The hypsochromic shifts reflect the same trends as found in B–X bond dissociation energies.[16] The conclusion that may be drawn is that the extent of the shifts may be proportional to the thermodynamic stability of the compounds investigated.

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Kinetics and Equilibria in Substitution of Nitro by Iodide and Thiourea in Nitrodiethylenetriamineplatinum(II) Nitrate

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In displacement at platinum(II), there is little direct evidence for the associative mechanism[2–4] which seems most reasonable and is supported by considerable data.[4] We have therefore investigated the kinetics of displacement in a complex in which the leaving group is difficult to displace, since this is a likely case in which kinetic evidence for association[2] might be found. The rates of reaction of nitrodiethylenetriamineplatinum(II) cation (**1**) with two displacing agents have been measured.[5] Although kinetic evidence for association has not been found, the results are of concern in interpretation of published kinetic data and in the design of future kinetic experiments.

Results

We studied the reactions (eq 1 and 2)[6] of **1** with I^- (eq 1) and thiourea (eq 2). With iodide present in excess, apparent first-order rate constants were obtained for reaction 1 in the usual way.[7] Although k_1(apparent) was linear in $[I^-]$ at high $[I^-]$, k_1(apparent) was higher than predicted by linear dependence on $[I^-]$ at low $[I^-]$ (Table I). The reactions were followed spectrophotometrically by product absorption at 310 mμ. Examination of the A_∞ values (Table I) for 0.02 and 0.04 M I^- indicated an equilibrium for reaction 1 and incomplete formation of **2**. This explains the nonlinear dependence of k_1(apparent) at low $[I^-]$.

$$\underset{\mathbf{1}}{\mathrm{Pt(dien)NO_2^+}} + \mathrm{I^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{2}}{\mathrm{Pt(dien)I^+}} + \mathrm{NO_2^-} \qquad (1)$$

$$\mathbf{1} + \mathrm{tu} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{3}}{\mathrm{Pt(dien)tu^{2+}}} + \mathrm{NO_2^-} \qquad (2)$$

TABLE I
RATE AND EQUILIBRIUM CONSTANTS FOR REACTION OF 1 WITH I^- (EQ 1) AT 74.4°[a]

$[I^-]$, M	10^4k(apparent),[b] sec^{-1}	A_∞[c]	10^4k_1,[d] sec^{-1}	k_{-1},[d] M^{-1} sec^{-1}
0.02	1.59	0.514	0.59	0.059
0.04	2.07	0.570	1.25	0.051
0.06	2.75	0.601	1.77	0.047
0.08	3.57	0.615	2.47	0.053
0.10	4.38	0.618	3.23	0.065

[a] Aqueous solution; [**1**] = 0.00174 M; ionic strength maintained at 0.10 M by addition of $NaNO_3$. [b] k(apparent) = the apparent first-order rate constant obtained by treatment of the data by the rate equation for a nonreversible, first-order reaction. [c] Optical density at 310 mμ at the end of the reaction. [d] From treatment of eq 1 as reversible.

Therefore, reaction 1 was treated as a reversible reaction[8] with k_1 first order and k_{-1} second order. This gave the values for k_1 and k_{-1} in Table I. The resulting k_1 values are now linear in $[I^-]$ and give a nearly zero intercept using the rate law (3) usually found for displacements at platinum(II).[4] Therefore we cannot evaluate k_S, but $k_{I^-} = 3.25 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$.

$$k = k_S + k_{I^-}[I^-] \qquad (3)$$

When thiourea is used as a displacing agent (eq 2), spectrophotometric data indicate that at equilibrium products predominate and k_{-2} can be neglected. When eq 3 is applied to the data (Table II), a straight line is obtained with $k_S = 1.2 \times 10^{-5}\ \mathrm{sec}^{-1}$ and $k_{tu} = 1.73 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$.[9] The value of k_S is so small that considering the standard deviations there can be considerable uncertainty in the exact value of k_S. The complete reaction in this case is consistent with (1) the greater displacing power of thiourea than of iodide ion noted previously[10] and also here (at the same tempera-

TABLE II
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE THIOUREA SUBSTITUTION OF NITRODIETHYLENETRIAMINEPLATINUM(II) NITRATE IN AQUEOUS SOLUTIONS AT 48.6°[a]

[Thiourea], M	10^4k_2,[b] sec^{-1}	[Thiourea], M	10^4k_2,[b] sec^{-1}
0.02	0.44	0.08	1.56
0.04	0.80	0.09	1.62
0.06	1.05	0.11	1.98
0.07	1.30		

[a] [Complex] = 0.00174 M. [b] Determined by least-squares treatment of first-order rate equation with spectrophotometric data at 320 mμ.

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(1) Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, Conn. 06457.

(2) P. Haake, *Proc. Chem. Soc.*, 278 (1962); there may have been complications due to HONO in this study.[3] Further work is needed.

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(5) For other work on diethylenetriamine complexes, see (a) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Amer. Chem. Soc.*, **82**, 4200 (1960); (b) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962); (c) H. B. Gray, *J. Amer. Chem. Soc.*, **84**, 1548 (1962); (d) U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

(6) Abbreviations: dien, diethylenetriamine; tu, thiourea, $(H_2N)_2CS$.

(7) (a) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Amer. Chem. Soc.*, **82**, 4200 (1960); (b) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962); (c) H. B. Gray, *J. Amer. Chem. Soc.*, **84**, 1548 (1962).

(8) E. A. Moelwyn-Hughes, "Physical Chemistry," Cambridge University Press, London, 1947, p 636.

(9) This is in reasonable agreement with an extrapolated value based on an energy of activation reported for this reaction.[5d]

(10) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Amer. Chem. Soc.*, **87**, 241 (1965).

ture k_{tu} will be considerably greater than k_I) and (2) the rapid displacement of I^- compared to other ligands which would be expected to be similar to thiourea in ease of displacement.[4]

Discussion

The data obtained in this study appear to follow eq 3 even though the leaving group is difficult to displace and the displacing agents might be expected to associate well with the substrate. This suggests that if the associative mechanism is valid for platinum(II), it is peculiarly difficult to get enough association to observe kinetically.[2,4] This important question needs further work.

Our observation that reaction 1 failed to go to completion is important, along with ionic strength effects,[11] in interpretation of previous data on this and related complexes. Many studies have been done with poor displacing agents. It seems possible that an equilibrium situation may have been present, and some of the reported rate constants may be apparent rather than true rate constants for the reactions which were studied.

Experimental Section

Materials.—Nitrodiethylenetriamineplatinum(II) nitrate was prepared by a known method.[7a] *Anal.* Calcd for $[Pt(dien)NO_2]NO_3$: C, 11.8; H, 3.2; Pt, 48.0. Found: C, 11.9; H, 3.2; Pt, 48.1.

Iododiethylenetriamineplatinum(II) iodide was prepared by Mann's method.[12] *Anal.* Calcd for [Pt(dien)I]I: ionic I, 22.9; coordinated I, 22.9; Pt, 35.3. Found: ionic I, 22.9; coordinated I, 22.7; Pt, 35.5.

Kinetics.—Thermostats were constant to ±0.1°. The reactions were followed by spectrophotometry on reaction samples which had been placed in sealed tubes. The rates of iodide substitutions in cationic platinum(II) complexes are known to be sensitive to ionic strengths,[11] so ionic strength was kept constant at 0.1 *M* by adding appropriate amounts of sodium nitrate. The iodide reactions were followed at 310 mμ, where there is a maximum difference between the extinction coefficients of reactant and product.

The treatment of reaction 1 as reversible involved eq 4–6[8] where a is the initial concentration of $Pt(dien)NO_2^+$ in the reaction mixture whose absorbances at times 0, t, and equilibrium are A_0, A_t, and A_{eq}, respectively. A_p represents the absorbance of a solution of $Pt(dien)I^+$ in the same solvent, having the same concentration as the reaction mixture. In all cases, good straight lines were obtained in plots of ln X against t.

$$\frac{2mk_1t}{K} = \ln\left[\frac{(A_p - A_0) + (A_t - A_0)\frac{m}{K} - \frac{1}{2}}{(A_p - A_0) - (A_t - A_0)\frac{m}{K} + \frac{1}{2}}\right] = \ln X \tag{4}$$

$$m = \left(aK + \frac{1}{4}K^2\right)^{1/2} \tag{5}$$

$$K = \frac{a(A_{eq} - A_0)^2}{(A_p - A_0)(A_p - A_{eq})} = \frac{k_1}{k_{-1}} \tag{6}$$

The reaction with thiourea was followed spectrophotometrically at 320 mμ. Since one of the reactants is now uncharged, the reaction is not sensitive to ionic strength changes. Furthermore, the reaction was complicated by a slower secondary process (involving probable replacements at one or more coordination positions originally occupied by the tridentate ligand) so that A_{eq} could not be observed, and the Guggenheim method[13] was used.

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Tricarbonyl(dimethyldivinylsilane)iron

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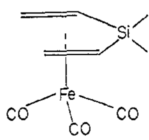
Although iron carbonyls have long been known to react with conjugated dienes[1] and to isomerize 1,4-dienes to 1,3-dienes,[2] there has been very little work on the reactions of the divinyl derivatives of the group IV metals with the metal carbonyls. Sterically, the divinyl derivatives of the group IV metals are similar to 1,4-dienes. However, electronically, they are considerably different due to dπ–pπ bonding effects,[3] and, because of these effects, the double bonds should be somewhat electron deficient when compared to normal double bonds.

Manuel and Stone[4] have reported that $(CH_3)_2Si(CH{=}CH_2)_2$ reacts with both $Mo(CO)_6$ and $W(CO)_6$ to give the compounds $(CH_3)_2Si(CH{=}CH_2)_2 \cdot Mo(CO)_4$ and $(CH_3)_2Si(CH{=}CH_2)_2 \cdot W(CO)_4$, respectively. On the other hand $(CH_3)_2Sn(CH{=}CH_2)_2$ was observed to react with $Fe(CO)_5$ to give $[(CH_3)_2SnFe(CO)_4]_2$. King and Stone suggested that the latter reaction might proceed through an unstable intermediate π complex between the vinylstannane and iron carbonyl.[5] However, to our knowledge, this intermediate complex has not been isolated, and no work has been reported on the analogous reaction between dimethyldivinylsilane and the iron carbonyls. We now wish to report that dimethyldivinylsilane reacts with triiron dodecacarbonyl to form tricarbonyl(dimethyldivinylsilane)iron. The proposed structure for this compound is shown below.



Experimental Section

Materials.—Dimethyldivinylsilane was prepared as described in the literature.[6] *Anal.* Calcd for $C_6H_{12}Si$: C, 64.29; H,

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