

Trifluoromethanesulphonato-O Complexes of Platinum(II) and Palladium(II)

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Reaction of chloroplatinum(II) and chloropalladium(II) complexes containing amine, pyridine (py), or phosphine ligands at or above room temperature with anhydrous $\text{CF}_3\text{SO}_3\text{H}$ leads to formation of trifluoromethanesulphonato-O complexes, characterized spectroscopically. The complexes *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{OSO}_2\text{CF}_3)_2]$, *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{OSO}_2\text{CF}_3)]$, $[\text{Pt}(\text{en})\text{Cl}(\text{OSO}_2\text{CF}_3)]$ (en = 1,2-diaminoethane), $[\text{Pt}(\text{dppe})(\text{OSO}_2\text{CF}_3)_2]$, $[\text{Pt}(\text{py})_2\text{Cl}(\text{OSO}_2\text{CF}_3)]$, $[\text{Pt}(\text{terpy})(\text{OSO}_2\text{CF}_3)]$ [CF_3SO_3], (terpy = 2,2':6',2''-terpyridine), *trans*- $[\text{Pd}(\text{NH}_3)_2\text{Cl}(\text{OSO}_2\text{CF}_3)]$, $[\text{Pd}(\text{en})(\text{OSO}_2\text{CF}_3)_2]$, $[\text{Pd}(\text{bipy})(\text{OSO}_2\text{CF}_3)_2]$ (bipy = 2,2'-bipyridine), and $[\text{Pd}(\text{PPh}_3)_2(\text{OSO}_2\text{CF}_3)_2]$ were isolated. Aquation reactions of selected complexes showed that trifluoromethanesulphonate hydrolysis is rapid for complexes of both Pt^{II} and Pd^{II} . Bis(trifluoromethanesulphonato)platinum(II) complexes exhibit two consecutive rate processes, with k_1/k_2 ca. 5, consistent with sequential hydrolysis of both anions. Preliminary investigations indicate that co-ordinated CF_3SO_3^- in these complexes may be substituted even by neutral co-ordinating O-donor solvents.

Syntheses of complexes of inert metal ions containing co-ordinated trifluoromethanesulphonate have been promoted by the recognition that CF_3SO_3^- is a labile leaving group under most circumstances.¹ Consequently, trifluoromethanesulphonato complexes can serve as valuable precursors to a range of derivatives formed by the substitution of this labile ligand by others of greater nucleophilicity.² For example, the simple complex $[\text{Co}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$ has been shown to hydrolyze rapidly and completely with simple Co-O cleavage in aqueous solution,³ and has been employed as a precursor for a range of penta-aminocobalt(III) complexes.⁴ Lability relative to other common ligands is apparently a general phenomenon in the co-ordination chemistry of trifluoromethanesulphonate, and this has been demonstrated for a range of metal ions.¹

To date, most examples of co-ordination complexes with bound CF_3SO_3^- have involved octahedral complexes of inert metal ions, notably Co^{III} , Rh^{III} , Ir^{III} , Cr^{III} , Ru^{III} , and Os^{III} .⁴⁻¹³ Few examples of square-planar complexes have appeared, although $[\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{OSO}_2\text{CF}_3)]^{14}$ and $[\text{Pd}(\text{NH}_2\text{Et}_2)(\text{OCCH}_2\text{CH}_2\text{NEt}_2)(\text{OSO}_2\text{CF}_3)]^{15}$ have been reported. Given the continuing interest particularly in platinum(II) chemistry, related to the antitumour properties of *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and later analogues,¹⁶ and the limited examples of trifluoromethanesulphonate complexes of platinum(II) and palladium(II) with amine, imine, or phosphine ligands in other co-ordination sites, we have extended our study of complexes of CF_3SO_3^- into this area. Details of syntheses, characterization, hydrolysis kinetics, and some preliminary ligand-substitution reactions for a range of complexes of Pt^{II} and Pd^{II} are now reported.

Experimental

Precursor Complexes.—The platinum(II) complexes \dagger $\text{K}_2[\text{PtCl}_4]$,¹⁷ *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$,¹⁷ *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$,¹⁷ *cis*- $[\text{Pt}(\text{py})_2\text{Cl}_2]$,¹⁸ $[\text{Pt}(\text{dppe})\text{Cl}_2]$,¹⁹ and $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl}\cdot 3\text{H}_2\text{O}$ ²⁰ were prepared as described earlier. Further, $[\text{Pt}(\text{en})\text{Cl}_2]$ was prepared as described,²¹ except the neutral complex was purified by passing through short columns of cation- and anion-exchange resins (Sephadex C-25 and A-25) in turn to remove

ionic impurities, concentrated by rotary evaporation, and crystallized by cooling.

The palladium(II) complexes $[\text{Pd}(\text{en})\text{Cl}_2]$ and $[\text{Pd}(\text{bipy})\text{Cl}_2]$ were prepared as described elsewhere,²² while *trans*- $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ were purchased from Strem Chemicals.

Platinum(II) Trifluoromethanesulphonato Complexes.—*cis*-Diamminebis(trifluoromethanesulphonato)platinum(II), *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{OSO}_2\text{CF}_3)_2]$. Dry *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (0.7 g) was placed in a three-necked flask (50 cm³) fitted with nitrogen gas inlet and outlet ducts. The vessel was purged with a gentle stream of dry nitrogen, and anhydrous $\text{CF}_3\text{SO}_3\text{H}$ (4 cm³) was added slowly. The mixture was stirred in an oil-bath at 100 °C for 2 h, removed and cooled in an ice-bath, then the nitrogen gas flow was disconnected. Sodium-dried diethyl ether (ca. 50 cm³) was added very carefully with mechanical stirring. The precipitated complex was recovered by filtration on a fine-porosity sintered-glass funnel, washed with diethyl ether, and dried in a vacuum desiccator (1.1 g) (Found: C, 4.9; H, 1.5; N, 4.9; S, 12.0. Calc. for $\text{C}_2\text{H}_6\text{F}_6\text{N}_2\text{O}_6\text{PtS}_2$: C, 4.55; H, 1.15; N, 5.3; S, 12.15%).

Chloro(1,2-diaminoethane)(trifluoromethanesulphonato)platinum(II), $[\text{Pt}(\text{en})\text{Cl}(\text{OSO}_2\text{CF}_3)]$. A sample of $[\text{Pt}(\text{en})\text{Cl}_2]$ (0.5 g) and anhydrous $\text{CF}_3\text{SO}_3\text{H}$ (4 cm³) were allowed to react and the product isolated exactly as described above (0.6 g) (Found: C, 8.4; H, 1.9; Cl, 7.8; N, 6.6. Calc. for $\text{C}_3\text{H}_8\text{ClF}_3\text{N}_2\text{O}_3\text{PtS}$: C, 8.15; H, 2.25; Cl, 8.05; N, 6.35%).

[1,2-Bis(diphenylphosphino)ethane]bis(trifluoromethanesulphonato)platinum(II), $[\text{Pt}(\text{dppe})(\text{OSO}_2\text{CF}_3)_2]$. A mixture of $[\text{Pt}(\text{dppe})\text{Cl}_2]$ (0.8 g) and $\text{CF}_3\text{SO}_3\text{H}$ (8 cm³) was allowed to react and the product isolated exactly as described above (Found: C, 37.6; H, 3.2; P, 6.7. Calc. for $\text{C}_{28}\text{H}_{24}\text{F}_6\text{O}_6\text{P}_2\text{PtS}_2$: C, 37.7; H, 2.7; P, 6.95%).

(2,2':6',2''-Terpyridine)(trifluoromethanesulphonato)platinum(II) trifluoromethanesulphonate, $[\text{Pt}(\text{terpy})(\text{OSO}_2\text{CF}_3)][\text{CF}_3\text{SO}_3]$. A mixture of $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl}$ (0.06 g) and anhydrous $\text{CF}_3\text{SO}_3\text{H}$ (1 cm³) was allowed to stand at room temperature under a nitrogen atmosphere for 24 h. The product was isolated by precipitation on addition of diethyl ether (20 cm³), collected by filtration, and dried in a vacuum desiccator. As isolated, the compound analyzed for one extra mole of $\text{CF}_3\text{SO}_3\text{H}$ per mole of complex (Found: C, 24.8; H, 1.8; N, 4.9. Calc. for $\text{C}_{18}\text{H}_{12}\text{F}_9\text{N}_3\text{O}_9\text{PtS}_3$: C, 24.65; H, 1.4; N, 4.8%).

cis- $[\text{Pt}(\text{py})_2\text{Cl}(\text{OSO}_2\text{CF}_3)]$ and *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{OSO}_2\text{CF}_3)]$

[†] Abbreviations: py = pyridine; dppe = 1,2-bis(diphenylphosphino)ethane; terpy = 2,2':6',2''-terpyridine; en = 1,2-diaminoethane; bipy = 2,2'-bipyridine.

CF₃]. These complexes were prepared by reaction of *cis*-[Pt(py)₂Cl₂] and *trans*-[Pt(NH₃)₂Cl₂] (*ca.* 100 mg) respectively with anhydrous CF₃SO₃H (*ca.* 3 cm³) as described above for the terpy complex. Chemical and spectroscopic analyses support the formulations, but microanalyses were not obtained, given the similarity to earlier examples.

Palladium(II) Trifluoromethanesulphonato Complexes.—*trans*-Diamminechloro(trifluoromethanesulphonato)-palladium(II), *trans*-[Pd(NH₃)₂Cl(OSO₂CF₃)]. Anhydrous CF₃SO₃H (8 cm³) was added to *trans*-[Pd(NH₃)₂Cl₂] (1.0 g) in a nitrogen-purged three-necked flask, and the solution was left for 24 h. Careful, initially dropwise, addition of dry diethyl ether (*ca.* 40 cm³) to the vigorously stirring solution precipitated the product (1.3 g). The solid was collected, washed with diethyl ether, and dried in a vacuum desiccator (Found: C, 3.8; H, 2.15; Cl, 10.7; N, 8.3. Calc. for CH₆ClF₃N₂O₃PdS: C, 3.7; H, 1.85; Cl, 10.9; N, 8.6%).

(1,2-Diaminoethane)bis(trifluoromethanesulphonato)-palladium(II), [Pd(en)(OSO₂CF₃)₂]. A solution of [Pd(en)Cl₂] (0.59 g) in anhydrous CF₃SO₃H (6 cm³) was allowed to react under nitrogen at room temperature for 11 d. The product was isolated as above, and tests of a sample using AgNO₃ indicated the absence of chloride ion. A reaction mixture after 4 d gave a positive test for chloride, and microanalysis best fitted a chloro-(trifluoromethanesulphonato) formulation. Although microanalyses of the final product were not particularly good, vibrational spectroscopy indicated no obvious or significant impurity (Found: C, 9.7; H, 2.2; N, 6.6. Calc. for C₄H₈F₆N₂O₆PdS₂: C, 10.3; H, 1.75; N, 6.05%).

(2,2'-Bipyridine)bis(trifluoromethanesulphonato)palladium(II), [Pd(bipy)(OSO₂CF₃)₂]. A mixture of [Pd(bipy)Cl₂] (0.68 g) and CF₃SO₃H (6 cm³) was allowed to react under nitrogen at room temperature for 24 h. Slow addition of a small volume of diethyl ether (*ca.* 20 cm³) to the stirring solution precipitated the complex, which was collected and dried as above. Large volumes of ether resulted in some redissolution of the product, and should be avoided (Found: C, 26.0; H, 1.6; N, 5.4. Calc. for C₁₂H₈F₆N₂O₆PdS₂: C, 25.7; H, 1.45; N, 5.0%).

Bis(trifluoromethanesulphonato)bis(triphenylphosphine)-palladium(II), [Pd(PPh₃)₂(OSO₂CF₃)₂]. A mixture of [Pd(PPh₃)₂Cl₂] (1.0 g) and anhydrous CF₃SO₃H (8 cm³) was allowed to react and the product isolated as described for the bipy complex above. For analysis, a sample was hydrated, and analyzed well as a trihydrate (Found: C, 46.4; H, 3.5; P, 6.35. Calc. for C₃₈H₃₆F₆O₉P₂PdS₂: C, 46.4; H, 3.7; P, 6.3%).

Reactions with Co-ordinating Solvents.—The reactivity of co-ordinated CF₃SO₃⁻ was probed qualitatively by reactions of complexes with a range of potentially co-ordinating solvents [dimethylformamide (dmf), dimethyl sulphoxide (dmsO), trimethyl phosphate, and acetonitrile], as well as with water. Reactions were performed on a small scale, with products characterized by vibrational spectroscopy and/or ¹H n.m.r. spectroscopy. The general methods employed were as follows.

(i) The complex (*ca.* 50 mg) was dissolved in dried solvent (<3 cm³), and stirred at room temperature for a period of hours. The solvent was then removed on a vacuum line, the solid residue was washed with ethanol briefly, and again dried under high vacuum for several hours. Complexes investigated were *cis*-[Pt(NH₃)₂(OSO₂CF₃)₂] (1 h, dmf), *trans*-[Pt(NH₃)₂Cl(OSO₂CF₃)] (24 h, dmsO), [Pt(en)Cl(OSO₂CF₃)] [1 h, PO(OMe)₃; 24 h, MeCN], and *trans*-[Pd(NH₃)₂Cl(OSO₂CF₃)] (1 h, dmsO).

(ii) The complex (*ca.* 50 mg) was refluxed in dried solvent (<5 cm³) for several hours, the mixture filtered, and the product isolated as in (i) above or by addition of a large volume of ethanol–diethyl ether (1:10) to precipitate the product. Com-

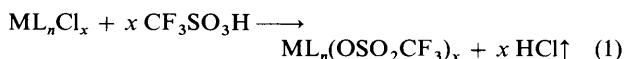
plexes investigated were: [Pt(en)Cl(OSO₂CF₃)] (5 h, MeCN; 4 h, dmf) and *trans*-[Pd(NH₃)₂Cl(OSO₂CF₃)] (3 h, dmsO; 1.5 h, dmf). In all cases metal was formed during reaction, suggesting a disproportionation reaction.

(iii) The complex (*ca.* 20 mg) was dissolved in a minimum volume of warm 0.1 mol dm⁻³ aqueous HClO₄, and crystals deposited on evaporation and cooling. These were collected, washed with alcohol and diethyl ether, and dried in a vacuum desiccator. Complexes investigated were [Pt(terpy)(OSO₂CF₃)] [CF₃SO₃]⁻ and *trans*-[Pd(NH₃)₂Cl(OSO₂CF₃)]⁻.

Physical Methods.—Infrared spectra of compounds dispersed in KBr discs or mulls were recorded using a Nicolet MX-1 Fourier-transform i.r. spectrometer. Proton n.m.r. spectra were recorded in D₂O versus trimethylsilylpropionate as internal reference using a JEOL FX-90Q spectrometer, and electronic spectra using an Hitachi 220A spectrometer. Hydrolysis reactions were followed using the latter spectrometer in 0.1 mol dm⁻³ aqueous CF₃SO₃H, with rate constants calculated by standard computational methods.

Results and Discussion

The general reaction of chlorometal complexes with anhydrous trifluoromethanesulphonic acid to form complexes with co-ordinated trifluoromethanesulphonate¹ [equation (1)] has



been shown in this study to occur for a range of platinum(II) and palladium(II) complexes. In all cases, simple substitution of chloro by trifluoromethanesulphonato ligands occurs alone. Infrared resonances of the other co-ordinated molecules are preserved from precursor to product, as illustrated for two examples in the Figure. In general, substitution in the complexes of Pd^{II} is more facile than in the platinum(II) analogues, consistent with the general chemistries of these ions. Reactions with chloroplatinum(II) complexes can usually be performed at elevated temperatures without any decomposition. However, because of the expected and observed greater instability of complexes of Pd^{II} compared with Pt^{II}, reactions of the former in CF₃SO₃H were carried out at room temperature, successfully.

With dichloro precursors, stepwise loss of chloro ligands occurs, and both chloro(trifluoromethanesulphonato) and bis-(trifluoromethanesulphonato) complexes of Pt^{II} and Pd^{II} are observed. With other second- and third-row octahedral metal ions, where substitution chemistry is slow, intermediates such as *trans*-[Ir(en)₂Cl(OSO₂CF₃)⁺ and *cis*-[Ru(en)₂Cl(OSO₂CF₃)⁺ are isolated after reaction for hours above or at room temperature.^{5,23} Reaction of dichloro complexes of first-row metal ions such as cobalt(III) at elevated temperature commonly leads to rapid and complete substitution,² and it is only from reaction below 0 °C that intermediates such as *trans*-[Co(en)₂Cl(OSO₂CF₃)⁺ have been isolated.²⁴ Replacement of the second chloro ligand in intermediates such as *trans*-[Ir(en)₂Cl(OSO₂CF₃)⁺ and even in *trans*-[Co(cyclam)Cl(OSO₂CF₃)⁺ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) occurs much more slowly than the initial step.^{5,13} In both the current and earlier studies, there is evidence that the lability of a second chloro *cis* to a CF₃SO₃⁻ ligand is greater than one *trans* to CF₃SO₃⁻ in anhydrous CF₃SO₃H.

Although co-ordination of the CF₃SO₃⁻ was anticipated, formulations with bidentate or bridging CF₃SO₃⁻ are unlikely in view of the low nucleophilicity of the ion,¹ and unidentate O-bonding is assumed as most reasonable. There may be feasible structures where it could be present as an unco-ordinated anion, and evidence for co-ordination needs to be detailed. Impor-

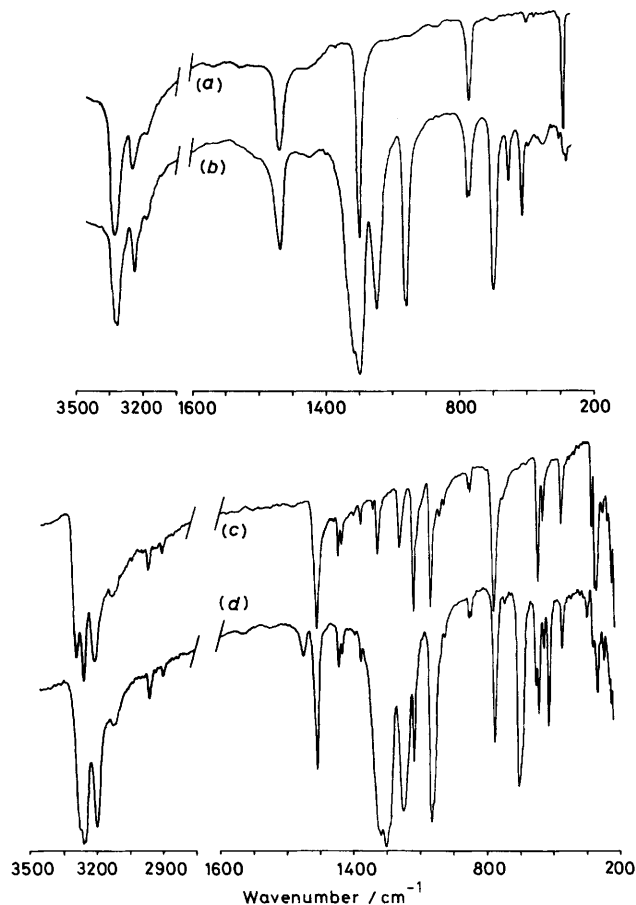


Figure. Infrared spectra of (a) $\text{trans-[Pd(NH}_3)_2\text{Cl}_2]$; (b) $\text{trans-[Pd(NH}_3)_2\text{Cl(OSO}_2\text{CF}_3)]$; (c) $[\text{Pt(en)Cl}_2]$; and (d) $[\text{Pt(en)Cl(OSO}_2\text{CF}_3)]$ dispersed in KBr

tantly, the ability of the CF_3SO_3^- complexes of Pd^{II} and Pt^{II} readily to form complexes with co-ordinated solvents (discussed later) is clearly indicative of a labile co-ordinated group, and CF_3SO_3^- is the most reasonable candidate. A crystal structure analysis of $[\text{Pd}(\text{NHEt}_2)(\text{OCCH}_2\text{CH}_2\text{NEt}_2)(\text{OSO}_2\text{CF}_3)]$ shows a unidentate O-bound CF_3SO_3^- with a longer than usual Pd–O bond,¹⁵ possibly reflecting the low nucleophilicity and potential lability of the anion. The electronic spectra of $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ (λ_{max} , 300 nm, ϵ 125 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; shoulder at 270 nm) and $\text{cis-[Pt(NH}_3)_2(\text{OH}_2)_2]^{2+}$ (broad λ_{max} , 260 nm, ϵ ca. 50 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) have been reported in water.²⁵ The spectrum of the putative $\text{cis-[Pt(NH}_3)_2(\text{OSO}_2\text{CF}_3)_2]$ in anhydrous $\text{CF}_3\text{SO}_3\text{H}$ (λ_{max} , 310, ϵ 190; 260 nm, ϵ 130 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) is similar to the spectrum of the dichloro analogue, consistent both with the formulation of the complex and the previously established⁵ adjacent location of Cl^- and CF_3SO_3^- in the spectrochemical series. Shifts and multiplicities of various i.r. resonances of CF_3SO_3^- upon co-ordination have, on occasions, proved significant enough to permit characterization.¹ The best examples of the variation from co-ordinated to ionic CF_3SO_3^- in these complexes come from the solvolysis studies; for example, the $\nu[\text{SO}_3(\text{E})]$ band in the spectrum of $\text{trans-[Pt(NH}_3)_2\text{Cl(OSO}_2\text{CF}_3)]$ occurs at 1275 cm^{-1} compared with 1260 cm^{-1} for $\text{trans-[Pt(NH}_3)_2\text{Cl(OSMe}_2)]$ [CF_3SO_3]. Clear evidence that CF_3SO_3^- is lost from the co-ordination sphere was obtained by crystallizing the hydrolysis products in the cases of reaction of $[\text{Pt(terpy)(OSO}_2\text{CF}_3)]^+$ and $\text{trans-[Pd(NH}_3)_2\text{Cl(OSO}_2\text{CF}_3)]$ in aqueous HClO_4 . In both cases, i.r. resonances

Table. Rate constants for aquation of trifluoromethanesulphonato complexes at 25 °C

Complex	$k_{\text{obs.}}/\text{s}^{-1}$	Ref.
$\text{trans-[Pt(NH}_3)_2\text{Cl(OSO}_2\text{CF}_3)]$	0.10	a
$[\text{Pt(en)Cl(OSO}_2\text{CF}_3)]$	0.075	a
$[\text{Pt(terpy)(OSO}_2\text{CF}_3)]^+$	0.10	a
$\text{cis-[Pt(NH}_3)_2(\text{OSO}_2\text{CF}_3)_2]$	0.10, ^b	a
$[\text{Pt(dppe)(OSO}_2\text{CF}_3)_2]$	0.05 ^c	a
$\text{trans-[Pd(NH}_3)_2\text{Cl(OSO}_2\text{CF}_3)]$	0.013	a
$[\text{Pd(PPh}_3)_2(\text{OSO}_2\text{CF}_3)_2]$	0.19 ^d	a
$[\text{Co(NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$	0.027	4
$[\text{Rh(NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$	0.019	5
$[\text{Ir(NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$	0.000 26	5
$[\text{Cr(NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$	0.12 ₅	5
$[\text{Ru(NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$	0.093	5
$[\text{Os(NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$	0.0018	6
$[\text{Pt(NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{3+}$	<0.0001	5

^a This work; determined in 0.1 mol dm^{-3} $\text{CF}_3\text{SO}_3\text{H}$. ^b $k_2 = 0.015 \text{ s}^{-1}$; $k_1/k_2 = 7.0$. ^c $k_2 = 0.011 \text{ s}^{-1}$; $k_1/k_2 = 4.5$. ^d Not resolved into two steps.

from CF_3SO_3^- were absent, while resonances from ClO_4^- and H_2O were observed.

Determined rate constants (Table) indicate that both $\text{Pt}^{\text{II}}\text{-OSO}_2\text{CF}_3$ and $\text{Pd}^{\text{II}}\text{-OSO}_2\text{CF}_3$ bonds are quite labile, consistent with behaviour shown by other metal ions.^{4–6} The lability on Pd^{II} is not markedly different from that on Pt^{II} or several other metal ions, suggesting lability is more a function of the poor nucleophilicity of the ligand than the inherent lability or inertness of the complexed metal ion.²⁶ For complexes of both Pd^{II} and Pt^{II} , the lability of CF_3SO_3^- relative to Cl^- is also substantial, with $k_{\text{obs.}}(\text{CF}_3\text{SO}_3^-)/k_{\text{obs.}}(\text{Cl}^-)$ ca. 10^3 {e.g. ca. 300 comparing $\text{trans-[Pd(NH}_3)_2\text{Cl(OSO}_2\text{CF}_3)]$ and $\text{trans-[Pd(NH}_3)_2\text{Cl}_2]$,²⁷ and ca. 1400 comparing $[\text{Pt(en)Cl(OSO}_2\text{CF}_3)]$ and $[\text{Pt(en)Cl}_2]$ ²⁷}. For $\text{cis-[Pt(NH}_3)_2(\text{OSO}_2\text{CF}_3)_2]$ and $[\text{Pt(dppe)(OSO}_2\text{CF}_3)_2]$, two rapid consecutive aquation steps were detected, with $k_1/k_2 < 10$ in each case. This rapid consecutive loss parallels behaviour of compounds such as $\text{cis-[Co(en)}_2(\text{OSO}_2\text{CF}_3)_2]^+$, where k_1/k_2 approaches the statistical substitution-rate ratio of 2.0.⁴ Only one rate constant fitted data for $[\text{Pd(PPh}_3)_2(\text{OSO}_2\text{CF}_3)_2]$, although in that case the short half-life suggests that a faster first process may have been missed, or alternatively $k_1/k_2 = 2$, when resolution of two components is not possible.²⁸ For all compounds studied, low solubility of the neutral precursors in aqueous $\text{CF}_3\text{SO}_3\text{H}$ limited the accuracy of determinations, and dependencies on acid concentration, anion, or temperature were not pursued.

Preliminary substitution reactions with common co-ordinating solvents were examined. In all cases where reactions were performed by refluxing a mixture, metal was detected, and presumably disproportionation to M^0 and M^{IV} occurred. Although diamagnetic compounds were isolable, characterization was not pursued, since our primary interest lay in the isolation of simple substitution products. Reactions performed at room temperature led to simple substitution in water, dmf, dmsO, and PO(OMe)_3 . Both i.r. and n.m.r. spectroscopy indicate reaction. For example, in the ^1H n.m.r. spectrum of the product $[\text{Pt(en)Cl}\{\text{PO(OMe)}_3\}][\text{CF}_3\text{SO}_3]$ the signal of co-ordinated en appears near 2.6 p.p.m. and there is a doublet at 3.76 and 3.88 p.p.m. downfield from some free PO(OMe)_3 at 3.65 and 3.52 p.p.m. The downfield chemical shift is characteristic of co-ordination, whereas the free PO(OMe)_3 probably arises from hydrolysis of the O-bound ligand in the D_2O during spectrum accumulation. Co-ordination of the weak PO(OMe)_3 ligand in place of CF_3SO_3^- is an indication of the poor nucleophilicity of the latter, and suggests that the $\text{Pt}^{\text{II}}\text{-OSO}_2\text{CF}_3$ and

$\text{Pd}^{\text{II}}\text{-OSO}_2\text{CF}_3$ compounds may prove to be useful precursors for synthesis of a range of new compounds, a proposition yet to be tested in detail.

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Received 23rd April 1987; Paper 7/737