

Comparative Rates of Ligand Substitution Reactions of Pt–C-Bonded Complexes in Aqueous Solution and the X-ray Crystal Structure of [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)] [OSO₂CF₃]

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The substitution behavior of the organometallic complex cation [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)]⁺ (**1**) has been studied with a series of nucleophiles (Cl[−], Br[−], I[−], N₃[−], NCS[−], thiourea, *N,N*-dimethylthiourea, *N,N,N,N*-tetramethylthiourea) as a function of nucleophile concentration ([Nu]), pH, temperature, and pressure. Complex **1** affords pseudo-first-order rate constants, *k*_{obs}, for the complex-formation reaction given by *k*_{obs} = *k*₁[Nu] + *k*_{−1}; the *k*_{−1} term is due to the reverse aquation reaction and is insignificant for the stronger, S-donor nucleophiles. The mechanism for the substitution of the coordinated water molecule is associative, as demonstrated by the large negative values of Δ*S*[‡] and Δ*V*[‡]. The results are compared to those obtained earlier for the geometrically related neutral zwitterionic complex [Pt{C₆H₄(CH₂NMe₂)₂}(NC₅H₄SO₃[−])(OH₂)] (**2**). Both cyclometalated complexes **1** and **2** have very high substitution reactivities that can be ascribed to labilization which arises from the σ-bonded carbon atom of the ortho-metalated aryl ligand in combination with back-bonding to the in-plane aryl ligand that increases the electrophilic character of the Pt(II) center. In complex **1** the σ-donicity of the second chelating dimethylamine group and/or the increased chelation effect of the tridentate ligand lead to a significantly increased lability of the coordinated water molecule, compared to complex **2**. The X-ray structure of the ionic complex [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)]⁺ [OSO₂CF₃][−] (**1a**) is described. The crystal structure comprises an aggregate of two complex cations and two triflate anions. The structure contains two fully equivalent square-planar coordinated Pt(II) centers with an O-ligated neutral H₂O molecule (Pt–O = 2.186 (2) Å) trans to the Pt–C_{aryl} bond (Pt–C = 1.903(2) Å); the aggregate results from the involvement of both H atoms of the two H₂O molecules in asymmetric hydrogen bonding to O atoms of the two triflate anions.

Introduction

The mechanistic behavior of palladium and platinum complexes is of general interest because of their widespread use as catalysts in synthetic processes, and as illustrated by recent publications, there is current interest for environmental and economic reasons in the aqueous (catalytic) chemistry of transition-metal species.² One important characteristic of the reactivity of metal complexes is the kinetic trans effect, which is a long-known and well-studied phenomenon.^{3–6} It has been found that C-bonded organic ligands (e.g. alkyl,

aryl) are among the strongest σ-donors and have a large kinetic trans effect; i.e., they increase the rate of substitution of a trans-positioned group.⁵ Substitution reactions of Pt(II) complexes containing a single metal–carbon bond were first investigated more than 30 years ago,⁷ and later studies with complexes containing two,^{8–10} three,¹¹ and four^{12,13} metal–carbon bonds have shown interesting kinetic and mechanistic features.

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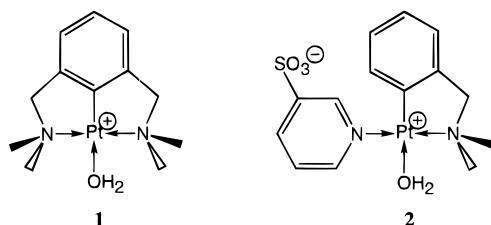


Figure 1. Schematic presentation of **1** and **2**.

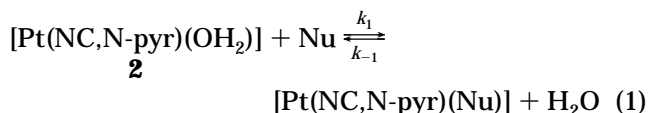
Complexes of the type *cis*-[PtR₂S₂] (R = Me, Ph; S = Me₂S, DMSO) have, for example, been found to exchange the solvent molecules via a dissociative mechanism, characterized by a positive volume of activation.¹⁴ Complexes of the type ML₄ (M = Pd(II), Pt(II); L = CN⁻, MeNC)^{12,13} show remarkably similar rates for ligand exchange reactions, independent of M. Most of these investigations of the kinetic trans effect have been performed, for solubility and chemical reasons, in organic solvents.

We are currently investigating the chemistry of cyclometalated complexes and have prepared the ionic complexes [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(OH₂)]⁺X⁻ (X = OSO₂CF₃ (**1a**),^{15a} BF₄ (**1b**)^{15b}) and the geometrically related, but neutral, zwitterionic complex [Pt{C₆H₄(CH₂NMe₂)₂}(NC₅H₄SO₃-3)(OH₂)] (**2**, ≡ [Pt(NC,N-pyr)(OH₂)]¹⁶ see Figure 1.

Nickel triad complexes containing the {C₆H₃(CH₂NMe₂)_{2-2,6}}⁻ ligand¹⁷ are worthy of detailed study because of their interesting chemistry, which includes catalytic behavior.¹⁸ Isolated neutral platinum(II) species of this ligand include unusual five-coordinate adducts of SO₂^{19a} and I₂^{19b} as well as the first mononuclear platinum phosphido complex,²⁰ whereas ionic **1** itself shows a unique reactivity that includes not only a (reversible) MeI addition reaction to form Wheland-type species^{21a} (studied theoretically by Hoffmann and co-workers^{21b}) but also the stabilization of monohalide and -hydride bridges.²²

Both cyclometalated platinum complexes **1** and **2** prove to be sufficiently soluble in water to enable detailed kinetic studies of complex-formation reactions with nucleophiles in aqueous solution. Our studies of complex **2**, for which the general complex-formation

reaction is given in eq 1, have already allowed us to



determine the forward and reverse rate constants (*k*₁ and *k*₋₁) and the associated activation parameters Δ*H*[‡], Δ*S*[‡], and Δ*V*[‡], as well as the p*K*_a value of the coordinated water molecule.¹⁶ We can clearly demonstrate the expected increase in reactivity and prove that no changeover occurs in the substitution mechanism, i.e. the complex still reacts via an associative substitution pathway.¹⁶

We now report on our study with complex **1** whose integrity as a ionic species in the solid state has been verified with an X-ray crystallographic determination. The detailed kinetic results demonstrate a high reactivity for this cyclometalated Pt(II) complex, and using results from our earlier study on complex **2**, we discuss the influence of charge, steric hindrance, and σ-donicity of the second chelating amine donor ligand on the overall substitution behavior in such cyclometalated complexes.

Experimental Section

Materials. The ionic complex [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(H₂O)][OSO₂CF₃] (**1a**) was prepared by following the literature procedure^{15a} from [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}Cl]^{15b} and [AgOSO₂CF₃] in wet acetone. Colorless crystals suitable for the X-ray crystallographic study were obtained by slow evaporation of a solution of **1** in wet acetone/dichloromethane to which hexane had been added. The preparation and characterization of the complexes [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}I]^{15b} and [Pt{C₆H₄(CH₂NMe₂)₂}(NC₅H₄SO₃-3)(OH₂)]¹⁶ (**2**) are described in the literature. All other chemicals used were of analytical reagent quality (Merck), and Millipore water was used in the preparation of all solutions.

Solution Measurements. UV-vis spectra were recorded in the thermostated (±0.1 °C) cell compartment of a Varian Cary 1 spectrophotometer. Kinetic measurements at ambient pressure were performed on a Dionex D 110 stopped-flow instrument. Kinetic measurements at elevated pressure (up to 125 MPa) were performed on a homemade high-pressure stopped-flow instrument.²³ Kinetic traces were analyzed using the OLIS KINFIT set of programs. pH measurements were performed with an Ingold electrode and a Metrohm E 520 pH meter.

Preparation of Solutions of [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(H₂O)]⁺ (1**).** The water-insoluble complex [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}I]^{15b} (10 mg) was dissolved in ca. 3 mL of dimethylformamide (DMF) to afford a solution of the ionic solvento complex [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(DMF)]⁺I⁻. This solution was diluted with H₂O (ca. 6 mL), and the iodide counteranion was exchanged with perchlorate on a Dowex anion exchanger. This preparation of [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(H₂O)]⁺ClO₄⁻ (**1c**) is outlined in Scheme 1. To the eluate (ca. 90 mL) was added solid NaClO₄ to adjust the ionic strength to 0.1 M, and then dilute HClO₄ was added to bring the pH to 4. The solution was further diluted to 100 mL to afford solutions of **1c** in which the concentration of [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(H₂O)]⁺, (**1**) was 1 × 10⁻⁴ M and the concentration of DMF was not more than 5–10% v/v.

Preliminary measurements had shown, notwithstanding the fact that DMF has a higher nucleophilicity than water, that

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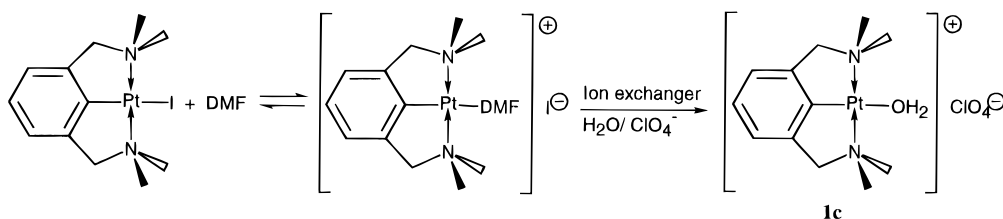
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Scheme 1

**Table 1. Crystal Data and Details of the Structure Analysis of [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)](OSO₂CF₃) (1a)**

formula	C ₁₃ H ₂₁ F ₃ N ₂ O ₄ PtS
mol wt	553.45
cryst syst	triclinic
space group	P1 (No. 2)
a, b, c, Å	8.9360(10), 9.0223(10), 11.5637(10)
α, β, γ, deg	103.165(11), 101.212(10), 97.836(10)
V, Å ³	874.4(2)
Z	2
D _{calc} , g cm ⁻³	2.101
F(000), e	532
μ(Mo Kα), cm ⁻¹	82.7
ref rflns	0.3, -3; 410; 202 (no decay)
data set	h, -13 to 14; k, -14 to +14; l, -22 to 0
total no. of data	5326
total no. of unique data	5031
no. of obsd data (I > 2.5σ(I))	4752
final R, R _w , S	0.020, 0.026, 1.14
⟨Δ/σ⟩ in final cycle	0.03
(Δ/σ) _{max} in final cycle	0.5

the addition of up to 10% DMF does not influence either the UV-vis spectra or the kinetic traces. We can therefore conclude that the aqua complex cation **1** is the reactive species under these conditions.

X-ray Crystallographic Structure Determination and Refinement of [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)](OSO₂CF₃) (1a). A colorless transparent crystal, 0.17 × 0.26 × 0.83 mm, was mounted on a glass fiber and used for data collection at 100 K on an Enraf-Nonius CAD-4F diffractometer. Crystal data and numerical details of data collection and refinement are given in Table 1. Data were collected in the ω/2θ mode: λ(Mo Kα) = 0.710 73 Å (Zr filtered); θ in the range 1.86–30.26°; scan angle Δω = (0.70 + 0.35 tan θ)°. Unit cell parameters were derived from a least-squares treatment of the SET4 diffractometer angles of 25 reflections in the range 14.0 < θ < 17.9°. The triclinic unit cell was checked for higher symmetry.²⁴

Three reference reflections (0,3, -3, 410, 202) were monitored during the 68 h of X-ray exposure time and showed no decay. The intensity data were corrected for absorption effects (Gaussian integration, grid 24 × 10 × 6; maximum and minimum correction, 10.73 and 3.40) and Lorentz and polarization effects. The variance σ²(I) was calculated on the basis of counting statistics plus an instability constant term (0.029I) as derived from the excess variance in the reference reflections.²⁵ A total of 5326 reflections were collected, of which 5031 were independent. The position of Pt was resolved by using the Patterson method. The remaining non-hydrogen atoms were determined from subsequent difference-Fourier maps. Refinement on F was carried out by full-matrix least-squares techniques (SHELX-76). Convergence was reached at R = 0.020, R_w = 0.026, S = 1.14 for 255 parameters and 4752 reflections with I > 2.5σ(I). No residual density was found outside the range -1.53 and +1.38 e Å⁻³ with highest

Table 2. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 1a

atom	x	y	z	U _{eq} (Å ²) ^a
Pt(1)	0.32606(1)	0.18750(1)	0.19384(1)	0.0089(1)
O(1)	0.4032(3)	0.3724(2)	0.3636(2)	0.0170(5)
N(1)	0.4074(3)	0.0066(3)	0.2543(2)	0.0123(6)
N(2)	0.2304(3)	0.3255(3)	0.0894(2)	0.0131(6)
C(1)	0.2636(3)	0.0343(3)	0.0416(2)	0.0112(6)
C(2)	0.1653(3)	0.0652(3)	-0.0557(2)	0.0129(7)
C(3)	0.1236(3)	-0.0443(3)	-0.1682(3)	0.0146(7)
C(4)	0.1820(3)	-0.1827(3)	-0.1803(2)	0.0148(7)
C(5)	0.2818(3)	-0.216(3)	0.0825(3)	0.0145(7)
C(6)	0.3235(3)	-0.1017(3)	0.0303(2)	0.0128(6)
C(7)	0.4386(3)	-0.1027(3)	0.1441(3)	0.0141(7)
C(8)	0.5515(3)	0.0561(3)	0.3543(3)	0.0164(7)
C(9)	0.2842(3)	-0.0793(3)	0.2977(3)	0.0170(7)
C(10)	0.1126(3)	0.2180(3)	-0.0219(3)	0.0139(7)
C(11)	0.3563(3)	0.4074(3)	0.0462(3)	0.0151(7)
C(12)	0.1537(3)	0.4428(3)	0.1554(3)	0.0178(8)
S	0.26978(9)	0.35487(9)	0.63918(6)	0.0174(2)
F(1)	-0.0163(3)	0.3794(3)	0.6459(3)	0.0580(9)
F(2)	0.0153(4)	0.1492(3)	0.5687(4)	0.073(1)
F(3)	0.0237(4)	0.3214(3)	0.4671(3)	0.072(1)
O(2)	0.3350(3)	0.2599(3)	0.5504(2)	0.0240(7)
O(3)	0.3003(3)	0.5177(3)	0.6440(3)	0.0348(8)
O(4)	0.2933(4)	0.3192(4)	0.7548(3)	0.047(1)
C(13)	0.0626(5)	0.2972(5)	0.5760(4)	0.035(1)

^a U_{eq} = one-third of the trace of the orthogonalized U matrix.

density near Pt. All non-hydrogen atoms were refined with anisotropic thermal parameters.

The hydrogen atoms of the structure, except those of H₂O, were introduced in the refinement riding on their carrier atoms. Three electron densities were located in a difference Fourier map in close proximity of oxygen but could not be identified unequivocally with the two H₂O hydrogens. These hydrogen atoms were therefore placed at calculated positions (on a straight line connecting the O atoms of H₂O and OSO₂-CF₃ of the asymmetric unit). The hydrogens were sorted into four separate groups (phenyl, methyl, methylene, and H₂O), and these were each assigned a separate common isotropic thermal parameter.

The empirical extinction parameter X was refined from the relationship $F_c^* = F_c(1 - (0.0001XF_c^2/\sin \theta))$ with X = 0.0034(1). Weights were introduced in the final refinement cycles ($w = 1/\sigma^2(F)$).

Final atom coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 2. Neutral atomic scattering factors were taken from ref 26 and were corrected for anomalous dispersion.²⁷

All calculations were performed with SHELX76²⁸ and the Euclid package²⁹ (PLATON and PLUTON for geometrical calculations) on a MicroVAX-II cluster.

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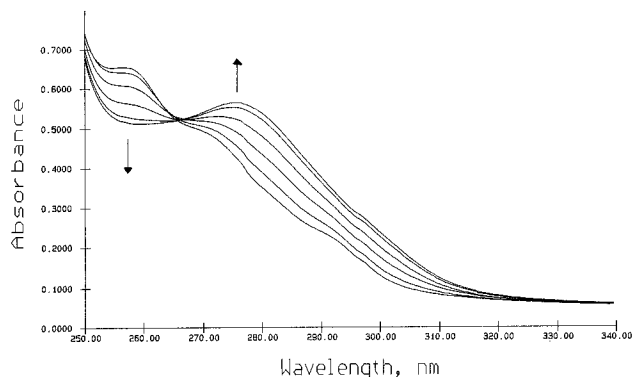


Figure 2. UV-vis spectra of complex **1** at pH 8.5, 9.8, 10.3, 10.8, 11.4, and 12.3.

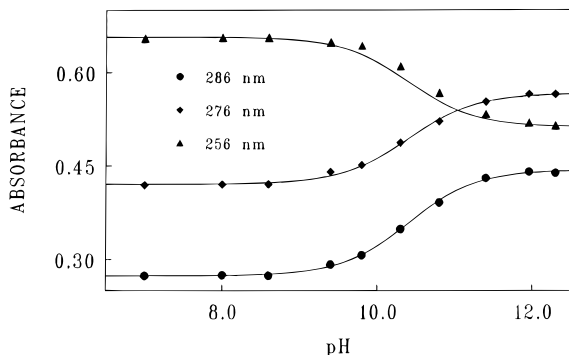
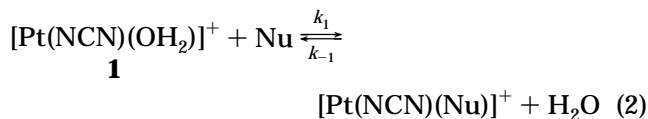


Figure 3. Plot of absorbance vs pH at different wavelengths for complex **1**.

Results

The nucleophilic substitution reaction for the cation $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}(\text{H}_2\text{O})]^+$ (**1**; $\equiv [\text{Pt}(\text{NCN})(\text{OH}_2)]^+$) in aqueous media with a neutral nucleophile (Nu) is shown in a general form in eq 2; with an anionic nucleophile the product will be a neutral species.



For the current studies of **1** solutions of the ionic species $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}(\text{H}_2\text{O})]\text{ClO}_4$ (**1c**) were prepared as outlined in Scheme 1 (see Experimental Section). To investigate the similarities and differences between the cation $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}(\text{H}_2\text{O})]^+$ (**1**) and complex **2**, we first determined the $\text{p}K_a$ value of the coordinated water molecule in the former. Then from studies of the formation of this complex with nucleophiles, wherein nucleophile concentration [Nu], pH, and temperature have been varied, we have determined equilibrium constants K as well as the forward and reverse rate constants (k_1 and k_{-1}), together with the associated activation parameters ΔH^\ddagger and ΔS^\ddagger in a manner analogous to that used earlier for **2**.¹⁶

Aqueous solutions of **1** (**2**) are characterized by an absorption maximum at 257 (247) nm at $\text{pH} \leq 8.5$ (8.3) and at 275 (267) nm at $\text{pH} \geq 12.3$ (11.5) with an isosbestic point at 265 (261) nm (Figure 2). The $\text{p}K_a$ of the coordinated water molecule, determined by a non-linear least-squares fit of the data from plots of absorbance vs pH (shown in Figure 3), is found to be 10.8 ± 0.1 (9.75 ± 0.05). The $\text{p}K_a$ value was also determined

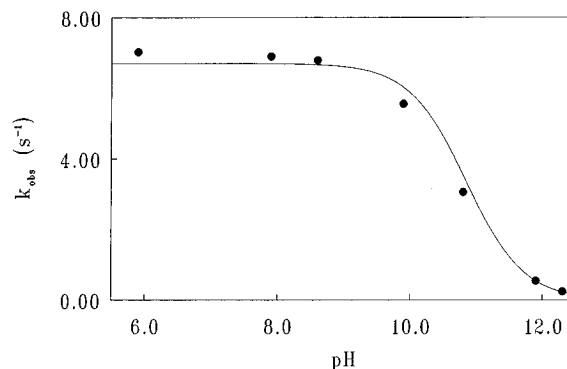


Figure 4. Plot of k_{obs} vs pH for the reaction of complex **1** with tmtu as entering nucleophile. Experimental conditions: $[\text{Pt}] = 5 \times 10^{-5}$ M, $T = 25^\circ\text{C}$, $[\text{I}^-] = 0.1$ M (NaClO_4), $[\text{tmtu}] = 6 \times 10^{-4}$ M.

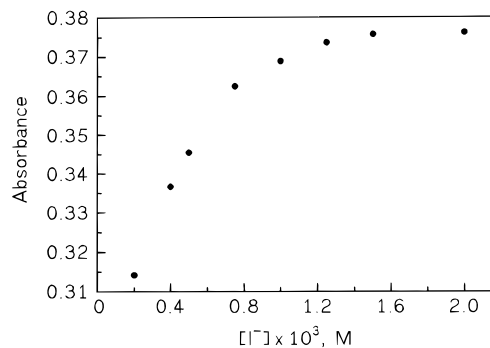


Figure 5. Plot of absorbance at 275 nm vs $[\text{I}^-]$ for the reaction of complex **1** with I^- . Experimental conditions: pH 4, $[\text{Pt}] = 5 \times 10^{-5}$ M, $T = 25^\circ\text{C}$, $I = 0.1$ M (NaClO_4).

kinetically from the substitution reaction of complex **1** (**2**) with tetramethylthiourea (tmtu) as a function of pH, and the resulting plot of k_{obs} vs pH is shown in Figure 4.

Addition of a nucleophile, Nu, to an aqueous solution of **1** (**2**) at a pH of ~ 4 shifts the absorbance maximum to higher wavelengths, and for Cl^- and Br^- a single isosbestic point is found at 261 (252) nm, in agreement with the 1:1 complexation reaction shown in eq 2. A representative plot of absorbance at a fixed wavelength versus nucleophile concentration [Nu] is shown in Figure 5. The equilibrium constant K_1 is derived from the linear anamorphoses of that plot by use of eq 3,

$$\frac{A - A_0}{[\text{Nu}]} = K_1 A_\infty - K_1 A \quad (3)$$

where A_0 and A are absorbances in the absence and presence of added Nu, respectively, and A_∞ is the absorbance at infinite concentration of Nu. The kinetically and spectrophotometrically determined values of K_1 for complexes **1** (and **2**) are summarized in Table 3.

The kinetic data of the complex-formation reaction (eq 2) of **1** with incoming nucleophiles of differing nucleophilicity were gathered under pseudo-first-order conditions, i.e. with at least a 10-fold excess of [Nu], and at a pH where complex **1** is present in its aqua form, i.e. as $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}(\text{OH}_2)]^+$. For most nucleophiles the pH was ~ 4 , but for N_3^- the measurements were carried out at pH 7.5. The kinetic traces at various temperatures were used to determine the pseudo-first-order rate constants k_{obs} , and second-order rate constants k_1 (for complexation) and k_{-1} (for the reverse

Table 3. Equilibrium Constants K_1 for **1 and **2**^a at 25 °C from UV–Vis Data and from Kinetic Data^b for Various Nucleophiles**

nucleophile	complex 1		complex 2 ^a	
	k_1/k_{-1} , M ⁻¹	K_1 , M ⁻¹	k_1/k_{-1} , M ⁻¹	K_1 , M ⁻¹
Cl ⁻	258 ± 28	279 ± 21	117 ± 9	90 ± 16
Br ⁻	770 ± 45	760 ± 52	159 ± 19	141 ± 9
I ⁻	5180 ± 760	4270 ± 200	730 ± 50	760 ± 20
N ₃ ⁻	3470 ± 650	4070 ± 650	3200 ± 960	3170 ± 120

^a Data taken from ref 15. ^b Measured at ionic strength 0.1 M (NaClO₄) and pH 4.

aquation reaction) were derived from the plot of k_{obs} vs [Nu], according to eq 4. The values for k_1 and k_{-1} are

$$k_{\text{obs}} = k_1[\text{Nu}] + k_{-1} \quad (4)$$

summarized in Table 4 together with the associated activation parameters ΔH^\ddagger and ΔS^\ddagger , calculated with use of the Eyring equation from the temperature dependence of the rate constants. Complex **1** has a high reactivity, and it only proved possible to determine the volume of activation, ΔV^\ddagger , with tmtu as entering nucleophile; for this system we obtained a value for ΔV^\ddagger of $-12.0 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ (Table 5).

Crystal and Molecular Structure of [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)](OSO₂CF₃) (1a**).** The interesting and sometimes unexpected chemistry of complexes containing the C₆H₃(CH₂NMe₂)₂-2,6 ligand,¹⁷ together with the temperature- and pH-dependent NMR spectra of **1**,³⁰ was sufficient motive to ensure that the complex cation was well characterized as an aqua solvento species before proceeding with the kinetic studies. To this end, we have carried out an X-ray crystallographic study of complex **1a**.^{15a} An ORTEP plot of the molecular structure together with the adopted numbering scheme is shown in Figure 6. Selected relevant bond distances and interbond angles are listed in Table 6.

The crystal structure of **1a** consists of the packing of two OSO₂CF₃ anions and two [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)] complex monocations, in a triclinic unit cell. The ions are linked by hydrogen bonds from the coordinated water molecules to form a dimeric cluster around an inversion center. The individual platinum centers have a slightly distorted square-planar coordination sphere that comprises the N, C, N atoms of the terdentate C₆H₃(CH₂NMe₂)₂-2,6 ligand (Pt–N(1) = 2.080(3) Å, Pt–N(2) = 2.077(3) Å, and Pt–C(1) = 1.903(2) Å) and the O atom of a water molecule situated trans to Pt–C(1) (Pt–O = 2.186(2) Å). The principal distortions emanate from the geometrical constraints of the terdentate ligand that afford C(1)–Pt–N(1) and C(1)–Pt–N(2) angles of 82.41(10) and 82.57(10)°, respectively. In neutral Pt(II) complexes containing this terdentate ligand, the range for Pt–C distances is 1.901–2.010 Å and the Pt–N range is 2.070–2.316 Å;^{15a,19,31} in the complex cation of **1a** the Pt–C_{aryl} bond and the Pt–N bonds are seen to be at the shorter end of these ranges.

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The Pt–O bond length of 2.186(2) Å in **1a** is a little shorter than that in the related complex [Pt(Ph)(PEt₃)₂(OH₂)]BF₄ (2.191 Å);^{32a} these distances are not exceptional for Pt(OH₂) units^{32b,c} but are significantly longer than Pt–O bonds in hydroxo-bridged complexes (1.98–2.17)^{32d,e} and other hydroxy species.^{32f} As is usual for Ni(II), Pd(II), and Pt(II) complexes of this terdentate ligand, the aryl nucleus is rotated about the Pt–C_{aryl} bond out of the metal coordination plane; in **1a** the dihedral angle between the aryl ring and the plane through C(1), N(1), N(2), and O(1) amounts to 13.19(12)°. The complex cation exhibits approximate non-crystallographic C₂ symmetry with respect to Pt–C(1) with a $\Delta C_2[\text{Pt}–\text{C}(2)]$ asymmetry parameter³³ of 3.5(3)° for the eight-membered ring Pt–N(1)–C(7)–C(6)–C(1)–C(2)–C(10)–N(2).

From the O-ligated water molecules the hydrogen atoms (which were not determined unequivocally but which were placed at calculated positions) are positioned nonsymmetrically above and below the metal coordination planes in the direction of the O atom of the OSO₂CF₃ anions. The S–O bonds of the anions involved in hydrogen bonding (1.448(3) and 1.443(3) Å) are significantly longer than the other S–O bonds of 1.428(3) Å; such differences in S–O bond lengths have been observed and accounted for earlier.³⁴

Discussion

The ligand order of increasing trans effect for square-planar Pt(II) complexes has been generally accepted for many years to be H₂O ≈ NO₃⁻ < OH⁻ < NH₃ < Cl⁻ < Br⁻ < I⁻ ≈ SCN⁻ ≈ NO₂⁻ ≈ PR₃ < CO ≈ C₂H₄ ≈ CN⁻ ≈ CH₃⁻ ≈ H⁻.³⁵ For both **1** and **2**, it is therefore reasonable to expect that their reactivities in substitution, which in both cases occurs *trans* to an aryl C_{ipso} donor atom, should have significant parallels and the rates should be high. This has indeed been found to be the case. However, although both ionic **1** and zwitterionic **2** have a similar N,C,N' donor atom array with a mutually trans arrangement of the N-donor sites, they do exhibit significant rate differences that are a reflection of their individual structures.

The pK_a value of 10.8 for the coordinated water molecule in complex **1** is 1 unit higher than that of complex **2**, and one can infer from this that the water molecule in **1** is likely to be more labile, i.e. closer in nature to free water (pK_a = 15.7). This argument, however, ignores the fact that **1** reacts as a complex cation with a +1 charge whereas complex **2** is a zwitterion, and this factor will also affect the lability of the coordinated water molecule. A further influence on

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Table 4. Rate Constants and Thermodynamic Parameters ΔH^\ddagger and ΔS^\ddagger for Complex-Formation Reactions of **1 and **2**^a with Various Nucleophiles at 25 °C^b**

complex	Nu	$k_1, \text{M}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$	k_{-1}, s^{-1}	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$
1	Cl [−]	$(13.7 \pm 0.2) \times 10^3$	31.4 ± 1.0	-60 ± 3	53 ± 5	30.0 ± 3.0	-112 ± 9
2	Cl [−]	$(4.0 \pm 0.1) \times 10^3$	30.0 ± 3.0	-112 ± 9	34 ± 2	47.5 ± 5.4	-56 ± 18
1	Br [−]	$(36.2 \pm 0.6) \times 10^3$	24.5 ± 1.5	-75 ± 5	47 ± 2	47.5 ± 0.9	-54 ± 3
2	Br [−]	$(11.3 \pm 0.2) \times 10^3$	25.1 ± 0.7	-83 ± 2	71 ± 7	50.3 ± 1.5	-41 ± 5
1	I [−]	$(12.1 \pm 0.2) \times 10^4$	22.1 ± 1.3	-74 ± 4	23 ± 3	43.6 ± 3.5	-72 ± 12
2	I [−]	$(42.9 \pm 0.5) \times 10^3$	27.6 ± 2.2	-63 ± 6	53 ± 3	38.7 ± 1.3	-82 ± 4
1	N ₃ [−]	$(46 \pm 1) \times 10^3$	20.9 ± 0.7	-86 ± 2	13.3 ± 2.2	29.6 ± 3.0	-124 ± 8
2	N ₃ [−]	$(15.2 \pm 0.2) \times 10^3$	25.6 ± 0.8	-79 ± 3	4.8 ± 1.8	43.8 ± 2.0	-85 ± 6
1	NCS [−]	$(14.4 \pm 0.3) \times 10^4$	18.8 ± 1.1	-83 ± 4			
2	NCS [−]	$(40.7 \pm 0.8) \times 10^3$	16.9 ± 0.3	-100 ± 1			
1	tu	$(77.7 \pm 0.4) \times 10^3$	18.5 ± 0.3	-89 ± 1			
2	tu	$(55.0 \pm 0.4) \times 10^3$	20.9 ± 0.8	-84 ± 3			
1	dmtu	$(40.8 \pm 0.2) \times 10^3$	21.3 ± 0.8	-85 ± 3			
2	dmtu	$(57.7 \pm 0.4) \times 10^3$	22.0 ± 0.6	-80 ± 2			
1	tmtu	$(10.4 \pm 0.3) \times 10^3$	37.7 ± 1.6	-41 ± 5			
2	tmtu	$(16.8 \pm 0.2) \times 10^3$	31.8 ± 1.2	-57 ± 4			

^a Data taken from ref 16. ^b [NaClO₄] = 0.1 M at pH 4 except for Nu = N₃[−] at pH 7.5.

Table 5. Activation Volumes for Reactions of **1 and **2**^a with Azide and Tetramethylthiourea (tmtu) as Nucleophiles**

complex	nucleophile	rate constant	$T, ^\circ\text{C}$	$\Delta V^\ddagger, \text{cm}^3 \text{mol}^{-1}$
1	tmtu	k_1	25	-12.0 ± 0.5
2	tmtu	k_1	25	-10.5 ± 0.1
2	N ₃ [−]	k_1	10	-10.1 ± 0.6
2	N ₃ [−]	k_{-1}	10	-12.4 ± 0.9

^a Data taken from ref 16.

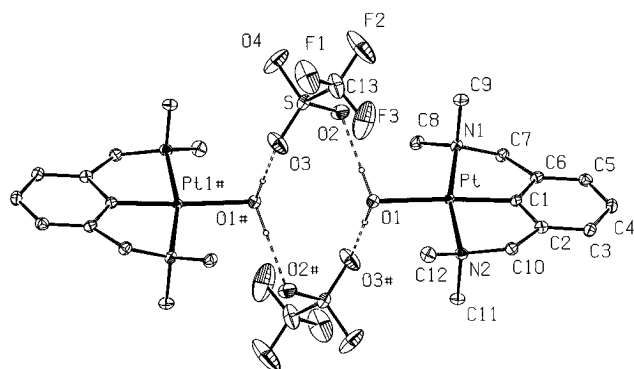


Figure 6. ORTEP thermal motion ellipsoid plot (50% probability level) of two molecules of [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(OH₂)] [OSO₂CF₃] (**1a**) contained by one unit cell with the adopted numbering scheme. Hydrogen atoms (except those of H₂O) are omitted for clarity. Atoms indicated by # are related by an inversion center (1 − *x*, 1 − *y*, 1 − *z*).

reactivity comes from differences in the steric hindrance, chelation mode, and σ -donicity of the coordinated ligands in these two complexes. It is difficult to separate these factors, but from a comparison of the second-order rate constants (k_1) listed in Table 4 some conclusions can be drawn.

Substitution reactions with the sterically hindered nucleophiles *N,N*-dimethylthiourea (dmtu) and *N,N,N,N*-tetramethylthiourea (tmtu) are significantly slower for complex **1** than for complex **2**; i.e., the latter appears to be sterically less hindered. This result may, on the one hand, be a reflection of the geometric rigidity and restrictions that the two coupled five-membered chelate rings in **1** impose on the mutual positioning of the Me groups of the two trans-positioned NMe₂ functionalities. On the other hand, it may result from the fact that the flat coordinated pyridine in **2** can wag about the Pt–N_{pyr} bond, although full rotation that would require the

Table 6. Selected Bond Distances (Å) and Angles (deg) for **1a, with Esd's in parentheses**

(a) Bond Distances			
Pt–O(1)	2.186(2)	N(2)–C(12)	1.485(4)
Pt–N(1)	2.080(3)	C(1)–C(2)	1.393(3)
Pt–N(2)	2.077(3)	C(1)–C(2)	1.394(4)
Pt–C(1)	1.903(2)	C(2)–C(3)	1.390(4)
N(1)–C(7)	1.521(4)	C(2)–C(10)	1.509(4)
N(1)–C(8)	1.491(4)	C(3)–C(4)	1.406(4)
N(1)–C(9)	1.491(4)	C(4)–C(5)	1.396(4)
N(2)–C(10)	1.527(4)	C(5)–C(6)	1.394(4)
N(2)–C(11)	1.490(4)	C(6)–C(7)	1.507(4)
S–O(2)	1.448(3)	F(1)–C(13)	1.339(5)
S–O(3)	1.443(3)	F(2)–C(13)	1.323(5)
S–O(4)	1.428(3)	F(3)–C(13)	1.315(6)
S–C(13)	1.808(5)		
(b) Bond Angles			
O(1)–Pt–N(1)	99.73(8)	C(10)–N(2)–C(12)	109.6(2)
O(1)–Pt–N(2)	95.24(9)	C(11)–N(2)–C(12)	108.6(2)
O(1)–Pt–C(1)	176.83(9)	Pt–C(1)–C(2)	118.8(2)
N(1)–Pt–N(2)	164.95(9)	Pt–C(1)–C(6)	118.6(2)
N(1)–Pt–C(1)	82.4(1)	C(2)–C(1)–C(6)	122.5(2)
N(2)–Pt–C(1)	82.6(1)	C(1)–C(2)–C(3)	118.9(3)
Pt–N(1)–C(7)	106.7(2)	C(1)–C(2)–C(10)	113.4(3)
Pt–N(1)–C(8)	114.3(2)	C(3)–C(2)–C(10)	127.7(2)
Pt–N(1)–C(9)	109.5(2)	C(2)–C(3)–C(4)	119.0(3)
C(7)–N(1)–C(8)	109.4(2)	C(3)–C(4)–C(5)	121.5(2)
C(7)–N(1)–C(9)	108.3(2)	C(4)–C(5)–C(6)	119.4(3)
C(8)–N(1)–C(9)	108.5(2)	C(1)–C(6)–C(5)	118.6(2)
Pt–N(2)–C(10)	107.4(2)	C(1)–C(6)–C(7)	113.0(2)
Pt–N(2)–C(11)	108.5(2)	C(5)–C(6)–C(7)	128.3(2)
Pt–N(2)–C(12)	114.2(2)	N(1)–C(7)–C(6)	109.5(2)
C(10)–N(2)–C(11)	108.4(2)	N(2)–C(10)–C(2)	109.2(2)
O(2)–S–O(3)	113.7(2)	S–C(13)–F(1)	111.2(3)
O(2)–S–O(4)	114.2(2)	S–C(13)–F(2)	110.8(3)
O(2)–S–C(13)	103.4(2)	S–C(13)–F(3)	111.3(3)
O(3)–S–O(4)	115.5(2)	F(1)–C(13)–F(2)	107.5(4)
O(3)–S–C(13)	103.5(2)	F(1)–C(13)–F(3)	106.5(4)
O(4)–S–C(13)	104.5(2)	F(2)–C(13)–F(3)	109.4(4)

aryl ring at some point to lie flat in the coordination plane of the metal center seems to be prohibited by ortho protons on the pyridine and the ortho-metalated rings. With sterically less hindered thiourea (tu) the complex-formation reaction is faster for complex **1** by a factor of 1.5; this rate acceleration is only moderate, and the most reasonable explanation for this result is that the dimethylamine group in **1** has a higher σ -donicity than the pyridine function in **2**.

In substitution reactions with negatively charged nucleophiles such as halides the k_1 values show complex **1** to react faster than complex **2**, as expected on the basis of charge neutralization, and the accelerating effect is

Table 7. Rate Constants and Activation Parameters for Solvent Exchange and Solvolysis Reactions of Pd(II) and Pt(II) Complexes

(a) Solvent Exchange							
complex ^a	solvent	k_1 , M ⁻¹ s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹	ΔV^\ddagger , cm ³ mol ⁻¹	temp, °C	ref
[Pd(H ₂ O) ₄] ²⁺	H ₂ O	10.2 ± 0.7	50 ± 2	-60 ± 6	-2.2 ± 0.2	51	41
[Pd(MeNC) ₄] ²⁺	CD ₃ CN	(10.6 ± 0.7) × 10 ⁵	16 ± 1	-75 ± 4	-3.1 ± 0.1	-9	13
[Pt(H ₂ O) ₄] ²⁺	H ₂ O	(7.1 ± 0.5) × 10 ⁻⁶	90 ± 2	-43 ± 8	-4.6 ± 0.2	24	42
[Pt(MeNC) ₄] ²⁺	CD ₃ CN	(6.2 ± 0.4) × 10 ⁵	14 ± 1	-88 ± 4	-3.7 ± 0.1	-9	13
[Pd(dien)H ₂ O] ²⁺	H ₂ O	93	38	-80	-2.8 ± 0.4	23	43
[Pd(Me ₅ dien)H ₂ O] ²⁺	H ₂ O	3.4 ± 0.5	62 ± 3	-27 ± 7	-7.2 ± 0.6	47	44
[Pd(Et ₅ dien)H ₂ O] ²⁺	H ₂ O	(5.3 ± 0.2) × 10 ⁻²	63 ± 1	-58 ± 2	-7.7 ± 1.3	96	44
(b) Solvolysis							
complex ^a	solvent	k_{-1} , s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹	ΔV^\ddagger , cm ³ mol ⁻¹	temp, °C	ref
[Pd(dien)Cl] ⁺	H ₂ O	43.8 ± 0.5	43 ± 3	-69 ± 12	-10.0 ± 0.6	25	45
[Pd(Me ₅ dien)Cl] ⁺	H ₂ O	(2.76 ± 0.04) × 10 ⁻¹	50 ± 1	-88 ± 3	-10.9 ± 0.3	25	46
[Pd(Et ₅ dien)Cl] ⁺	H ₂ O	(7.2 ± 0.1) × 10 ⁻⁴	59 ± 3	-106 ± 9	-8.2 ± 0.3	25	45
[Pt(dien)Cl] ⁺	H ₂ O	1.04 × 10 ⁻⁴	84	-42	-10.5 ± 0.3	25	47, 48
[Pt(C ₆ H ₃ (CH ₂ NMe ₂) ₂)Cl]	H ₂ O	53 ± 5	30 ± 3	-112 ± 9			this work
[Pt(C ₆ H ₄ CH ₂ NMe ₂)(py-3-SO ₃)Cl] ⁻	H ₂ O	34 ± 2	47 ± 5	-56 ± 18			16
trans-[Pt(SMe ₂) ₂ (Ph)Cl]	MeOH	0.96	52 ± 2	-71 ± 7	-11.6 ± 0.6	25	49
trans-[Pt(SMe ₂) ₂ (mesityl)Cl]	MeOH	0.45	54 ± 1	-70 ± 3	-16.3 ± 3.3	25	49

^a Abbreviations: dien = diethylenetriamine, Me₅dien = 1,1,4,7,7-pentamethyl-dien, Et₅dien = 1,1,4,7,7-pentaethyl-dien.

a factor of approximately 3. Since this result is a combined effect of the charge and σ -donicity, we can deduce that the influences of these two factors are therefore similar.

On the basis of the activation parameters given in Table 4, there is no direct correlation to be found between the reactivity and activation enthalpy, ΔH^\ddagger , and this indicates that the activation entropy is playing an important role in these reactions. It is, however, true that ΔH^\ddagger is much higher for the significantly slower solvolysis reaction (notice k_{-1} is given in s⁻¹) than for the complexation reaction. This difference in activation enthalpy is due to the fact that water is more weakly nucleophilic than the other nucleophiles studied.

From Table 4 it can be seen that for both **1** and **2** the rate of aquation k_{-1} is directly related to the nucleophilicity of the coordinated ligand and, excepting Cl⁻ with complex **2** and N₃⁻ with both **1** and **2**, a stronger nucleophile affords a slower rate of aquation. On the basis of nucleophilicity ρ_{Pt} values of Cl⁻, Br⁻, and N₃⁻ (3.04, 4.18, and 3.58, respectively)³⁶ azide should be faster than Cl⁻ but slower than Br⁻ in complex-formation reactions. However, the reaction of **1** and **2** with N₃⁻ is faster than with Br⁻. This observation that azide behaves differently from what is expected from its nucleophilicity has been made before, and the explanation is related to steric effects.³⁷ With our complexes it is worth noting that the slowest aquation reaction we find is with azide as nucleophile. This result could be due to bond stabilization in the four-coordinate product arising from an interaction of the π bonds on the azide ligand with the metal center and, eventually, with the π^* aryl orbitals (i.e. back-bonding). For both **1** and **2** the reaction with NCS⁻ exhibits a subsequent, slow, step that is independent of nucleophile concentration. Since we found no evidence with any other nucleophiles used in this study for either consecutive complex-formation reaction or μ -halide association,²² we believe that this concentration-indepen-

dent reaction is possibly an intramolecular linkage isomerization, from initially S-bonded to N-bonded;³⁸ in the product [Pt{C₆H₃(CH₂NMe₂)₂-2,6}NCS] isolated from the reaction of **1** with NCS⁻, the isothiocyanate ligand is known to be N-bonded.³⁹

In reactions of complex **2** with azide and tmtu the significantly negative values for ΔS^\ddagger and the activation volume ΔV^\ddagger (Table 5) are evidence for the operation of an associative substitution mode and the ΔV^\ddagger value now obtained for the corresponding reaction of **1** with tmtu is also consistent with this type of mechanism. Thus, the labilization caused by the presence of a single metal-carbon (aryl) bond is accompanied by retainment of the substitution mechanism usually found for square-planar complexes.⁴⁰ That this was not a foregone conclusion is illustrated by a study of solvent exchange in the complexes *cis*-[PtPh₂(Me₂S)₂], *cis*-[PtPh₂(DMSO)₂], and *cis*-[PtMe₂(DMSO)₂]; for these complexes, which have two metal-carbon bonds on a Pt(II) center, there is a changeover in substitution mechanism from associative to dissociative.¹³

In an associative substitution reaction the metal center changes its hybridization from originally dsp² (square-planar) to dsp³ (trigonal bipyramidal) with involvement of the p_z orbital in the five-coordinate transition state. That an aryl ligand such as that found in **1** and **2** has a high trans effect can be adequately explained by the stabilization it affords of a trigonal-bipyramidal transition state, although for **1** chelation restraints may favor a square-pyramidal transition state.

In this context it is worth remarking that, although we have not succeeded in isolating trigonal-bipyramidal Pt(II) species based on the C₆H₃(CH₂NMe₂)₂-2,6⁻ ligand, the neutral square-planar species [Pt{C₆H₃(CH₂NMe₂)₂-

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2,6}X] do have a unique chemistry that includes a notable propensity for five-coordination and square-pyramidal adducts such as $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}\text{Br}(\eta^1\text{-SO}_2)]^{19\text{a}}$ and $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}\text{I}(\eta^1\text{-I}_2)]^{19\text{b}}$ have been isolated and structurally characterized.

The literature data^{41–49} summarized in Table 7, including the results of this and our earlier studies, nicely demonstrate that the lability of square-planar d⁸ complexes can be systematically tuned through electronic and steric effects. For example, the metal ion itself plays a very important role, as is illustrated by the fact that solvent exchange and aquation reactions of the Pd(II) complexes $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Pd}(\text{dien})\text{Cl}]^+$ are 6 orders of magnitude faster than those of the corresponding Pt(II) complexes $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Pt}(\text{dien})\text{Cl}]^+$.

Complexes **1** and **2** are most readily discriminated electronically from the $[\text{Pt}(\text{dien})\text{Cl}]^+$ system by the presence of an additional platinum–carbon bond, and their solvolysis rate constants are 5 orders of magnitude greater than that of $[\text{Pt}(\text{dien})\text{Cl}]^+$. This result is consistent with a conference report that there is a significant acceleration for the solvolysis of a chloro ligand trans to a carbon-bonded aromatic substituent.⁴⁹

When H₂O is replaced by MeNC in $[\text{M}^{\text{II}}\text{L}_4]^{2+}$ systems, the solvent exchange rate constant increases by 5 orders of magnitude for Pd(II)^{13,41} and by 11 orders of magnitude for Pt(II).^{13,42} This clearly demonstrates the significant lability introduced by the metal–carbon bond, the effect being even more significant for the less labile Pt(II) system. These increases in solvent exchange rate constants are accompanied by a drastic decrease in ΔH^\ddagger (e.g. from 90 to 14 kJ mol^{–1} for Pt(II)) and also a decrease in ΔS^\ddagger , whereas ΔV^\ddagger remains small and negative. The exchange process is clearly associative in all these cases.

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The observed fast rate of exchange in complexes **1** and **2** can be ascribed to destabilization of the ground state and stabilization of the five-coordinate transition state. On the one hand the metal–carbon bond will introduce a ground-state trans effect which will weaken the bond with the leaving group. On the other hand, since the substitution process is basically associative in nature, there must be an effect that will cause a more efficient binding of the entering nucleophile. The shortest aryl–metal bond is encountered when the aryl ligand and the metal are in the same plane such that effective back-bonding from the d_{xz} metal orbital into the aromatic antibonding π^* orbital can occur. This will increase the electrophilic character of the metal center and favour axial nucleophilic attack. The difference in reactivity between complexes **1** and **2** must be due to the additional σ -donicity of the second chelating dimethylamino group in **1** and/or the stronger chelation effect of the tridentate versus the bidentate ligand that will affect the lability of the remaining coordination site.

The above discussion based on the data in Table 7, as well as the results of this and our earlier studies,¹⁶ clearly demonstrates that steric and electronic effects can be used to tune the lability of Pt(II) and Pd(II) complexes. The large changes in lability one finds are in general not associated with a changeover in mechanism and can be accounted for in a rather straightforward manner. A promising result from these studies is the possibility to perform organometallic chemistry in an aqueous solution. Thus, the study of catalytic processes in aqueous medium, employing complexes related to those used in this study, presents a challenge for future investigations.

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Supporting Information Available: Tables containing all the k_{obs} , k_1 , and k_{-1} data and complete tables of final fractional coordinates and (an)isotropic thermal parameters of all atoms and of bond distances and angles (14 pages). Ordering information is given on any current masthead page.

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