TABLE II

REACTION BETWEEN $\mathrm{Fe(phen)_3^{2+}}$ AND CHLORINE AT 25° AND IONIC STRENGTHS LOWER THAN 1.0 *M*[a]

I, *M*	A_0[b]	[Total oxidant], m*M*	[$\mathrm{Cl_2}$ species], m*M*	*k*,[c] M^{-1} sec^{-1}
0.1	1.164	8.51	8.09	1.26
0.1	0.357	8.51	8.09	1.19
0.1	1.135	9.54	9.06	1.20
0.1	1.190	3.29	3.13	1.19
0.1	0.774	7.72	7.33	1.23
0.1	1.217	1.90	1.80	1.16
0.1[d]	1.250	7.39	5.75	1.10
0.1[d]	1.250	7.08	5.43	1.17
0.01[e]	1.237	9.12	3.76	1.06
0.01[e]	0.615	9.10	3.74	1.12

[a] Ionic strength maintained at 0.1 *M* with HCl. [b] Calculated initial absorbance. [c] Rate constant with $\mathrm{Cl_2}$ species concentration used in the rate law. [d] Hydrogen ion concentration was 0.01 *M* with HCl and the ionic strength was maintained with HCl and NaCl. [e] Hydrogen ion concentration was maintained at 0.01 *M* with HCl.

not reveal conclusively whether or not $\mathrm{Cl_3^-}$ is a significant reactant. The data reported in Tables I and II suggest that the $\mathrm{Fe(phen)_3^{2+}}$–$\mathrm{Cl_2}$ reaction rate is independent of both hydrogen ion and chloride ion concentration in the 0.01–1.0 *M* range. Under the conditions of these experiments and those of Crabtree and Schaefer,[11] the concentration of $\mathrm{Cl_3^-}$ changes from 2 to 16% of the total oxidant concentration while the concentration of $\mathrm{Cl_2}$ changes from 98 to 84% of the total oxidant by varying the concentration of either hydrogen or chloride ions. Thus more significant changes in concentrations of $\mathrm{Cl_3^-}$ occur when the chloride ion is varied over a wider range than that reported in this and other[11] works.

The species HClO was found to be less reactive than $\mathrm{Cl_2}$. In experiments where excess HClO was added to $\mathrm{Fe(phen)_3^{2+}}$ in dilute sulfuric acid (5×10^{-5} to 5×10^{-2} *M*) and at an ionic strength of 1.0 *M*, the decrease in absorbance due to $\mathrm{Fe(phen)_3^{2+}}$ at 5100 Å was found to be slower in the first few minutes than in the latter portion of reaction. Analyses of the absorbance–time data suggest that in the first portion of reaction where only about 2% of $\mathrm{Fe(phen)_3^{2+}}$ disappears, HClO reacts with $\mathrm{Fe(phen)_3^{2+}}$ to produce chloride ion which reacts rapidly with the excess HClO to form $\mathrm{Cl_2}$ in accordance with eq 5. Beyond the initially slow portion of reaction, deviation from linearity in absorbance–time plots occurs and the rate of disappearance of $\mathrm{Fe(phen)_3^{2+}}$ increases with time. The $\mathrm{Fe(phen)_3^{2+}}$–HClO reaction appears to be autocatalytic in that the $\mathrm{Cl_2}$ formed reacts faster with $\mathrm{Fe(phen)_3^{2+}}$ than does HClO. The kinetic details of the HClO–$\mathrm{Fe(phen)_3^{2+}}$ reaction will be reported elsewhere.

In conclusion, it should be pointed out that $\mathrm{Cl_2}$ reacts much faster than HClO with $\mathrm{Fe(phen)_3^{2+}}$ as in the case when $\mathrm{Fe(CN)_6^{4-}}$ is the reducing agent,[12] but HClO reacts more rapidly than $\mathrm{Cl_2}$ with $\mathrm{Fe^{2+}}$.[13] Furthermore, $\mathrm{Cl_2}$ reacts with $\mathrm{Fe(phen)_3^{2+}}$ *via* an outer-sphere path and involves a one-electron step. Formation of $\mathrm{FeCl^{2+}}$ as an initial product in the $\mathrm{Fe^{2+}}$–$\mathrm{Cl_2}$ and $\mathrm{Fe^{2+}}$–HClO reactions[13] strongly suggests that an inner-sphere path is involved. The mode of reaction seems to change significantly as iron(II) is complexed with phenanthroline or cyanide ion but, unfortunately, specific comparison of rates can be made only when all of the reactions proceed *via* the same path.

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Substitution Reactions of the Bromo(1,1,7,7-tetraethyldiethylenetriamine)palladium(II) Cation in Nonaqueous Solvents

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It was found that substitution reactions (eq 1) in

$$\mathrm{Pd(Et_4dien)^1Br^+ + Y^{n-} \longrightarrow Pd(Et_4dien)Y^{(2-n)+} + Br^-} \quad (1)$$

water are first order in complex but zero order in Y, even for good ligands like $\mathrm{SO_3^{2-}}$, $\mathrm{SCN^-}$, and $\mathrm{I^-}$.[2,3] The mechanism was explained by a slow solvolysis step (eq 2) (S = $\mathrm{H_2O}$ in this case), followed by a rapid anation step (eq 3). The direct reagent path (eq 4), a parallel

$$\mathrm{Pd(Et_4dien)Br^+ + S \xrightarrow[k_1]{slow} Pd(Et_4dien)S^{2+} + Br^-} \quad (2)$$

$$\mathrm{Pd(Et_4dien)S^{2+} + Y^{n-} \xrightarrow{fast} Pd(Et_4dien)Y^{(2-n)+} + S} \quad (3)$$

$$\mathrm{Pd(Et_4dien)Br^+ + Y^{n-} \xrightarrow{k_2'} Pd(Et_4dien)Y^{(2-n)+} + Br^-} \quad (4)$$

reaction so common in square-planar substitution kinetics in which a dependence of rate on nucleophile Y is found,[4] was observed[2,3] only for the ligands $\mathrm{OH^-}$ and $\mathrm{S_2O_3^{2-}}$. Hydroxide ion can remove the proton from the central amine nitrogen of $\mathrm{Et_4dien}$, creating the reactive conjugate-base species (SN1CB mechanism), and thiosulfate ion has a very large nucleophilic reactivity constant (n_{Pt})[5] toward a "soft" ion like Pd(II),[6] enabling it to form the necessary five-coordinate species even in this sterically hindered system.

In the present study, kinetics were carried out in $\mathrm{CH_3OH}$, $\mathrm{(CH_3)_2SO}$, and $\mathrm{CH_3CN}$ in an attempt to de-

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(1) $\mathrm{Et_4dien = HN[C_2H_4N(C_2H_5)_2]_2}$.

(2) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2944 (1966).

(3) J. B. Goddard and F. Basolo, *Inorg. Chem.*, **7**, 936 (1968).

(4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 377.

(5) R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, **90**, 319 (1968).

(6) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

termine the role of steric hindrance in depressing the direct reagent (k_2') path of substitution in these nonaqueous solvents.

Experimental Section

Materials.—The preparation of the palladium complexes used here was reported earlier.[2,3] Methanol (Baker Reagent grade) was dried by refluxing with magnesium metal and was then distilled. Acetonitrile (Fisher Reagent grade) was distilled over P_2O_5 and then over K_2CO_3. Dimethyl sulfoxide (Matheson Coleman and Bell anhydrous) was used without further drying (maximum H_2O, 0.05%).

Kinetics.—Kinetics were followed on a Beckman DU spectrophotometer, equipped with a water-jacketed cell compartment, at a uv wavelength where the spectral change was large. Reactions were run with sufficient excess ligand to ensure pseudo-first-order conditions.

The bromide salt of the complex was used for the kinetics, and sodium salts of the ligand were used, along with $NaClO_4$ for ionic strength control, where solubility permitted. In $(CH_3)_2SO$, LiCl and $LiClO_4$ were used for $[Cl^-] > 0.005$ *M;* in CH_3CN, $(C_2H_5)_4NCl$ and $(C_2H_5)_4NClO_4$ were used in the chloride rate study.

Results

The observed rate constants for reaction 5 are given

$$Pd(Et_4dien)Br^+ + Y^- \longrightarrow Pd(Et_4dien)Y^+ + Br^- \quad (5)$$

in Table I. In the reaction of iodide with $[Pd(Et_4dien)Br]Br$ in CH_3CN and $(CH_3)_2SO$, the observed rate constants *decreased* with increasing $[I^-]$. This is consistent with a reaction that approaches an equilibrium rather than goes to completion. These rate constants were obtained from the slope of a graph of log $(A_e - A_t)$ *vs. t*, where A_e is the observed infinity (equilibrium) absorbance and A_t is the absorbance at time t. All of these plots were linear. The "true" first-order rate constants were obtained from the plot of log $(A_\infty - A_t)$ *vs. t*, where A_∞ is the infinity absorbance found for the 0.100 M I^- reaction (which goes to completion). These plots are linear only for the initial part of the reaction.

Where pertinent, approximate values of the equilibrium constants for reaction 5, defined by eq 6, were obtained from the kinetic data. Concentrations of the complexes were based on the observed spectral change at equilibrium at the wavelength at which the kinetics were carried out and on the expected spectral change for reaction 5 going 100% as written. Data are given in Table II. The most accurate values of K_{eq} will be obtained when the equilibrium of reaction 5 lies *ca.* 50% to the right.

$$K_{eq} = [Pd(Et_4dien)Y^+][Br^-]/[Pd(Et_4dien)Br^+][Y^-] \quad (6)$$

TABLE I

OBSERVED RATE CONSTANTS FOR REACTION 5, $\mu = 0.100$

$[Y^-]$, *M*	10^5k_{obsd}, sec^{-1}
CH_3OH, 3.2×10^{-4} *M* $Pd(Et_4dien)Br^+$, 47°	
0.010 NO_2^- [a]	1.47
0.020 NO_2^- [a]	1.36
0.002 NO_2^-	15.8
0.005 NO_2^-	15.9
0.010 NO_2^-	16.2, 16.1,[b] 14.2[c]
0.020 NO_2^-	15.8
0.100 NO_2^-	20.0
0.001 I^-	13.2
0.005 I^-	14.2
0.020 I^-	14.8
0.100 I^-	14.7
$(CH_3)_2SO$, 1.7×10^{-4} *M* $Pd(Et_4dien)Br^+$, 25°	
0.001 Cl^-	4.91
0.005 Cl^-	4.82
0.010 Cl^-	4.74
0.050 Cl^-	4.54
0.100 Cl^-	4.87
$(CH_3)_2SO$, 1.4×10^{-4} *M* $Pd(Et_4dien)Br^+$, 25°	
0.002 I^-	7.55 (2.73)[d]
0.010 I^-	6.38 (5.22)[d]
0.020 I^-	5.93 (5.07)[d]
0.050 I^-	5.53 (5.63)[d]
0.100 I^-	5.28 (5.28)[d]
$(CH_3)_2SO$, 1.6×10^{-4} *M* $Pd(Et_4dien)Br^+$, 25°	
0.001 NO_2^-	4.93
0.002 NO_2^-	5.41, 5.89[e]
0.005 NO_2^-	6.47
0.010 NO_2^-	8.13, 11.1[f]
0.050 NO_2^-	22.5, 25.0[g]
0.100 NO_2^-	37.7
$(CH_3)_2SO$, 1.5×10^{-4} *M* $[Pd(Et_4dien)I]I$,[h] 25°	
0.001 Br^-	8.28
0.002 Br^-	8.32
0.010 Br^-	8.43
CH_3CN, 1.6×10^{-4} *M* $Pd(Et_4dien)Br^+$, 47°	
0.001 Cl^-	4.70
0.005 Cl^-	5.28
0.010 Cl^-	7.64
0.050 Cl^-	11.47
0.100 Cl^-	24.1, 24.2,[i] 24.0[j]
0.001 I^-	9.28 (4.24)[d]
0.005 I^-	6.63 (6.16)[d]
0.010 I^-	6.05 (5.44)[d]
0.050 I^-	6.60 (6.28)[d]
0.100 I^-	7.62 (7.62)[d]

[a] At 25°. [b] 0.002 *M* $HClO_4$ present. [c] 0.20 *M* H_2O present. [d] Recalculated k_{obsd} using the expected A_∞ for 100% reaction. [e] 0.0005 *M* *p*-toluenesulfonic acid (TSA) present. [f] 0.001 *M* TSA present. [g] 0.002 *M* TSA present. [h] The reaction of the iodo complex with bromide ion was run to verify the reversibility of the reaction of the bromo complex with iodide ion. [i] 0.033 *M* H_2O present. [j] 0.058 *M* H_2O present.

TABLE II

APPROXIMATE VALUES OF EQUILIBRIUM CONSTANTS FOR EQ 6 AT $\mu = 0.100$

$[Y^-]$, *M*	Obsd absorbance change	% $Pd(Et_4dien)Y^+$ at equilibrium	K_{eq}
CH_3OH, 47°, λ 300 mμ, Initial $[[Pd(Et_4dien)Br]Br] = 3.22 \times 10^{-4}$ *M*			
0.001 NO_2^-	0.389	56.6	0.80
0.002 NO_2^-	0.485	72.4	0.82
0.005 NO_2^-	0.568	84.8	0.70
0.100 NO_2^-	0.670	100[a]	. . .
$(CH_3)_2SO$, 25°, λ 300 mμ, Initial $[[Pd(Et_4dien)Br]Br] = 1.41 \times 10^{-4}$ *M*			
0.002 I^-	0.272	37.3	0.059
0.005 I^-	0.430	59.0	0.065
0.010 I^-	0.544	74.6	0.073
0.020 I^-	0.630	86.4	0.084
0.100 I^-	0.729	100[a]	. . .
CH_3CN, 47°, λ 300 mμ, Initial $[[Pd(Et_4dien)Br]Br] = 1.60 \times 10^{-4}$ *M*			
0.001 I^-	0.338	51.7	0.28
0.002 I^-	0.435	66.5	0.28
0.100 I^-	0.654	100[a]	. . .

[a] By definition.

Discussion

The rate constants for the ligand-independent path (reactions 2 and 3) and ligand-dependent path (reaction 4) are summarized in Table III, together with the previous data from the aqueous work.

As can be seen from Table III, k_1 decreases in the order $H_2O > (CH_3)_2SO > CH_3OH > CH_3CN$. This order depends mainly on two factors: the ability of the solvent to coordinate with Pd(II)[7] and to solvate the leaving group.[7,8] The similarity of the k_1 values for different nucleophiles reacting in a given solvent indicates the same common solvento intermediate as had been found previously for the aqueous reactions.[2,3]

Normally for Pt(II), k_1 is greater for DMSO than for water; *e.g.*, for $^{36}Cl^-$ substitution in *trans*-$Pt(py)_2Cl_2$,

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[7] Reference 4, p 390.

[8] R. S. Drago, V. A. Mode, and J. G. Kay, *Inorg. Chem.*, **5**, 2050 (1966).

TABLE III

RATE AND EQUILIBRIUM CONSTANTS FOR REACTION 5 IN VARIOUS SOLVENTS AT $\mu = 0.100$

Y	Temp, °C	10^5k_1,[a] sec^{-1}	$10^3k_2'$,[b] $M^{-1}\ \text{sec}^{-1}$	K_{eq}[c]
Solvent H_2O[d]				
I^-, N_3^-, NO_2^-, SCN^-, SO_3^{2-}	25	130–150	0	>1
$S_2O_3^{2-}$	25	150	5930	>>1
OH^-	25	130	55	. . .
Solvent CH_3OH				
NO_2^-	25	1.4	0	. . .
NO_2^-	47	17.2	0	0.8
I^-	47	14.1	0	. . .
Solvent $(CH_3)_2SO$				
I^-	25	5.4	0	0.06
Cl^-	25	4.8	0	>1
NO_2^-	25	4.5	3.6	. . .
Br^-[e]	25	8.3	0	17[f]
Solvent CH_3CN				
I^-	47	4.9	0.27	0.3
Cl^-	47	4.5	1.97	>1

[a] As defined in reaction 2. [b] As defined in reaction 4. [c] As defined by eq 6. [d] Data from ref 2 and 3. [e] Reaction of iodo complex with bromide ion. [f] Reciprocal of K_{eq} for reaction of bromo complex with iodide ion.

$k_1(\text{DMSO}) = 108k_1(H_2O)$.[9] This behavior was attributed to the relative stability of the Pt–S bond of the DMSO solvento complex over that of the Pt–O bond in the corresponding aquo complex. Although Pd(II) is not as selective as Pt(II), the same order of stability is expected for these soft Lewis acids. The fact that $k_1(H_2O) = 25k_1(\text{DMSO})$ for $\text{Pd(Et}_4\text{dien)Br}^+$ indicates the effect of steric hindrance in this system; the bulkier DMSO has more difficulty than the smaller H_2O in approaching the palladium.

It is also evident that the reagent-dependent path (eq 4) exists for certain ligands in $(CH_3)_2SO$ and CH_3CN, where it is experimentally nonexistent in CH_3OH and H_2O. Both chloride and iodide ions show this dependence in CH_3CN (although the evidence for iodide ion is marginal) but not in $(CH_3)_2SO$. This may indicate a solvation by CH_3CN of the ethyl groups of Et_4dien, permitting them to spread out from the palladium, thereby allowing easier entrance of the nucleophile. This solvation of the ethyl groups is less important in $(CH_3)_2SO$, since only nitrite ion shows this rate dependence, and a nitrite dependence in CH_3OH or H_2O was not observed, indicating a solvation effect of much less significance. Thus the better solvating solvents (for the ethyl groups) allow a more "square-planar" behavior for this sterically hindered system in that the two-term law (eq 7) is now followed to a higher degree.

$$\text{rate} = \{k_1 + k_2'[\text{Y}]\}[\text{Pd(Et}_4\text{dien)Br}^+] \qquad (7)$$

These results may also be attributed to the solvation of the reagent ions. Thus in the protonic solvents the solvation energy of the reagent anions is large, making their reactivity small compared with the aprotic systems where the energy of solvation of the reagent anions is small. Extensive studies have been made of solvent effect on substitution reactions of platinum(II) complexes.[10] The results show that the effect of solvent on reagent reactivity is not large and that the order of reactivity is the same in protonic and in aprotic solvents. In spite of this the solvation of reagent anions may be more significant for reactions of Pd(II) which is less discriminating than is Pt(II). Note that changes in solvent have not been found to cause a reversal in the order of nucleophilic strength toward Pt(II) substrates, but for $\text{Pd(Et}_4\text{dien)Br}^+$ the order of reactivity is $Cl^- > I^-$ for the solvent CH_3CN (Table III).

Furthermore it is seen from the equilibrium constants that the formation of bromo complex over iodo complex is actually favored in CH_3CN and $(CH_3)_2SO$. For water, Hewkin and Poë[11] have estimated that $K_{eq} \cong 10$ for reaction 8, but in CH_3CN and $(CH_3)_2SO$, $K_{eq} < 1$

$$\text{Pd(Et}_4\text{dien)Br}^+ + I^- \rightleftharpoons \text{Pd(Et}_4\text{dien)I}^+ + Br^- \qquad (8)$$

(Table III). This reversal in stability may be explained by the ability of the "soft" solvents to solvate the "soft" iodide ion to a greater degree than the somewhat harder bromide ion;[6] on this basis alone, the bromide ion would tend to remain bound, whereas the iodide ion would prefer to remain free in its solvated state.

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Some Reactions of Dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin with Thiols

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Organotin halides are smoothly converted into the corresponding thio derivatives on treatment with thiols in the presence of a base.[1,2] We have found that dichlorobis(dicarbonyl-π-cyclopentadienyl)tin, $[\pi\text{-}C_5H_5Fe(CO)_2]SnCl_2$ (I), reacts under similar conditions with thiophenol and with dithiols by replacement of the Sn–Cl bonds by Sn–S, while the iron–tin bonds remain intact.

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