

Ligand Substitution Reactions of a Dinuclear Platinum(I) Complex

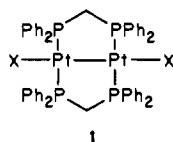
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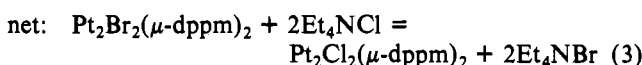
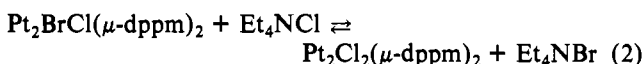
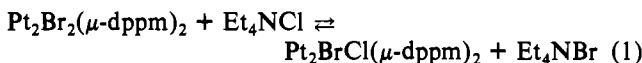
The complex $\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2$ reacts with Et_4NCl in dichloromethane and dichloroethane to form $\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2$. The reaction is reversible and proceeds via stepwise formation of the mixed-ligand (Br, Cl) complex. The reaction follows biphasic kinetics, and each step shows a linear dependence on $[\text{Et}_4\text{NCl}]$, with rate constants 93 ± 20 and $19.4 \pm 1.2 \text{ M}^{-1} \text{ s}^{-1}$ for the respective steps (10.0°C in CH_2Cl_2). The identification of a rate constant with an individual step is a process that inherently admits of dual solutions; the assignment of $k_1 = 93 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 19.4 \text{ M}^{-1} \text{ s}^{-1}$ was made on the basis that only this model gave a consistent and reasonable value for the molar absorptivity of the mixed-halide intermediate. The reaction in 1,2-dichloroethane shows a quite different kinetic pattern, with a single pseudo-first-order rate law and a more complex variation of k_{obsd} with $[\text{Et}_4\text{NCl}]$.

Introduction

Although the kinetics of ligand substitution reactions of Pt(II) complexes have been studied extensively,^{1,2} little is known about analogous reactions of Pt(I) complexes. The availability³ of well-characterized dinuclear Pt(I) halide complexes, $\text{Pt}_2\text{X}_2(\mu\text{-dppm})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; dppm = bis(diphenylphosphino)methane) (1), presents an opportunity in this



regard. This system holds additional interest because these dihalides react with small molecules (e.g., CH_2N_2 , CO , S_8 , SO_2) to insert atoms or molecules into the metal-metal bond;⁴⁻⁶ indeed, ligand substitution may be one step in the insertion process. In this paper we report on a kinetic study of the reaction of $\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2$ with chloride ions in dichloromethane solvent, which is shown to yield ultimately the dichloro complex by way of the mixed bromo-chloro complex:



Experimental Section

$\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ was prepared according to the literature.³ Tetraethylammonium chloride was recrystallized from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$. Dichloromethane and 1,2-dichloroethane were distilled before use. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker WM-300 spectrometer using external 85% phosphoric acid as a reference. Kinetic measurements were made at 10.0°C under pseudo-first-order conditions (excess Et_4NCl) by following the absorbance changes at 300 or 340 nm with a Cary 219 spectrophotometer.

Results

Reactions and Products. The UV-visible absorption spectra and the NMR spectra showed complete conversion to the dichloro complex in the presence of excess Et_4NCl . The re-

Table I. Rate Constants, k_f and k_s , and Calculated ϵ_B Values (λ 300 nm) for Case 1 and Case 2^a

$10^3 \times [\text{Et}_4\text{NCl}]/\text{M}$	$10^2 k_f/\text{s}^{-1}$	$10^2 k_s/\text{s}^{-1}$	$10^{-4} \epsilon_B/\text{M}^{-1} \text{ cm}^{-1}$	
			case 1	case 2
0.525	2.42 ± 0.33	0.87 ± 0.27	1.41	-0.72
0.788	7.91 ± 2.65	2.19 ± 0.23	1.54	-1.29
1.05	6.79 ± 3.08	2.43 ± 0.30	1.53	-0.44
1.05	5.79 ± 1.28	2.23 ± 0.50	1.47	-0.37
1.31	9.76 ± 1.23	3.00 ± 0.19	1.70	-0.38
1.58		4.21 ± 0.36		
1.58	28.4 ± 0.3	3.30 ± 0.11	1.39	-8.0
1.58	21.7 ± 8.7	4.15 ± 0.19	1.63	-2.58
1.84	35.6 ± 7.2	4.78 ± 0.14	1.65	-4.58
2.10	30.8 ± 7.7	4.60 ± 0.15	1.59	-4.24
2.10	25.4 ± 3.3	4.75 ± 0.09	1.65	-2.57
2.10	15.7 ± 2.8	4.00 ± 0.15	1.81	-0.54
2.10 ^b	9.66 ± 3.48	3.10 ± 1.37	(0.58)	(-0.21) ^b
2.10 ^b		5.10 ± 0.24		
2.63	39.7 ± 13.7	6.31 ± 0.19	1.74	-2.91
3.15	19.2 ± 4.6	5.65 ± 0.57	1.52	-1.11
3.15	32.0 ± 14.1	6.87 ± 0.69	1.68	-1.75
3.68		8.80 ± 0.26		
4.20	30.6 ± 21.4	8.34 ± 1.24	1.45	-1.67
4.20	47.00 ± 0.02	7.90 ± 0.02	1.51	-3.98
5.25		10.7 ± 0.4		

^a $[\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2]_0 = 3.51 \times 10^{-5} \text{ M}$. ^b At 340 nm.

verse transformation occurs even more readily, suggesting, as expected, that bromide is more tightly bound than chloride. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a mixture of $\text{Pt}_2\text{Br}(\mu\text{-dppm})_2$ and Et_4NCl ($\sim 1:1$) in CD_2Cl_2 consisted of three resonances as shown in Figure 1. In addition to the resonance corresponding to $\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2$ (3.56 ppm) and $\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2$ (6.07 ppm), a new resonance appeared at 4.80 ppm, which could be assigned to the mixed-halide complex, $\text{Pt}_2\text{BrCl}(\mu\text{-dppm})_2$. The latter peak is slightly broadened, which is reasonable since two sets of phosphorus atoms occur in the mixed-halide complex. The relative intensities also confirm the inferred stability sequence and the stepwise reactions written earlier.

Kinetics. The absorbance-time curves monitored at 300 nm (or 340 nm in two kinetic runs) for reactions 1 and 2 in CH_2Cl_2 solutions were obtained in the presence of large stoichiometric excesses of Et_4NCl , such that its concentration remained effectively constant in each experiment. The kinetic data were in accord with the occurrence of two sequential first-order reactions. In terms of the values of absorbance per unit path length (D), the data were resolved⁷ by eq 4, to yield the values

$$\frac{D_t - D_\infty}{[\text{Pt}_2]_0} = a_f \exp(-k_f t) + a_s \exp(-k_s t) \quad (4)$$

(7) The computer program for the kinetic analyses by eq 4 was developed by Dr. Marcel Maeder, University of Basel, Switzerland, 1980.

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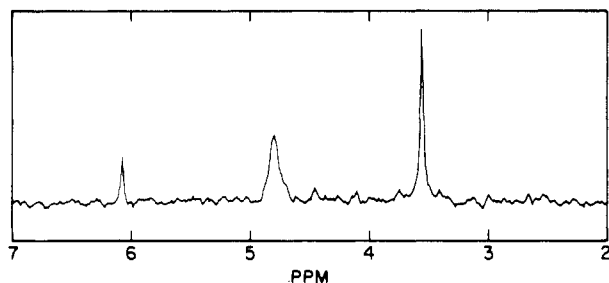


Figure 1. ^{31}H NMR spectrum of the reaction mixture of $\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2$ (4.4×10^{-3} M) and $(\text{C}_2\text{H}_5)_4\text{NCl}$ (4.2×10^{-3} M) in CD_2Cl_2 .

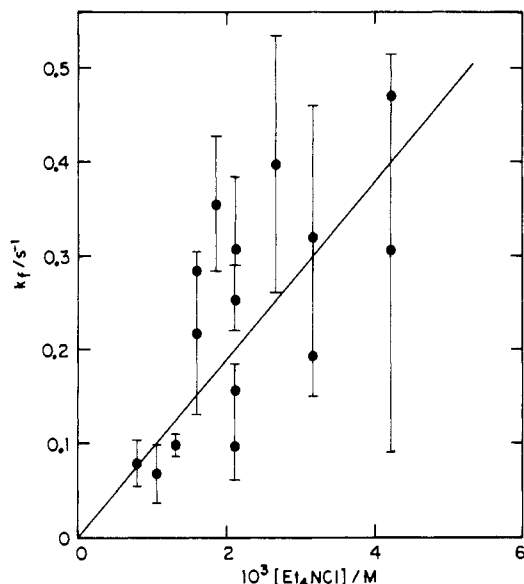


Figure 2. Plot of k_f vs. $[(\text{C}_2\text{H}_5)_4\text{NCl}]$ for the reaction of $\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2$ with $(\text{C}_2\text{H}_5)_4\text{NCl}$ in CH_2Cl_2 at 10.0°C . The slope is $93 \pm 20 \text{ M}^{-1} \text{ s}^{-1}$.

given in Table I. In this form, with “fast” and “slow” terms—amplitudes (a) and rate constants (k)—one or the other term is not identified with a particular reaction step. Indeed, such an assignment cannot be made unambiguously without further analysis.⁸⁻¹⁰ That point aside, both of the rate constants show a variation with $[\text{Et}_4\text{NCl}]$ that is linear within the experimental error (Figures 2 and 3). A least-squares analysis gives the second-order rate constants $k_f/[\text{Et}_4\text{NCl}] = 93 \pm 20 \text{ M}^{-1} \text{ s}^{-1}$ and $k_s/[\text{Et}_4\text{NCl}] = 19.4 \pm 1.2 \text{ M}^{-1} \text{ s}^{-1}$ at 10.0°C in CH_2Cl_2 . It is clear, of course, that the larger of the two has been resolved by this procedure with relatively low precision, as is evident from its standard deviation and the scatter in Figure 2.

Rate Constant Assignments. Returning to the ambiguity of the rate constant assignments, we consider two cases pertaining to a sequence of pseudo-first-order reactions:

$$\text{case 1: } k_1 = k_f > k_2 = k_s \quad \text{case 2: } k_1 = k_s < k_2 = k_f$$

Depending upon which situation prevails, the amplitudes assume a different significance. If ϵ_A , ϵ_B , and ϵ_C are used to symbolize the molar absorptivities of the dibromo, bromochloro, and dichloro complexes, respectively, then the molar absorptivity of intermediate complex B can be calculated from the rate constants and amplitudes. *The substance of this*

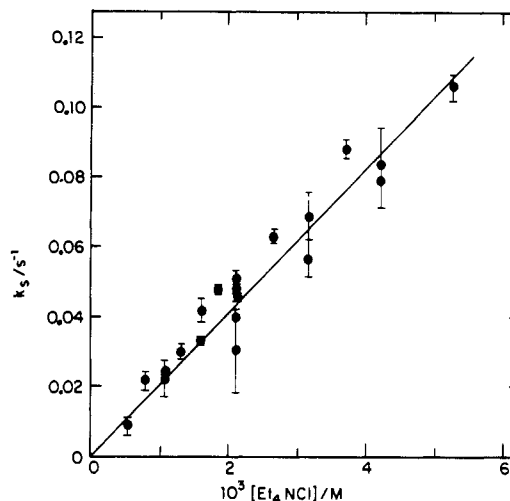


Figure 3. Plot of k_s vs. $[(\text{C}_2\text{H}_5)_4\text{NCl}]$ for the reaction of $\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2$ with $(\text{C}_2\text{H}_5)_4\text{NCl}$ in CH_2Cl_2 at 10.0°C . The slope is $19.4 \pm 1.2 \text{ M}^{-1} \text{ s}^{-1}$.

Table II. Kinetic Data for the Reaction of $\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2$ with Et_4NCl in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 10.0°C ^a

$10^4 \times [\text{Et}_4\text{NCl}]/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$	$10^4 \times [\text{Et}_4\text{NCl}]/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
5.44	0.102	13.6	0.171
6.35	0.105	18.1	0.199
7.26	0.117	18.1	0.202
7.26	0.120	22.7	0.224
9.07	0.140		

^a $[\text{Pt}_2\text{Br}_2(\mu\text{-dppm})_2]_0 = 3.41 \times 10^{-5} \text{ M}$.

analysis is that different expressions apply in each case, and different numerical values for ϵ_B result, depending upon which case is applicable. The equations are as follows:

$$\text{case 1: } \epsilon_B = \epsilon_C + a_s(1 - k_s/k_f) \quad (5)$$

$$\epsilon_B = (\epsilon_A - a_f)(1 - k_s/k_f) + \epsilon_C k_s/k_f \quad (6)$$

$$\text{case 2: } \epsilon_B = \epsilon_C + a_f(1 - k_f/k_s) \quad (7)$$

$$\epsilon_B = (\epsilon_A - a_s)(1 - k_f/k_s) + \epsilon_C k_f/k_s \quad (8)$$

Our attempt to decide between the two cases is based on the values of ϵ_B obtained in each, as to both their consistency and their reasonableness. The values of ϵ_B calculated from the experimental data for each presumed case are given in Table I. The data for case 1 are preferable for two reasons. First, the value of ϵ_B in case 1 is constant for the 16 experiments at 300 nm, $\epsilon_B = 1.58 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ($\pm 8\%$ standard deviation), whereas large scatter and negative values are obtained for ϵ_B when case 2 is assumed. Second, the value of ϵ_B at 300 nm in case 1 lies nearly midway between ϵ_A ($2.62 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and ϵ_C ($1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), as one would expect for a mixed-halide complex, especially one with an NMR spectrum (Figure 1) that fails to signal any special features.

Kinetics in 1,2-Dichloroethane. In this solvent the kinetic data followed a single-step equation and fit to a pseudo-first-order rate law. The observed rate constants are listed in Table II. The variation of k_{obsd} with $[\text{Et}_4\text{NCl}]$ followed an equation of the form

$$k_{\text{obsd}} = \frac{kK[\text{Et}_4\text{NCl}]}{1 + K[\text{Et}_4\text{NCl}]} \quad (9)$$

as illustrated in Figure 4. A nonlinear least-squares analysis gave the values $k = 0.37 \pm 0.02 \text{ s}^{-1}$ and $K = (6.6 \pm 0.5) \times 10^2 \text{ M}^{-1}$ at 10.0°C .

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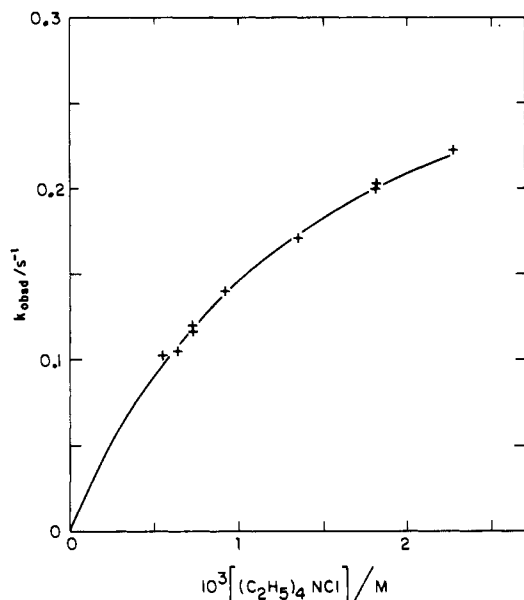
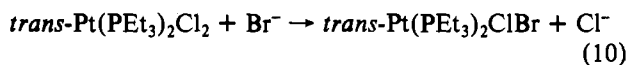


Figure 4. Plot of k_{obsd} vs. $[(C_2H_5)_4NCl]$ for the reaction of $Pt_2Br_2-(\mu-dppm)_2$ with $(C_2H_5)_4NCl$ in $ClCH_2CH_2Cl$ at $10.0^\circ C$. The solid line represents the nonlinear least-squares fit to eq 9.

Interpretation and Discussion

These Pt(I) (d^9) complexes have 16-electron square-planar structures, because they possess a Pt–Pt bond.¹¹ That the rate of substitution at Pt(I) is much greater than at Pt(II) is not surprising. A perfectly analogous comparison of the extent of the rate acceleration for Pt(I) as compared to that for Pt(II) is not feasible, however, although a reasonable assessment can be made by comparing these rate constants with those for *trans*-bis(phosphine) complexes^{12–14} (eq 10). The Pt(II)



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substitution rate constants are much lower; for example, $k = 4.7 \times 10^{-4} M^{-1} s^{-1}$ at $25^\circ C$ in methanol,¹⁴ which corresponds to a Pt(I) acceleration by $>10^5$.

In view of the molecular structure of the dinuclear complexes,^{3–5,11} it seems quite reasonable to view them in an alternative manner. The platinum atoms have square-planar coordination and 16-electron configurations, and in that respect these complexes are analogous to Pt(II) complexes. In this view, the rate enhancement may be said to arise from a profound trans effect of the metal–metal bond. This promotes associative attack at the metal center and thereby greatly increases the rate of ligand substitution.

The assignment of $k_1 > k_2$ was made on the basis of which model gave the more realistic value of ϵ_B . We particularly want to call attention to the method used since it may be of general applicability.

The answer obtained gave a rate constant ratio of $k_1/k_2 = 4.8$. This, too, is in the direction expected on statistical grounds, since there is twice the probability of bromide substitution in the parent dibromo complex than in the intermediate bromo-chloro complex.

The data in 1,2-dichloroethane are strikingly different, yet they are quite limited. More likely than not, however, the first-order kinetic pattern is simply a fortuitous happening (i.e., $k_1 \sim 2k_2$),¹⁵ and the denominator term may simply result from an outer-sphere complexation equilibrium. Further work is required before a reasonable interpretation can be offered.

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Registry No. 1, 61250-66-6; Br₂, 7726-95-6; Cl₂, 7782-50-5.

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 (15) Cases in which a sequence of two (pseudo-) first-order reactions appear to follow a monophasic kinetic equation rather than a biphasic one, known as "statistical" kinetics, and the conditions that need to be satisfied have been cited in the literature: (a) Buckingham, D. A.; Francis, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630. (b) Pohl, M. C.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 235. (c) Armstrong, F. A.; Henderson, R. A.; Sykes, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 6545. (d) Marty, W.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 1246.