rise to a signal at -24.8 ppm (^2J(Pt–F) = 847.2 Hz), suggesting NBD displacement had occurred. However, further studies to determine the identity of this complex were prevented by the subsequent attack on the CF_3 groups.

Reactions of cis-Pt(CF$_3$)$_2$L$_2$ (L$_2$ = tmen (2), bipy (3); L = py (4)) with aqueous acids

Addition of four molar equivalents of concentrated aqueous HCl to an acetone solution of **2** resulted in the formation of a new species. The Pt–F coupling of 717.8 Hz confirmed that this new species was a Pt^{II} complex. Complete conversion of **2** into this new complex was observed over 90 min, during which time the production of fluoride ion was also noted by the emergence of a ^{19}F peak at -182 ppm [18].

Concurrent dissociation of the protonated tmen ligand was detected by the gradual increase in intensity of two new peaks in the ^{1}H NMR spectrum of the reaction solution at 3.13 and 3.93 ppm, both devoid of platinum coupling. These shifts were similar to those exhibited by an acetone solution of tmen to which aqueous HCl had been added. The ^{195}Pt signal from this new complex appeared as a quartet at -3625 ppm (^2J(Pt–F) = 718 Hz), obviously from coupling to only three fluorine nuclei, indicating that only one CF_3 group remained bound to the platinum nucleus. The ^{13}C spectrum revealed the presence of coordinated CO by a quartet signal at 157.71 ppm with platinum satellites, ^1J(Pt–C) = 1936.7 Hz. The quartet splitting was a product of coupling with the three fluorine atoms of the CF_3 moiety, ^3J(C–F) = 8.1 Hz.

These NMR spectral data were consistent with the formation of either *cis*- or *trans*-$Pt(CF_3)(CO)Cl_2^-$ (**14** or **15**). Confirmation of this empirical formula came with the isolation of a solid from the reaction of **1** with $(n\text{-}Bu)_4NCl$ (described below) which analysed for $[(n\text{-}Bu)_4N][Pt(CF_3)(CO)Cl_2]$ and gave identical NMR spectra to those described above.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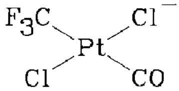
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In *cis*-$Pt(CH_3)_2(CO)_2$ and *cis*-$PtPh_2(CO)_2$ the ^{13}C chemical shifts of the coordinated CO groups are 178.0 and 175.8 ppm, with ^1J(Pt–C) values of 898 and 881 Hz [19]. As the NMR *trans* influence of CF_3 is only slightly less than that of CH_3 and Ph [20] one would expect ^1J(Pt–C) for a CO group *trans* to CF_3 to be of a similar magnitude. The value of ^1J(Pt–C) obtained for the species resulting from the action of HCl on **2** was 1936.7 Hz, considerably greater than those mentioned above, and indicative of CO *trans* to a ligand possessing low *trans* influence such as chloride. A marked difference was also evident between the ^{13}C shift of the CO group in this complex and those reported for the two complexes with CO *trans* to alkyl or aryl. From this it was reasoned that *cis*-$Pt(CF_3)(CO)(Cl_2^-$ (**14**) was the isomer that formed. The $^{13}C(O)\text{–}Pt\text{–}CF_3$ coupling constant was also similar to the value when CO is known to be *cis* to CF_3 (e.g. 7.4 Hz in $Pt(CF_3)(CO)(tmen)^+$ (see below)).

14 appeared to be resistant to further attack by the excess of HCl remaining in solution, since it was still present in solution after one month.

Compounds **3** and **4** also reacted with an excess of concentrated aqueous HCl (eight molar and four molar equivalents respectively) to yield **14**, with accompanying formation of fluoride ion. Compound **4** was completely converted to **14** in 1 h, while **3** required 16 h for conversion.

Attempts to detect by ^{19}F NMR the presence of the proposed $Pt(CF_3)(CF_2)py_2^+$ intermediate in a solution of **4** in dry CH_2Cl_2 containing one molar equivalent of dry HCl gas were not successful; only signals due to **14** and unreacted **4** being observed. It appears that this intermediate is extremely reactive, and rapid reaction with trace amounts of water occurs to generate **14**.

Addition of five molar equivalents of concentrated aqueous $HClO_4$ to a solution of **2** in acetone resulted in the rapid formation of a new species evidenced by a singlet with satellites at -21.18 ppm in the ^{19}F NMR spectrum (Fig. 2(b). The only other peaks present in the region corresponding to $Pt\text{–}CF_3$ were minor peaks in the

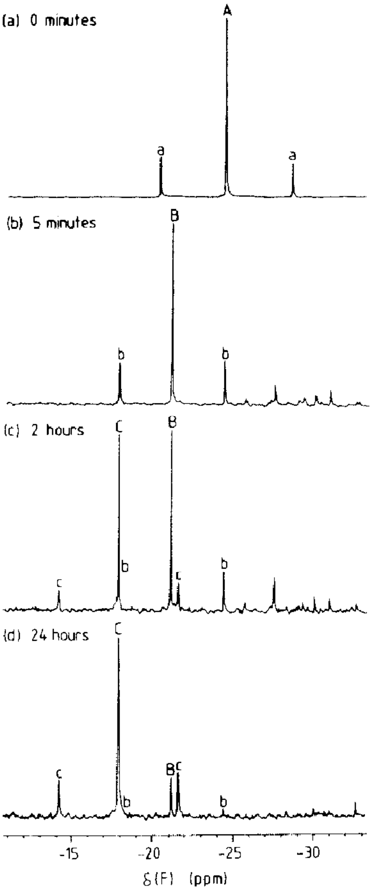


Fig. 2. 94.2 MHz ^{19}F NMR spectra of a solution of $Pt(CF_3)_2$(tmen) (**2**) in $(CD_3)_2CO$, to which excess $HClO_4/H_2O$ has been added, as a function of time after addition. Aa $Pt(CF_3)_2$(tmen) (**2**). Bb $Pt(CF_3)(CO)(tmen)^+$ (**16**). Cc *cis*-$Pt(CF_3)(CO)(OH_2)_2^+$ (**17**).

range -25 to -31 ppm. No peaks from **2** remained. The value of 600.6 Hz for ^2J(Pt–F), although considerably lower than the value for **2**, still indicated formation of a Pt^{II} complex. The 100 MHz ^{1}H spectrum of the solution (Fig. 3(b)) showed two strong singlets at 3.10 and 3.32 ppm each with platinum satellites, corresponding to the two sets of N-CH_3 protons of an unsymmetrically coordinated tmen ligand. The two Pt–N–CH_3 coupling constants were 38.8 and 23.8 Hz respectively. The ^{13}C NMR spectrum contained signals arising from the four different carbon atoms (two methyl and two methylene) of the tmen ligand, the CF_3 group, and coordinated CO (Table 3). No evidence could be found in either the ^{1}H or ^{13}C spectra to indicate that displacement of the tmen ligand had occurred at this stage. The only structure consistent with these data is $Pt(CF_3)(CO)(tmen)^+$ (**16**). This was confirmed by preparation of an authentic sample of $[Pt(CF_3)(CO)(tmen)]ClO_4$ from $Pt(CF_3)I$-(tmen) (described in Experimental section). When this solid was dissolved in acetone, NMR spectra were found to correlate with the spectra obtained upon treatment of **2** with $HClO_4$. In this complex, where the carbonyl ligand is necessarily *cis* to CF_3, the coupling between the carbonyl carbon and the fluorine nuclei is 7.4 Hz.

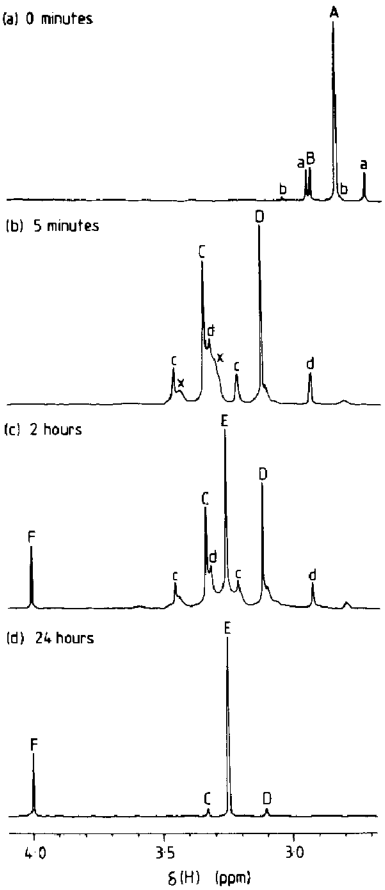
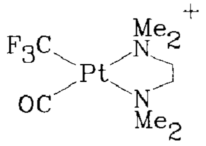


Fig. 3. 99.6 MHz ^1H NMR spectra of a solution of $Pt(CF_3)_2(tmen)$ (**2**) in $(CD_3)_2CO$, to which excess $HClO_4/H_2O$ has been added, as a function of time after addition. $Pt(CF_3)_2(tmen)$ (**2**): Aa *N*-methyl groups; Bb *N*-methylene groups. $Pt(CF_3)(CO)(tmen)^+$ (**16**): Cc *N*-methyl groups *trans* to CF_3; Dd *N*-methyl groups *trans* to CO. $(tmenH_2)^{2+}$: E *N*-methyl groups; F *N*-methylene groups. The *N*-methylene protons of **16** give a complex pattern (AA′BB′) under broad envelopes marked ×.

It was apparent that the reaction with $HClO_4$ differed from that of HCl, in that rapid formation of $Pt(CF_3)(CO)(tmen)^+$ (**16**) occurred upon addition of the $HClO_4$, without protonation of the tmen ligand occurring simultaneously. This difference is most likely to be a result of the greater ability of chloride, relative to water or perchlorate, to fill the coordination sites vacated by the N-donor group, hence displacement of the N-donor ligand is rapid in the reaction with HCl.



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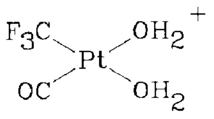


17

The significant lowering of the value of $^1J(Pt-F)$ from **2** to **16** is interesting when one considers that there is no change in the *trans* ligand; the factor primarily responsible for the magnitude of the Pt–F coupling. This leads to the assumption that the CO ligand must have a considerable *cis* influence. A similar effect has been observed in [Pt(CH_3)X(dppe)] complexes [4], where ^1J(Pt–P) *trans* to CH_3 was almost 200 Hz lower in [Pt(CH_3)(CO)(dppe)]$^+$ relative to [Pt(CH_3)$_2$(dppe)].

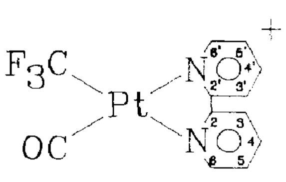
The greater NMR *trans* influence of CF_3 relative to CO has been well documented [4,20], thus enabling specific assignment of the proton and carbon resonances of the tmen ligand in **16** based on the relative magnitudes of the platinum couplings (Table 3). In this complex all the methylene protons would be inequivalent and yield a complex AA′BB′ spectrum of low intensity, accounting for the absence of any definite signals. In a spectrum recorded at higher field (400 MHz) two complex patterns centred at 3.29 and 3.46 ppm were observed.

After the solution had stood for several hours at room temperature the ^{19}F spectrum showed a second singlet with satellites to lower shielding (−17.98 ppm) from **16** (Fig. 2(c)). ^2J(Pt–F), 687.2 Hz, indicated formation of another Pt^{II} complex. This was accompanied by the appearance, in the ^1H spectrum (Fig. 3(c)), of two singlets devoid of platinum coupling at 3.24 and 3.99 ppm, arising from the presence of tmenH_2^{2+} in solution. Release of the tmen ligand presumably left *cis*-Pt(CF_3)(CO)(OH_2)$_2^+$ (**17**) as the new Pt^{II} complex since the perchlorate anions were not expected to coordinate.

After 24 h reaction little **16** remained (Fig. 2(d) and 3(d)). There was considerable deposition of a dark solid, presumably platinum metal. As an acetone solution of **16** in the absence of acid showed no tendency to decompose, this suggested that **17** was not very stable under the reaction conditions.

Generation of **17** was accompanied by a new quartet signal corresponding to coordinated CO in the ^{13}C spectrum at 155.05 ppm. The coupling between this nucleus and the ^{19}F nuclei (3.6 Hz) corresponded to a *cis* geometry. Satellites from coupling to platinum were too weak to be observed. Attempts to obtain the ^{195}Pt NMR signal for **17** were unsuccessful. The most likely explanation for this was the presence of protonation/deprotonation equilibria involving the coordinated water molecules, causing broadening of the platinum signal to the extent that it was not observed. However, following addition of LiCl to a solution containing **17** a ^{195}Pt NMR signal corresponding to **14** (the complex expected upon replacement of the aqua ligands of **17** with chloride) was easily detected.

Addition of ten molar equivalents of concentrated aqueous $HClO_4$ to a solution of **3** in acetone caused the immediate formation of Pt(CF_3)(CO)(bipy)$^+$ (**18**). None of complex **3** remained in solution. Confirmation that NMR peaks were correctly assigned to **18** came with the preparation of [Pt(CF_3)(CO)(bipy)]ClO_4 from Pt(CF_3)I(bipy) (described in Experimental section). When this solid was dissolved in acetone identical NMR spectra were obtained. The solid exhibited a ν(C≡O) band at 2144 cm^{-1} in the IR spectrum.



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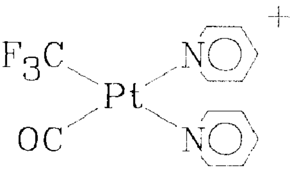

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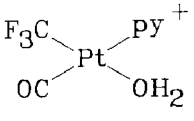
The bipyridyl ligand resisted dissociation from **18**. Even when the acid concentration was doubled no formation of **17** was noted.

The reaction between **4** and $HClO_4$ exhibited greater complexity in products and a much greater dependence on the concentration of acid than either of the two previous systems. Over 1 h following addition of approximately an equimolar amount of concentrated aqueous $HClO_4$ to an acetone solution of **4**, formation of a new Pt^{II} complex (and fluoride ion) occurred. NMR data (Table 3) were consistent with formation of *cis*-$Pt(CF_3)(CO)py_2^+$ (**19**). Unfortunately, only *trans*-$Pt(CF_3)Ipy_2$ was obtained from reaction of pyridine with $Pt(CF_3)I(NBD)$, and **19** could not be generated in an analogous manner to the carbonyl complexes in the two previous systems for further confirmation of its identity. Under the conditions of this preparation **19** appeared to be stable in solution for at least two days at room temperature.

Addition of five molar equivalents of $HClO_4$ to an acetone solution of **4** resulted in the immediate formation of four Pt^{II} complexes, two of which were easily identified as *cis*-$Pt(CF_3)(CO)py_2^+$ (**19**) and *cis*-$Pt(CF_3)(CO)(OH_2)_2^+$ (**17**) on the basis of previous studies. The two additional products in this system were probably complexes containing only one bound pyridine, isomers of $Pt(CF_3)(CO)(OH_2)py^+$ (**20** and **21**). The two additional signals in the ^{19}F spectrum were assigned to **20** and **21** (Table 3) on the basis of their similarity, both in chemical shift and coupling constant, to the signals from **17** and **19** respectively. The presence of significant amount of **17** early in the reaction (cf. **17** was first noticed after 1 h in the reaction of **2** with a similar amount of $HClO_4$) indicated that the pyridine ligands were very susceptible to protonation by acid.



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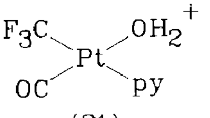

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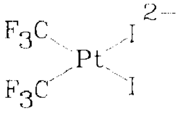
After the solution had stood for 18 h the ^{19}F spectrum showed an increase in intensity of the peaks due to **17** and **20** relative to those of **19** and **21**. At this stage the solution had darkened considerably and a black precipitate, presumably platinum metal, had formed. After the solution had stood a further 24 h more decomposition of the complexes had occurred (judging from the amount of additional black precipitate formed) and the ^{19}F spectrum showed a sharp decline in the intensities of the peaks due to **17** and **21**. The increase in the amount of **20** relative to **21** is most probably a result of slow isomerisation of **21** to **20**. Appleton et al. [21] have reported a similar process operating in Pt^{IV} complexes which places ligands of high *trans* influence *trans* to ligands of low *trans* influence.

The ^{19}F spectra of solutions involving reactions with $HClO_4$ displayed a number of additional minor signals in the range -25 to -31 ppm with Pt–F couplings indicative of Pt^{IV} complexes. Given that **17**, and possibly other of the Pt^{II} species, appear to be unstable under these conditions, these Pt^{IV} species could be arising from disproportionation of the Pt^{II} complex to give Pt^0 and a Pt^{IV} complex. No attempt was made to establish the identity of any of these Pt^{IV} complexes.

Displacement of the NBD ligand from $Pt(CF_3)_2(NBD)$ (1) by anionic ligands

Addition of an equimolar amount of NaI or $(n\text{-}Bu)_4NI$ to an acetone solution of **1** produced immediate and complete conversion to a complex giving rise to a signal in the ^{19}F spectrum at -17.4 ppm, $^2J(Pt–F) = 900.3$ Hz. Clearly this complex could not be *cis*-$Pt(CF_3)_2I_2^{2-}$ (**22**), as one would expect some unreacted **1** to be still present in solution with only one mole equivalent of iodide added. To account for complete conversion to a new Pt^{II} complex consistent with a $^2J(Pt-F)$ value indicating CF_3 *trans* to I, bridging by the iodo ligands to form $[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]^{2-}$ (**23**) must be occurring. Although the ^{19}F spectrum of **23** appeared to be first-order, the ^{195}Pt spectrum showed peaks in addition to the major septet, consistent with the X-part of the complex $A_6XX'A'_6$ spectrum expected for **23**. From this solution, when tetra-n-butylammonium was the counterion, could be isolated a pale yellow solid which analysed well for $[(n\text{-}Bu)_4N]_2[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]$ (Table 1).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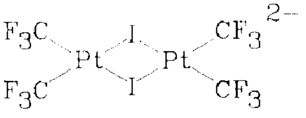
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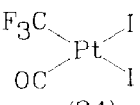
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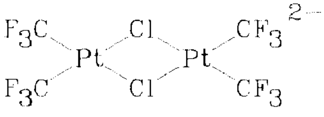
Subsequent addition of two molar equivalent of iodide ion to a solution of **23** in acetone resulted in the appearance of a new signal in the ^{19}F spectrum at −7.84 ppm, $^2J(Pt-F) = 764.8$ Hz. Formation of this new complex was slow at room temperature, but complete conversion was rapidly achieved by refluxing the solution. Addition of water or aqueous acid also increased the rate of conversion. This conversion was accompanied by the appearance of a peak at −182.5 ppm, from fluoride ion [18]. Addition of two molar equivalents of iodide ion to an acetone solution of **1** initially generated a mixture of **23** and this new complex, with subsequent slow conversion of **23** into this new complex as described above.

The ^{195}Pt signal of this new complex appeared as a quartet at −4293 ppm, indicating that only one CF_3 group still remained bound to the platinum nucleus, and that this signal could not be arising from **22**. If **22** were formed, at least temporarily, the product of attack on this complex by traces of water would be *cis*-$Pt(CF_3)(CO)I_2^-$ (**24**). Evidence for a coordinated CO group could be obtained from the ^{13}C spectrum. The chemical shift and Pt–C coupling constant (158.2 ppm and 1834.4 Hz) together with the C–F coupling constant 10.1 Hz) were consistent with the CO group being *cis* to the CF_3 group. This complex could be isolated as the tetra-n-butylammonium salt, and analyses (Table 1) support the formula $[(n\text{-}Bu)_4N][Pt(CF_3)(CO)I_2]$. An IR spectrum of this solid revealed a band at 2096 cm^{-1} corresponding to the C≡O stretch of the coordinated CO group.

Addition of an equimolar amount of chloride ion (either as LiCl or $(n\text{-}Bu)_4NCl$) to an acetone solution of **1** yielded two new signals in the ^{19}F spectrum at −13.65 ppm ($^2J(Pt-F) = 717.6$ Hz) and −16.07 ppm ($^2J(Pt-F) = 852.7$ Hz) in addition to a small amount of unreacted **1**. The signal at −13.65 ppm could be attributed to *cis*-$Pt(CF_3)(CO)Cl_2^-$ (**14**) from comparison with the product of reactions of $Pt(CF_3)_2L_2$ with HCl previously described. The small proportion of **1** remaining in solution immediately after addition of chloride ion indicated that the signal at −16.07 ppm resulted from $[(CF_3)_2Pt(\mu\text{-}Cl)_2Pt(CF_3)_2]^{2-}$ (**25**) rather than *cis*-$Pt(CF_3)_2Cl_2^{2-}$ (**26**). Initially **25** was the major component of the solution, but steady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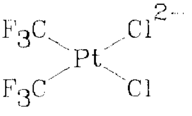
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reaction of this complex occurred over a 45-min period, generating additional **1** and **14**. This prevented further clarification of the structure of **25** by ^{13}C and ^{195}Pt NMR, and resulted in contamination of a solid derivative by the other complexes.

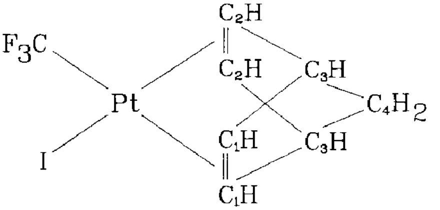
When two molar equivalents of LiCl or $(n\text{-Bu})_4$HCl were added to an acetone solution of **1**, both **25** and **14** were generated, with no **1** remaining. With the additional chloride ion present the reaction of **25** gave rise only to additional **14**, until, after 45 min, only **14** remained in solution. When $(n\text{-Bu})_4$NCl had been used, solid $[(n\text{-Bu})_4\text{N}][\text{Pt}(\text{CF}_3)(\text{CO})\text{Cl}_2]$ was isolated ($\nu(\text{C}{\equiv}\text{O}) = 2093\ \text{cm}^{-1}$).

In subsequent experiments where considerable precautions were taken to exclude water from these systems, no NMR evidence to suggest the presence of either **22** or **26** could be detected. Only peaks due to the dimeric complexes **23** or **25** were observed.

Preliminary studies indicate that bromide, thiocyanate and acetylacetonate anions also effect NBD displacement from **1**, but detailed studies of these systems have not been carried out.

Pentafluorophenyl complexes with bridging halide corresponding to **23** and **25** have been prepared by Usón et al. [22]. It is interesting that in this system the arylation of PtCl_2 with (C_6F_5)MgBr led to the formation of the binuclear complex $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Br})_2\text{Pt}(\text{C}_6\text{F}_5)_2]^{2-}$ exclusively. No evidence for the $[\text{Pt}(\text{C}_6\text{F}_5)_2\text{Br}_2]^{2-}$ complex was obtained, even when a large excess of the organomagnesium derivative was used. It is also noteworthy that reaction between PtCl_2 and (C_6F_5)MgBr resulted in the exclusive formation of a product with bromide as the bridging ligand from a solution in which chloride ions also exist. This parallels the lesser stability found for the chloro-bridged species in the trifluoromethylplatinum(II) complexes.

Although much more stable in solution than its chloro analogue, **23** did react further upon standing, forming **24** and **1** (when the displaced NBD ligand was still present in solution) (Fig. 4(b)), and fluoride ion. With longer standing, peaks due to **23** disappeared and new peaks grew in the spectrum (Fig. 4(b), 4(c)). After 8 d, the solution had darkened considerably, and crystals had deposited from solution. After recrystallisation, the solid analysed for $\text{Pt}(\text{CF}_3)\text{I}(\text{NBD})$ (**27**). NMR data (Table 3)



(27)

were consistent with this formulation. Particularly noteworthy are the large differences in coupling constants to platinum of carbon and proton nuclei for the olefin groups *trans* to CF_3 and iodide. The ^{19}F NMR spectrum of the reaction solution showed, in addition to peaks from **27**, two quartets with satellites, of equal intensity, which must be due to a bis(trifluoromethyl) complex in which the two trifluoromethyl groups are non-equivalent (i.e. *cis*-$\text{Pt}(\text{CF}_3)_2\text{LL}'$). From the Pt–F coupling constants (719.0 and 849.6 Hz) L and L′ must have low *trans* influence. As the ^{13}C spectrum of the reaction mixture indicated the presence of a carbonyl resonance, in addition to that of **24**, at 175.44 ppm, and the only other potential ligand in solution with a low trans influence was iodide, this complex was for-

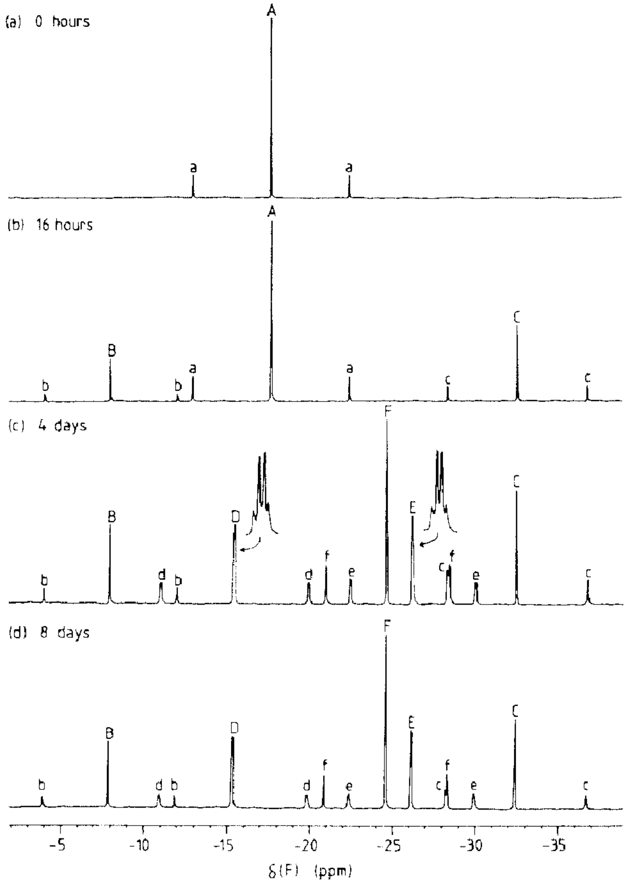
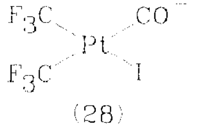


Fig. 4. 94.2 MHz ^{19}F NMR spectra of a $(CD_3)_2CO$ solution containing $[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]^{2-}$ (**23**) and NBD, as a function of time. Aa $[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]^{2-}$ (**23**). Bb *cis*-$Pt(CF_3)(CO)I_2^-$ (**24**). Cc $Pt(CF_3)_2(NBD)$ (**1**). *cis*-$Pt(CF_3)_2I(CO)^-$ (**28**): Dd CF_3 *trans* to I; Ee CF_3 *trans* to CO. (Insets are a five-fold frequency expansion) Ff $Pt(CF_3)I(NBD)$ (**27**).

mulated as *cis*-$Pt(CF_3)_2I(CO)^-$ (**28**). Attempts to isolate this complex as a solid with the purpose of obtaining analytical confirmation of its composition were unsuccessful. However, the NMR data all agree with the proposed structure. The splitting of the central signal of the CO group fitted well with the expected quartet of quartets from coupling to the two inequivalent sets of three fluorine nuclei. One C–F coupling (8.1 Hz) was similar to that previously observed when CO is *cis* to CF_4. The larger coupling (18.7 Hz) corresponded to coupling to the *trans* CF_3 group. The chemical shift of this signal (175.44 ppm compared with values of between 157 and 159 ppm for other carbonyl complexes reported in this work) was similar to that reported for the complexes *cis*-$PtR_2(CO)_2$ ($R = CH_3$, Ph) [19] where the CO group is *trans* to the alkyl or aryl group. Unfortunately the multiplicity of the signal from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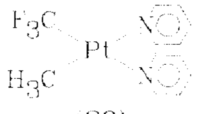
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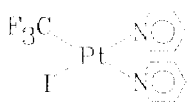
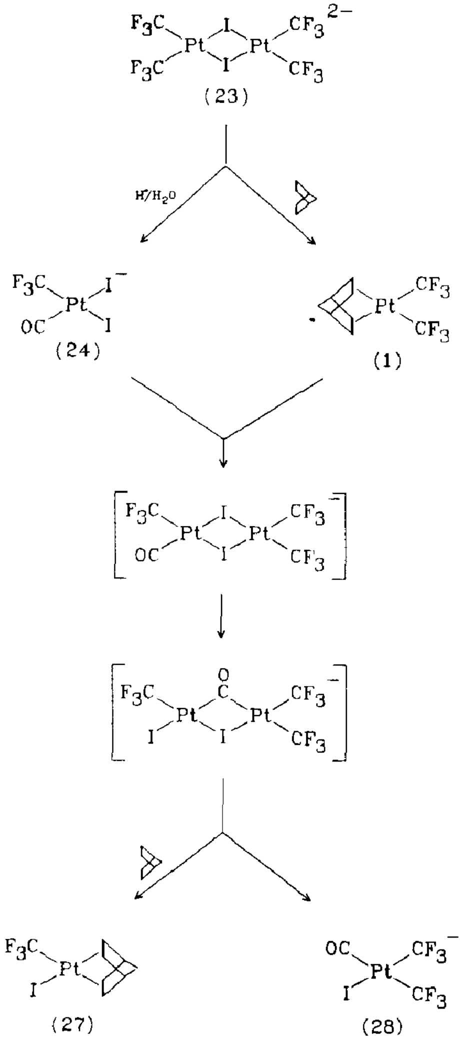

(30)

28 caused the platinum satellites to be took weak to be observed, and no comparison between ${}^1J$(Pt–C(O)) values could be made. The inequivalent CF_3 groups also caused the ^{195}Pt signal to appear as a quartet of quartets at −4293 ppm.

Further studies revealed that no reaction proceeded when an acetone solution of **24** (prepared by addition of two molar equivalents of iodide ion to **1**) was allowed to stand in the presence of the displaced NBD ligand. However, when an acetone solution of **1** was added to a solution of **24** generated from $[(n\text{-Bu})_4N]_2[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]$ (i.e. with no free NBD present) in approximately equal quantities, formation of **27** and **28** resulted. Thus, it appears that the role played by **23** is only generation of **1** and **24**, probably by cleavage of the binuclear unit, followed by rapid attack on the *cis*-$Pt(CF_3)_2I_2^{2-}$ complex yielding **24**, and recombination of the '$Pt(CF_3)_2$' moiety with the NBD ligand still present in solution forming **1**. The reaction between **1** and **24** is thought to result from displacement of the NBD ligand from **1** by **24** to form a binuclear complex, which then undergoes rearrangement to



Scheme 1

place the CO group as a bridging ligand. The binuclear complex then dissociates, with subsequent recombination of the NBD ligand with the 'Pt(CF_3)I' moiety, to yield **27** and **28**. This sequence of reactions is summarised in Scheme 1.

Monitoring, via ^{19}F NMR, of a solution of **14** to which an equimolar amount of **1** had been added, led to the discovery of several new signals. However, these did not seem to parallel the reaction of **24** with **1**, and no attempt was made to elucidate their identity. The reason for the inability of **14** to duplicate the reactions of **24** probably lies in the lower stability of the binuclear complex when the bridging groups are chloride.

Conclusions

As expected, displacement of the NBD ligand from **1** was achieved by a much greater range of weak donor ligands than that reported [8] for $Pt(CH_3)_2(NBD)$ where reaction was not observed with acetonitrile, benzonitrile, DMF, chloride or bromide. The reaction with iodide or thiocyanate was slow, and resulted in loss of the methyl groups. The range of $Pt(CF_3)_2L_2$ products prepared in this study was more extensive than those prepared by Clark and Manzer [2] from $Pt(CF_3)_2(COD)$.

It appears that, with the weaker donor groups and anionic ligands attached to the $Pt(CF_3)_2$ moiety, the CF_3 groups become more susceptible to attack by weakly acidic reagents such as water. This is most evident for the anionic complexes where the $Pt(CF_3)_2X_2^{2-}$ complexes could not be detected. This attack is probably responsible for the decomposition of the solid derivatives which are unstable if left exposed to the atmosphere.

It is surprising that both CF_3 groups in the $Pt(CF_3)_2L_2$ complexes are not attacked by electrophilic reagents. From a study by Michelin et al. [12] it appears that one factor influencing electrophilic attack on the F atoms of CF_3 groups is the electron density on the metal centre. This suggests that for $Pt(CF_3)_2L_2$ complexes conversion of one CF_3 group into a CO group decreases the electron density on the platinum centre sufficiently to render the remaining CF_3 group immune to further attack. This delicate balance is especially noticeable in complexes **14** and **24** which, although possessing an overall negative charge, do not undergo further attack.

One qualitative measure of the susceptibility of the CF_3 group in a complex to electrophilic attack may be gained from the relative positions of the ν(C–F) bands in the IR spectrum of these complexes. Unfortunately, direct comparisons between mono(trifluoromethyl) and bis(trifluoromethyl) complexes are not possible because interaction between the two CF_3 groups in bis(trifluoromethyl) complexes causes splitting of the two bands commonly observed in the IR spectrum of mono(trifluoromethyl) complexes [13]. In an attempt to gauge the effect of a change in electron-donating ability of a ligand on ν(C–F) values, the IR spectra of $Pt(CF_3)(CH_3)$(bipy) (**29**) [23] and $Pt(CF_3)$I(bipy) (**30**) were obtained. **29** was chosen because, from the similarity in *trans* influence between CH_3 and CF_3, it was thought that this compound would display similar IR characteristics to **3** while by-passing the problem of splitting of the two ν(C–F) bands. Its IR spectrum exhibited ν(C–F) bands at 1090 and 960 cm^{-1}. When the IR spectrum of **30** was obtained, the ν(C–F) bands appeared to higher wavenumber, at 1105 and 1010 cm^{-1}, showing the apparent sensitivity of the C–F bond to variations in electron density on the platinum centre.

Experimental

Instrumentation and general methods

99.6 MHz ^{1}H, 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 ^{1}H and 100.4 MHz ^{13}C spectra were obtained on a JEOL JNM GX-400 spectrometer, with a 5 mm dual ^{1}H/^{13}C probe. Chemical shifts (positive to lower shielding) are relative to internal tetramethylsilane (TMS) for ^{1}H and ^{13}C, to internal $CFCl_3$ for ^{19}F, and to external Na_2PtCl_6/H_2O for ^{195}Pt.

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) [24] and hence $Pt(CH_3)_2$(NBD) [8]. $Pt(CF_3)_2$(NBD) was prepared by the reaction of $Pt(CH_3)_2$(NBD) with excess CF_3I, as previously described [13].

Reactions of 1 with neutral ligands

Preparation of the $Pt(CF_3)_2L_2$ complexes was generally carried out by addition of the ligand to a solution of **1** in the appropriate solvent, followed by a brief period of heating to ensure complete reaction. Details of conditions used for each complex are given in Table 4. Isolation methods for each complex, and any variations to the general method described above, are given below.

$Pt(CF_3)_2$(tmen) (2)

The solution volume was reduced to 1–2 ml and the white solid filtered off, washed with chloroform (0.5 ml) and ether (3 × 5 ml), and dried under vacuum.

Table 4

Experimental conditions for preparation of $Pt(CF_3)_2L_2$ complexes

Complex		Reactants		Solvent (Volume)	Heating		Yield (%)
		1 (mmol)	Ligand (mmol)		Temperature	Time	
$Pt(CF_3)_2$(tmen)	**(2)**	1.18	1.99	$CHCl_3$ (10 ml)	reflux	5 min	89
$Pt(CF_3)_2$(bipy)	**(3)**	0.59	0.65	$CHCl_3$ (4 ml)	reflux	2 min	80
cis-$Pt(CF_3)_2py_2$	**(4)**	4.2	9.3	$CHCl_3$ (15 ml)	reflux	15 min	89
$Pt(CF_3)_2$(en)	**(5)**	0.16	0.22	Ether (3 ml)	–	–	99
cis-$Pt(CF_3)_2(NH_3)_2$	**(6)**	0.24	4.7	$CHCl_3$ (3 ml)	–	–	70
cis-$Pt(CF_3)_2(DMSO)_2$	**(7/8)**	0.24	0.94	Ether (5 ml)	reflux	2 h	–
cis-$Pt(CF_3)_2(NCCH_3)_2$	**(9)**	0.48	–	CH_3CN (2 ml)	reflux	5 min	61
cis-$Pt(CF_3)_2(NCPh)_2$	**(11)**	0.24	–	PhCN (1 ml)	85 °C	5 min	49
cis-$Pt(CF_3)_2(DMF)_2$	**(13)**	0.24	–	DMF (2 ml)	85 °C	10 min	–

$Pt(CF_3)_2(bipy)$ (3)

The bipyridine was added as a solution in 1 ml $CHCl_3$. The yellow precipitate was collected, washed with ether (3 ml), and dried under vacuum.

*cis-$Pt(CF_3)_2py_2$ (**4**)*

The solution volume was reduced to 1–2 ml and cyclohexane (5 ml) added to ensure complete precipitation of the product. The crystals were collected, washed with cyclohexane (5 ml), and dried under vacuum.

$Pt(CF_3)_2(en)$ (5)

Precipitation was immediate upon addition of the ethylenediamine, and no heating was carried out. The white precipitate was filtered off and dried under vacuum.

*cis-$Pt(CF_3)_2(NH_3)_2$ (**6**)*

The $Pt(CF_3)_2(NBD)$ solution was placed in a thick-walled Carius tube, degassed and frozen. The ammonia was subsequently condensed into the tube and the tube sealed and allowed to warm to room temperature. Upon reaching room temperature a white precipitate formed. After removal of any volatile substances remaining in the tube in vacuo, the white solid was filtered off and dried under vacuum.

*cis-$Pt(CF_3)_2(DMSO)_2$ (7 and **8**)*

Evaporation of the reaction solution yielded a yellow oil, which could not be crystallised. Attempts to separate **7** and **8** by passage down a Florisil column, eluting with chloroform, resulted in decomposition of the complexes.

*cis-$Pt(CF_3)_2(NCCH_3)_2$ (**9**)*

The reaction solution was evaporated to dryness on a rotary evaporator to yield an oily solid. Ether (2 × 1 ml) was added to remove any CH_3CN still adhering to the solid. The solid was finally dried briefly under vacuum.

*cis-$Pt(CF_3)_2(NCPh)_2$ (**11**)*

Addition of hexane (5 ml) precipitated the product. The solid was collected, washed with ether (2 ml), and dried under vacuum.

*cis-$Pt(CF_3)_2(DMF)_2$ (**13**)*

Isolation of a solid compound was unsuccessful as complete removal of the excess DMF under vacuum was not possible without heating to temperatures high enough to decompose the platinum(II) complex. Addition of solvents such as hexane to the DMF solution failed to cause precipitation.

*Reactions of **1** with anionic ligands*

*Preparation of $[(n\text{-}Bu)_4N]_2[(CF_3)_2Pt(\mu\text{-}I)_2Pt(CF_3)_2]$ (**23**)*

To a solution of **1** (0.20 g; 0.48 mmol) in 2 ml dry acetone was added a solution of $(n\text{-}Bu)_4NI$ (0.18 g; 0.48 mmol) in 2 ml dry acetone. The solution was stirred for 1 h, then the acetone removed under vacuum, yielding a yellow oil. 2 ml ether was added, and upon standing the oil crystallised. The pale yellow solid was washed with ether (2 × 2 ml) and dried under vacuum. Yield 0.25 g (74%).

*Preparation of $[(n\text{-}Bu)_4N][Pt(CF_3)(CO)I_2]$ (**24**)*

To a solution of **1** (0.03 g; 0.07 mmol) in 1 ml acetone was added a solution of $(n\text{-Bu})_4NI$ (0.06 g; 0.16 mmol) in 2 ml acetone, followed by 0.05 ml of 1 *M* aqueous $HClO_4$. The solution was stirred for 7 d at room temperature, its volume then reduced to 0.25 ml, and water (1 ml) added to yield a yellow oil. The water layer was removed, and another 1 ml water was added to ensure no excess $(n\text{-Bu})_4NI$ remained. After removal of the second aqueous layer and addition of 1 ml absolute ethanol, a yellow solid was obtained. The solid $[(n\text{-Bu})_4N][Pt(CF_3)(CO)I_2]$ was washed with a second 1 ml volume of absolute ethanol and dried under vacuum. Yield 0.03 g (54%).

*Preparation of $[(n\text{-}Bu)_4N][Pt(CF_3)(CO)Cl_2]$ (**14**)*

To a solution of **1** (0.03 g; 0.07 mmol) in 1 ml acetone was added a solution of $(n\text{-Bu})_4NCl$ (0.05 g; 0.18 mmol) in 2 ml acetone. After 2 h stirring the solution was removed under vacuum to leave a yellow oil. Ether (5 ml) was added and the solution cooled to 5 °C for 24 h, during which crystals formed. The ether was removed and water (0.25 ml) added to dissolve the excess of $(n\text{-Bu})_4NCl$ adhering to the crystals. After the aqueous solution was decanted off, the white solid was washed with a minimum quantity of absolute ethanol, then ether (2 × 1 ml), and finally dried under vacuum. Yield 0.01 g (23%).

*Preparation of $Pt(CF_3)I(NBD)$ (**27**)*

To a solution of **24** in 4 ml acetone (generated by addition of NaI (0.22 g; 1.5 mmol) to a solution of **1** (0.31 g; 0.73 mmol), followed by stirring for 2 d) was added another solution of **1** (0.31 g; 0.73 mmol) in 3 ml acetone. The combined solution was stirred overnight, and then allowed to stand for several days. Crystals of **27** deposited on the bottom of the reaction vessel. The solution was concentrated to 2 ml and the precipitated **27** filtered off. An additional crop of **27** could be obtained by evaporation of the remaining acetone solution to dryness and removal of any remaining **1** and anionic complexes by successive washings of the solid with acetone until only **27** remained. Elution with acetone from a column of Florisil could also be used to separate the mixture of complexes, any **1** being eluted first followed by **27**. The anionic complexes were not eluted from the column, probably due to decomposition as indicated by formation of a black band near the top of the column.

Reactions of $Pt(CF_3)_2L_2$ with acids

Except for **3**, throughout these studies NMR monitoring was carried out on solutions prepared by dissolving 0.06 g of the particular Pt^{II} complex in 1 ml acetone-d_6, to which 0.05 ml of the appropriate acid was added. The lower solubility of **3** meant that only about 0.03 g of solid could be dissolved in 1 ml acetone-d_6. For studies where equimolar quantities were required the amount of acid was reduced to 0.01–0.02 ml. Hydrochloric acid (32% w/w) and perchloric acid (70% w/w) were used.

Preparation of $Pt(CF_3)I(tmen)$

N,N,N′,N′-tetramethylethylenediamine (0.03 ml; 0.20 mmol) was added to a solution of **27** (0.075 g; 0.16 mmol) in 6 ml acetone and the solution stirred for 4 h. Concentration to 0.5 ml and addition of ether (5 ml) precipitated $Pt(CF_3)I(tmen)$ as a white solid, which was washed with ether (2 × 1 ml) and dried under vacuum. Yield 0.058 g (74%). NMR data: $\delta(F)$ −14.10, $^2J(Pt-F) = 562.7$ Hz.

*Preparation of [Pt(CF$_3$)(CO)(tmen)]ClO$_4$ (**16**)*

$Pt(CF_3)I(tmen)$ (0.052 g; 0.10 mmol) was dissolved in 1 ml acetone and a solution of $AgClO_4$ (0.021 g; 0.10 mmol) in 0.5 ml acetone added. After 16 h stirring of the mixture in the dark, the precipitated AgI was filtered off, and CO passed through the filtrate for 5 min. Reduction of the volume of the solution to 0.5 ml and addition of ether (5 ml) precipitated **16** as a white solid. This solid was washed with ether (2 × 2 ml) and dried under vacuum. Yield 0.025 g (48%).

*Preparation of Pt(CF$_3$)I(bipy) (**30**)*

To a solution of **27** (0.110 g; 0.23 mmol) in 10 ml acetone was added a solution of bipyridine (0.038 g; 0.24 mmol) in 2 ml acetone. The mixture was gently refluxed for 5 min, then concentrated to a volume of 1 ml. Upon addition of ether (3 ml), yellow $Pt(CF_3)I(bipy)$ precipitated. This solid was washed with ether (2 × 1 ml) and dried under vacuum. Yield 0.120 g (96%). NMR data: $\delta(F)$ −13.16, $^2J(Pt-F) = 531.0$ Hz.

*Preparation of [Pt(CF$_3$)(CO)(bipy)]ClO$_4$ (**18**)*

A solution of $AgClO_4$ (0.016 g; 0.08 mmol) in 0.5 ml acetone was added to a suspension of $Pt(CF_3)I(bipy)$ (0.043 g; 0.08 mmol) in 1 ml acetone. The solution was covered to exclude light and stirred for 1 h. The precipitate of AgI was filtered off. When CO was passed through the filtrate for 2 min, a pale yellow precipitate of **18** formed. The solid was separated and dried under vacuum. Yield 0.026 g (60%).

Preparation of trans-Pt(CF$_3$)Ipy$_2$

Compound **27** (0.042 g; 0.087 mmol) was dissolved in 2 ml acetone and pyridine (0.013 ml; 0.16 mmol) added. The solution was gently refluxed for 10 min, then the acetone was removed under vacuum. The white solid obtained was washed with ether (2 × 2 ml) and dried under vacuum. Yield 0.034 g (73%). NMR data (platinum coupling constants given in parenthesis): $\delta(F)$ −31.54 (697.6); $\delta(C)$: C_α 155.2 (15.4), C_β 126.6 (48.4), C_γ 139.7 (11.7); $\delta(H)$: H_α 8.98 (47.6), H_β 7.56, H_γ 8.03.

Attempted preparation of Pt(CF$_3$)(CF$_2$)py$_2^+$

$Pt(CF_3)_2py_2$ (0.123 g; 0.25 mmol) was placed in a thick-walled 10 mm NMR tube and the tube evacuated and heated at 60 °C for 24 h prior to addition of HCl to remove any traces of water from the solid. 5 ml of CH_2Cl_2 (previously distilled from P_2O_5 and stored over P_2O_5) was condensed into the NMR tube in vacuo, and then allowed to warm to room temperature and the solid dissolved. The solution was refrozen and one molar equivalent of HCl gas (dried by passage through a dry ice/acetone bath at −78 °C) condensed into the tube. The tube was sealed and the contents allowed to warm to room temperature. The NMR spectrum was recorded as soon as possible after the contents had thawed.

Acknowledgements

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References

1 C.R. Kistner, J.H. Hutchinson, J.R. Doyle, and J.C. Storlie, Inorg. Chem., 2 (1963) 1255.
2 H.C. Clark and L.E. Manzer, J. Organomet. Chem., 59 (1973) 411.
3 N. Chaudhury and R.J. Puddephatt, J. Organomet. Chem., 84 (1975) 105.
4 T.G. Appleton and M.A. Bennett, Inorg. Chem., 17 (1978) 738.
5 G.B. Young and G.M. Whitesides, J. Amer. Chem. Soc., 100 (1978) 5808.
6 C. Eaborn, K.J. Odell, and A. Pidcock, J. Chem. Soc., Dalton Trans., (1978) 357.
7 G.B. Deacon and K.T. Nelson-Reed, J. Organomet. Chem., 322 (1987) 257.
8 T.G. Appleton, J.R. Hall, and M.A. Williams, J. Organomet. Chem., 303 (1986) 139.
9 T.G. Appleton, J.R. Hall, D.W. Neale, and M.A. Williams, J. Organomet. Chem., 276 (1984) C73.
10 G.R. Clark, S.V. Hoskins, and W.R. Roper, J. Organomet. Chem., 234 (1982) C9.
11 T.G. Richmond, A.M. Crespi, and D.F. Shriver, Organometallics, 3 (1984) 314.
12 R.A. Michelin, G. Facchin, and R. Ros, J. Organomet. Chem., 279 (1985) C25.
13 T.G. Appleton, R.D. Berry, J.R. Hall, and D.W. Neale, J. Organomet. Chem., 342 (1988) 399.
14 T.G. Appleton and J.R. Hall, Inorg. Chem., 10 (1971) 1717.
15 Z. Dawoodi, C. Eaborn, and A. Pidcock, J. Organomet. Chem., 170 (1979) 95.
16 C. Eaborn, K. Kundu, and A. Pidcock, J. Chem. Soc., Dalton Trans., (1981) 933.
17 R. Usón, J. Forniés, M. Tomas, B. Menjon, and A.J. Welch, Organometallics, 7 (1988) 1318.
18 M. Hudlicky, J. Fluor. Chem., 28 (1985) 461.
19 G.K. Anderson, H.C. Clark, and J.A. Davies, Inorg. Chem., 20 (1981) 1636.
20 T.G. Appleton, H.C. Clark, and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
21 T.G. Appleton, M.H. Chisholm, H.C. Clark, and L.E. Manzer, Inorg. Chem., 11 (1972) 1786.
22 R. Usón, J. Forniés, F. Martinez, and M. Tomas, J. Chem. Soc., Dalton Trans., (1980) 888.
23 T.G. Appleton, J.R. Hall, M.T. Mathieson, and D.W. Neale, to be submitted.
24 D. Drew and J.R. Doyle, Inorg. Synth., 13 (1972) 48.