# Acid- and Base-catalysed Displacement of the Carboxylate Ligand from $[Pt(dien)(RCO_2)]^+$ (dien = 1,5-Diamino-3-azapentane; R = $CH_2Cl$, $CHCl_2$, or $CCl_3$) in Aqueous Solution

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The kinetics of the displacement of the carboxylate ligand from $[Pt(dien)(RCO_2)]^+$ (dien = 1,5-diamino-3-azapentane; R = $CHCl_2$ or $CCl_3$) have been studied and are compared with the data for R = $CH_2Cl$. Although the intrinsic reactivity is very sensitive to the basicity of the leaving group, the nucleophilic discrimination is independent of the nature of the leaving group and is the same as that of $[Pt(dien)Cl]^+$. The acid-catalysed pathway for solvolysis, which dominated the reaction of the chloroacetate complex, is far less important for the displacement of $CHCl_2CO_2^-$ and not observed for $CCl_3CO_2^-$. The solvolysis is accelerated by added hydroxide, the rate law taking the form $k_{obs.} = k_0 + k_1[OH^-] + k_2[OH^-]^2$. The relative contribution of the three pathways depends upon the basicity of the leaving group.

As part of our studies of the labilities of oxygen donor ligands in four-co-ordinate planar $d^8$ metal complexes[1] we examined the displacement of chloroacetate from $[Pt(dien)(CH_2ClCO_2)]^+$ (dien = 1,5-diamino-3-azapentane) and *cis*-$[Pt(NH_2Pr^i)_2(CH_2ClCO_2)_2]$. The behaviour of these two substrates differed in many respects, in particular the bis(carboxylato) complex displayed an unusually large nucleophile-independent pathway which served to swamp the nucleophilic-dependent pathway for entry by chloride and to make a major contribution to the entry of bromide. Such an effect was absent from the displacement of $CH_2ClCO_2^-$ from $[Pt(dien)(CH_2ClCO_2)]^+$ which showed a normal linear relationship between log $k_2$ and the nucleophilicity of the entering group (water included) relevant to a +1 substrate.

The solvolytic displacement of the carboxylate was acid catalysed in all cases, the rate law taking the form $k_{obs.} = k_0^{H_2O} + k_1^{H_2O}K_0[H^+]$, and it was suggested that the substrate was distributed between a protonated and an unprotonated form, equilibrium constant $K_0$, the two species solvolysing with rate constants $k_0^{H_2O}$ and $k_1^{H_2O}$ respectively. The linear dependence on $[H^+]$ was consistent with $K_0$ being small enough for $K_0[H^+]$ never to be significant compared to 1.

In a recently completed work[2] involving the ring-opening and displacement of the dicarboxylate ligand from $[Pt(NH_3)_2(cbdca)]$ (cbdca = cyclobutane-1,1-dicarboxylate) the rate law took the form $k_{obs.} = (k_0^{H_2O} + k_1^{H_2O}K_0[H^+])/(1 + K_0[H^+])$ where $K_0[H^+]$ became significant compared to 1 as the acid concentration is increased. In order to understand the relationship between $K_0$, $k_0^{H_2O}$, $k_1^{H_2O}$, and the basicity of the leaving group, we have prepared some other monocarboxylato complexes of the type $[Pt(dien)(RCO_2)]^+$ (R = $CCl_3$, $CHCl_2$, or $CH_2Cl$) and have studied the displacement of $RCO_2^-$ in the presence and absence of acid and in the presence of other nucleophiles. The results are reported in this paper.

## Experimental

*Preparation of Complexes.*—$[Pt(dien)(CH_2ClCO_2)]ClO_4$ was prepared as previously reported.[1]

$[Pt(dien)(CHCl_2CO_2)]ClO_4$. A suspension of compound $[Pt(dien)Br]Br$ (0.5 g, 1.09 mmol), prepared by the method of Mann,[3] in anhydrous methanol (30 $cm^3$) was treated with $AgClO_4$ (0.453 g, 2.18 mmol) and stirred in the dark for 24 h. The AgBr was filtered off and the filtrate treated with a slight excess of lithium dichloroethanoate (0.162 g, 1.20 mmol) prepared by neutralizing a solution of the acid in methanol with $Li_2CO_3$. After 1 h the solution was evaporated to dryness, diethyl ether was added, and the crude product separated as an oil. This was pumped free of the solvent, dissolved in the minimum amount of methanol, and an excess of $LiClO_4$ added. The pure compound was obtained as a white microcrystalline salt (Found: C, 13.65; H, 2.60; Cl, 19.9; N, 7.90. $C_6H_{14}Cl_3N_3O_6Pt$ requires C, 13.7; H, 2.70; Cl, 20.25; N, 8.00%).

$[Pt(dien)(CCl_3CO_2)]ClO_4$ was prepared in a similar way (Found: C, 12.7; H, 2.45; Cl, 25.45; N, 7.60. $C_6H_{13}Cl_4N_3O_6Pt$ requires C, 12.85; H, 2.35; Cl, 25.3; N, 7.50%).

Attempts to prepare $[Pt(dien)(CH_3CO_2)]ClO_4$ by this method were thwarted by our inability to crystallize the oil. Other reagents were either analytical grade or the best otherwise available.

*Kinetics.*—The reactions were initiated by adding a freshly prepared aqueous solution (0.03 $cm^3$, $5 \times 10^{-2}$ mol $dm^{-3}$) of the substrate in pre-thermostatted 1 mol $dm^{-3}$ $NaClO_4$ (or NaF) to an aqueous solution (3.00 $cm^3$) containing the nucleophile and $NaClO_4$ (or NaF) that had been brought to the reaction temperature in the thermostatted cell compartment of a Perkin-Elmer Lambda-5 u.v. spectrophotometer. The subsequent changes were followed spectrophotometrically either by repetitive scan over the wavelength range (220—380 nm) or by an absorbance *versus* time scan at the appropriate wavelength.

## Results

*Displacement of the Carboxylate from Complexes* $[Pt(dien)(CH_nCl_{3-n}CO_2)]^+$ *in Aqueous Solution.*—In aqueous 1.0 mol $dm^{-3}$ sodium perchlorate, a solution of $[Pt(dien)(CH_nCl_{3-n}CO_2)]^+$ changes to the aqua complex in a single stage, first-order process. The final spectrum is consistent with that of the aqua complex plus the carboxylate anion and the nature of the product is confirmed by its subsequent reaction with $Cl^-$ to give $[Pt(dien)Cl]^+$. In acid solution the aqua complex and the carboxylic acid are formed. In the presence of sodium hydroxide

**Table 1.** First-order rate constants, $k_{obs.}$, for the reactions of $[Pt(dien)(RCO_2)]^+$ substrates, in water at 25 °C ($I$ = 1.0 mol dm$^{-3}$, $NaClO_4$)

| R | Reagent (X) | [X]/mol dm$^{-3}$ | $10^4k_{obs.}$/s$^{-1}$ |
|---|---|---|---|
| $CCl_3$ | $H^+$ | 0.09 | 28 ± 1 |
| | $H^+$ | 0.18 | 29 ± 1 |
| | $H^+$ | 0.36 | 30 ± 1 |
| | $H^+$ | 0.55 | 28.5 ± 0.2 |
| | $H^+$ | 0.73 | 28.5 ± 0.2 |
| | $H^+$ | 0.91 | 28.5 ± 0.2 |
| | $Cl^-$ | 0.09 | 28.9 ± 0.2 |
| | $Cl^-$ | 0.18 | 32.9 ± 0.2 |
| | $Cl^-$ | 0.36 | 43.0 ± 0.2 |
| | $Cl^-$ | 0.55 | 51.6 ± 0.4 |
| | $Cl^-$ | 0.73 | 60.4 ± 0.5 |
| | $Cl^-$ | 0.91 | 75.0 ± 0.3 |
| | $Br^-$ | 0.045 | 44.3 ± 0.1 |
| | $Br^-$ | 0.09 | 61.1 ± 0.2 |
| | $Br^-$ | 0.18 | 96.6 ± 0.3 |
| | $Br^-$ | 0.36 | 161 ± 1 |
| | $Br^-$ | 0.455 | 192 ± 1 |
| | $OH^-$ | 0.045 | 29.9 + 0.4 |
| | $OH^-$ | 0.09 | 36.4 ± 0.7 |
| | $OH^-$ | 0.18 | 48.3 ± 1.8 |
| | $OH^-$ | 0.273 | 63.9 ± 1.6 |
| | $OH^-$ | 0.36 | 73.1 ± 2.3 |
| | $OH^-$ | 0.455 | 108 ± 3 |
| | $OH^-$ | 0.55 | 119 ± 4 |
| | $OH^-$ | 0.636 | 133 ± 3 |
| | $OH^-$ | 0.73 | 166 ± 5 |
| | $OH^-$ | 0.818 | 219 ± 4 |
| | $OH^-$ | 0.91 | 282 ± 5 |
| | $OH^-$* | 0.09 | 46.6 ± 0.8 |
| | $OH^-$* | 0.273 | 87.8 ± 8.2 |
| | $OH^-$* | 0.455 | 122 ± 4 |
| | $OH^-$* | 0.636 | 180 ± 5 |
| | $OH^-$* | 0.818 | 205 ± 5 |
| | $OH^-$* | 0.91 | 264 ± 7 |
| $CHCl_2$ | $H^+$ | 0.09 | 6.36 ± 0.02 |
| | $H^+$ | 0.18 | 6.42 ± 0.02 |
| | $H^+$ | 0.36 | 6.47 ± 0.03 |
| | $H^+$ | 0.55 | 6.65 ± 0.03 |
| | $H^+$ | 0.73 | 6.81 ± 0.04 |
| | $H^+$ | 0.91 | 7.01 ± 0.03 |
| | $Cl^-$ | 0.09 | 7.82 ± 0.03 |
| | $Cl^-$ | 0.18 | 8.96 ± 0.03 |
| | $Cl^-$ | 0.36 | 11.53 ± 0.06 |
| | $Cl^-$ | 0.55 | 14.67 ± 0.06 |
| | $Cl^-$ | 0.73 | 17.65 ± 0.08 |
| | $Cl^-$ | 0.91 | 20.8 ± 0.1 |
| $CHCl_2$ | $Br^-$ | 0.09 | 14.7 ± 0.4 |
| | $Br^-$ | 0.18 | 22.6 ± 0.1 |
| | $Br^-$ | 0.36 | 39.6 ± 0.2 |
| | $Br^-$ | 0.55 | 60.0 ± 0.4 |
| | $Br^-$ | 0.73 | 79.0 ± 0.3 |
| | $Br^-$ | 0.91 | 99.5 ± 0.4 |
| | $I^-$ | 0.036 | 82.8 ± 1 |
| | $I^-$ | 0.073 | 158 ± 2 |
| | $I^-$ | 0.146 | 312 ± 6 |
| | $I^-$ | 0.218 | 461 ± 7 |
| | $I^-$ | 0.291 | 593 ± 25 |
| | $OH^-$ | 0.045 | 7.33 ± 0.06 |
| | $OH^-$ | 0.09 | 8.14 ± 0.05 |
| | $OH^-$ | 0.18 | 9.08 ± 0.08 |
| | $OH^-$ | 0.273 | 10.13 ± 0.07 |
| | $OH^-$ | 0.36 | 12.44 ± 0.08 |
| | $OH^-$ | 0.455 | 13.52 ± 0.14 |
| | $OH^-$ | 0.55 | 16.25 ± 0.12 |
| | $OH^-$ | 0.636 | 17.83 ± 0.15 |
| | $OH^-$ | 0.73 | 21.62 ± 0.14 |
| | $OH^-$ | 0.818 | 24.24 ± 0.27 |
| | $OH^-$ | 0.91 | 27.78 ± 0.28 |
| | $OH^-$* | 0.09 | 11.22 ± 0.06 |
| | $OH^-$* | 0.273 | 14.50 ± 0.11 |
| | $OH^-$* | 0.455 | 18.38 ± 0.15 |
| | $OH^-$* | 0.636 | 22.07 ± 0.18 |
| | $OH^-$* | 0.818 | 26.83 ± 0.25 |
| | $OH^-$* | 0.91 | 28.2 ± 0.3 |
| $CH_2Cl$ | $OH^-$ | 0.045 | 2.02 ± 0.03 |
| | $OH^-$ | 0.09 | 2.13 ± 0.03 |
| | $OH^-$ | 0.18 | 2.31 ± 0.03 |
| | $OH^-$ | 0.273 | 2.66 ± 0.03 |
| | $OH^-$ | 0.36 | 3.03 ± 0.05 |
| | $OH^-$ | 0.455 | 3.23 ± 0.04 |
| | $OH^-$ | 0.55 | 3.73 ± 0.05 |
| | $OH^-$ | 0.636 | 3.88 ± 0.04 |
| | $OH^-$ | 0.73 | 4.43 ± 0.06 |
| | $OH^-$ | 0.818 | 5.19 ± 0.08 |
| | $OH^-$ | 0.91 | 5.86 ± 0.09 |
| | $OH^-$* | 0.09 | 2.79 ± 0.04 |
| | $OH^-$* | 0.273 | 3.49 ± 0.05 |
| | $OH^-$* | 0.455 | 4.43 ± 0.08 |
| | $OH^-$* | 0.636 | 5.03 ± 0.06 |
| | $OH^-$* | 0.818 | 5.73 ± 0.07 |
| | $OH^-$* | 0.91 | 6.02 ± 0.05 |

* Ionic strength with NaF.

the product is $[Pt(dien)(OH)]^+$ and the carboxylate. The rate constants for the solvolysis, determined by a non-linear, least-squares fit of the absorbance ($A_t$) *versus* time ($t$) data to the expression $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs.}t)$ with $A_0$, $A_\infty$, and $k_{obs.}$ as parameters to be optimized, are collected in Table 1. In the presence of acid or base the ionic strength was held constant, $I$ = 1.0 mol dm$^{-3}$, with $NaClO_4$. In the reactions with hydroxide a parallel series of reactions were studied using NaF to maintain the ionic strength.

In the presence of NaCl, the change is still first order and the product has a spectrum identical to that of an authentic sample of $[Pt(dien)Cl]^+$. The kinetics were studied at constant ionic strength maintained by $NaClO_4$. Rate constants are collected in Table 1.

Similar reactions were carried out with NaBr and NaI, and the products identified as $[Pt(dien)Br]^+$ and $[Pt(dien)I]^+$ respectively. The rate constants for the processes, determined in the usual way, are collected in Table 1.

## Discussion

The rate of the solvolytic displacement of $CH_2ClCO_2^-$ from $[Pt(dien)(CH_2ClCO_2)]^+$ was shown[1] to be acid dependent, obeying the rate law (1). The reaction of $[Pt(dien)(CHCl_2CO_2)]^+$ behaves in a similar fashion although the relative contribution of the acid-catalysed path is far less and $[Pt(dien)(CCl_3CO_2)]^+$ aquates at a rate that is independent of

$$k_{obs.} = k_0^{H_2O} + k_1^{H_2O}K_0[H^+] \qquad (1)$$

**Table 2.** Specific rate constants for the reactions of $[Pt(dien)(RCO_2)]^+$ substrates, in water at 25 °C, with various reagents (X) at $I$ = 1.0 mol dm$^{-3}$ ($NaClO_4$)

| | X | R = $CCl_3$ | R = $CHCl_2$ | R = $CH_2Cl$* |
|---|---|---|---|---|
| $k_0^{H_2O}$/s$^{-1}$ | $H_2O$ | $2.87 \times 10^{-3}$ | $6.26 \times 10^{-4}$ | $1.89 \pm 10^{-4}$ |
| $k_1^{H_2O}K_0$ | $H_2O$ | | $7.9 \times 10^{-5}$ | $1.88 \times 10^{-3}$ |
| $k_2(Cl^-)$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $Cl^-$ | $5.6 \times 10^{-3}$ | $1.58 \times 10^{-3}$ | $3.21 \times 10^{-4}$ |
| $k_2(Br^-)$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $Br^-$ | $3.61 \times 10^{-2}$ | $1.03 \times 10^{-2}$ | $2.5 \times 10^{-3}$ |
| $k_2(I^-)$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $I^-$ | | $2.05 \times 10^{-1}$ | |
| $k_2(CNS^-)$/ dm$^3$ mol$^{-1}$ s$^{-1}$ | $CNS^-$ | | | $7.72 \times 10^{-2}$ |

* Data from ref. 1.

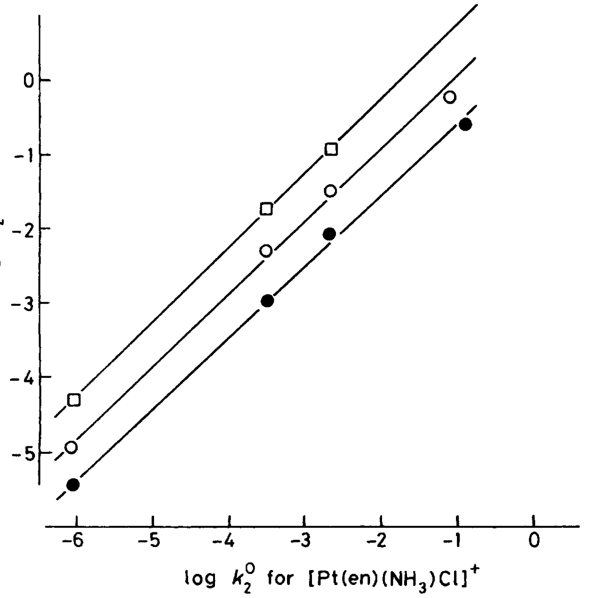


**Figure 1.** Plots of log $k_2^0$ *versus* $n_{Pt}^+$ {$n_{Pt}^+$ = log $k_2^0$ for the analogous reactions of $[Pt(en)(NH_3)Cl]^+$} for the complexes $[Pt(dien)(RCO_2)]^+$: (□) R = $CCl_3$, (○) R = $CHCl_2$, (●) R = $CH_2Cl$

$[H^+]$. The values of $k_0^{H_2O}$ and $k_1^{H_2O}$ are collected in Table 2. Since it was not possible to achieve conditions where $K_0[H^+]$ was significant compared to 1, $k_1^{H_2O}$ and $K_0$ could not be separated.

Although limited in scope this is the only systematic comparison of the effect of the basicity of the carboxylate ligand on the rate constant for its displacement from Pt$^{II}$. The data are too few for a quantitative discussion of the effect but it is obvious that the uncatalysed solvolytic rate constant decreases as the basicity of the leaving group increases, reflecting presumably the strength of its bond to platinum. This is consistent with what is found for the displacement of amines and the best line to fit $-\log k_0^{H_2O}$ *versus* p$K_a$ of $RCO_2H$ has a slope (0.45) that is of a comparable magnitude to that of a similar plot (*ca.* 0.5) for the displacement of amines and heterocyclic nitrogen bases (L′) from *trans*-$[PtL(L')Cl_2]$ under the *trans* influence of sulphur, phosphorus, and arsenic donors, L.[4] The contribution towards the acid-catalysed path, expressed as the inseparable product $k_1^{H_2O}K_0$, changes in the opposite direction and, in the case of the least basic carboxylate, $CCl_3CO_2^-$, is unmeasurable against the background of the uncatalysed solvolysis. Since it is likely that the variation of $k_1^{H_2O}$ with the basicity of the leaving group $RCO_2H$ should follow the same order as $RCO_2^-$, it is not unreasonable to conclude that the reversal of the leaving-group effect is due to the dominance of the variation of $K_0$ with the substituent R. Until $K_0$ and $k_1^{H_2O}$ can be separated and more data are available the effect cannot be treated quantitatively but it is reasonable to expect that the complexes of the most basic carboxylate ligands will have values of $K_0$ sufficiently large for it to be possible to protonate a reasonable fraction of the substrate at easily achieved acid concentrations.

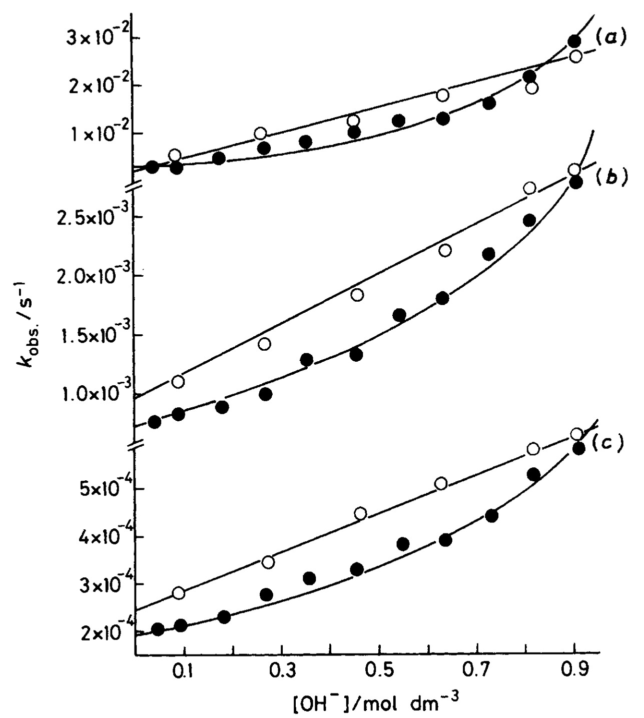
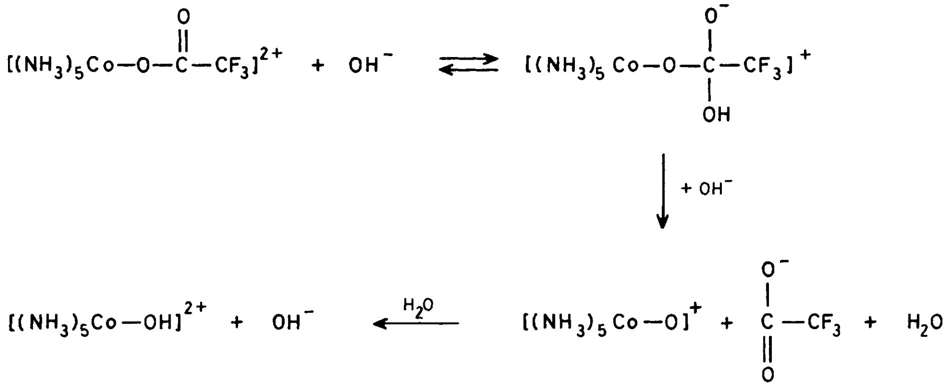


**Figure 2.** Plots of $k_{obs.}$ *versus* $[OH^-]$ for the reactions of the $[Pt(dien)(RCO_2)]^+$ complexes (from data in Table 1). (●) $I$ = 1 with $NaClO_4$; (○) $I$ = 1 mol dm$^{-3}$ with NaF. Curves correspond to the following best-fitting equations. (*a*) R = $CCl_3$, $10^4$ $k_{obs.}$ = 33.7 + 5.8 $[OH^-]$ + 274 $[OH^-]^2$. (*b*) R = $CHCl_2$; $10^4$ $k_{obs.}$ = 6.85 + 8.14 $[OH^-]$ + 16.1 $[OH^-]^2$. (*c*) R = $CH_2Cl$; $10^4$ $k_{obs.}$ = 1.96 + 1.47 $[OH^-]$ + 3.0 $[OH^-]^2$

The rate constants for the entry of other nucleophiles ($X^-$) in the absence of acid follow the usual two-term rate law, $k_{obs.} = k_0^{H_2O} + k_2[X^-]$, and the slopes and intercepts of plots of $k_{obs.}$ *versus* $[X^-]$ are collected in Table 2. The nucleophilic discriminations are compared in Figure 1, where log $k_2^0$ (the second-order rate constant extrapolated to zero ionic strength) is plotted against the logarithm of the analogous rate constants for the reactions of $[Pt(en)(NH_3)Cl]^+$ (en = 1,2-diaminoethane) with the same nucleophiles at 25 °C. This has been recommended as a nucleophilicity scale more suitable for the reactions of +1 charged substrates[5] than the classic $n_{Pt}^0$ scale.[6]

The extrapolation to zero ionic strength uses the Debye-Hückel relationship, $\log k_2\ (I = 0) = k_2\ (I = I) + 1.02I^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1}$, and becomes $\log k_2\ (I = 0) = \log k_2\ (I = 1.0) + 0.50$. Although the expression is inaccurate at these ionic strengths, the error introduced is less than that which would have arisen had the data for uninegative nucleophiles been untreated. A salt effect correction is necessary if the anionic nucleophiles are to be compared with the neutral nucleophile water. The data for the three substrates lie on almost parallel straight lines and the nucleophilic discrimination factors (the slopes) of these lines are



Scheme.

0.99 ± 0.02, 0.97 ± 0.04, and 0.95 ± 0.03 for $CCl_3CO_2$, $CHCl_2CO_2$, and $CH_2ClCO_2$ substrates respectively. It has already been pointed out that the nucleophilic discrimination factor for $[Pt(dien)(CH_2ClCO_2)]^+$ (0.95 ± 0.03) is only slightly smaller than that of $[Pt(dien)Cl]^+$ (1.03).[7]

In basic solution, the rate of displacement of ligand is dependent upon $[OH^-]$. Plots of $k_{obs.}$ *versus* $[OH^-]$ (Figure 2) are curved and the relationship takes the form $k_{obs.} = k_0 + k'[OH^-] + k''[OH^-]^2$. The rate constants for the best fit are given in the legend of the figure and the calculated curves are displayed. This type of hydroxide dependence has been observed before in the reactions of *cis*-$[Pt(NH_3)_2(SMe_2)_2]^{2+}$ [8] and is now being examined in great depth with a variety of substrates, *e.g.* *cis*-$[Pt(py)_2(SMe_2)_2]^{2+}$ (py = pyridine), $[Pt(SMe_2)_4]^{2+}$, and the results will be reported and discussed elsewhere.[9] It has been observed that if the ionic strength is held constant with NaF instead of $NaClO_4$, the dependence on $[OH^-]$ of the reactions of *cis*-$[Pt(py)_2(SMe_2)_2]^{2+}$ becomes linear.[9] Until now, a hydroxide dependence of this sort has been only found with doubly charged cations; the hydroxide dependence that is found in the second stage {displacement of L from *cis*-$[Pt(SMe_2)_2(OH)L]^+$ (L = $NH_3$, py, or $SMe_2$)} is strictly linear and the rate constants are unaffected by replacing the $ClO_4^-$ by $F^-$.[9] The $[Pt(dien)(RCO_2)]^+$ complexes are the first unipositive substrates to show this greater than first-order dependence on $[OH^-]$ and also to show the accelerating effect of replacing $ClO_4^-$ by $F^-$. The base hydrolysis of $[Co(NH_3)_5(CF_3CO_2)]^{2+}$ has a second-order dependence on $[OH^-]$, a rare observation for the base hydrolysis of acidoamine cobalt(III) complexes but this has been shown to be due to a parallel attack at the carboxylate carbon to promote a ligand loss through C–O fission (Scheme).[10]

The possibility that the extra hydroxide dependence observed in the reactions of $[Pt(dien)(RCO_2)]^+$ is due to a similar carbon–oxygen fission can be ruled out since the rate law for the reaction of $[Pt(dien)Br]^+$ with hydroxide is of the form $k_{obs.} = k_0^{H_2O} + k'[OH] + k''[OH]^2$, although the contributions from the hydroxide-dependent terms are not quite as important.

We do not, at this stage, feel able to provide an explanation of this phenomenon but we intend to discuss it elsewhere at much greater length when the work in progress has been completed.

## Acknowledgements

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