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Ruthenium(II) Tetraammines, a Useful Model to Compare *trans*-Effect and *trans*-Influence of Phosphanes

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Abstract

The substitution reaction

$$trans\text{-}[Ru(NH_3)_4P(III)H_2O]^{2+} + pz \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4P(III)pz]^{2+} + H_2O$$

where P(III) = PEt_3, PBu_3, PPh_3, $P(OBu)_3$ and $P(OPh)_3$ has been studied at 25.0 °C, $\mu = 0.10$ $NaCF_3COO$, $C_{H^+} = 1.0 \times 10^{-3}$ M. Assuming the second order specific rate k_1 for the substitution of the water molecule on the coordination sphere for pz as indicative of a relative order of the *trans*-effect of P(III), the following increasing *trans*-effect order can be written: $P(OPh)_3 < PPh_3 < P(OEt)_3 < P(OBu)_3 < PBu_3 < PEt_3$. The weakening of the Ru(II)–pz bond expressed as $1/K_{eq}$ permits us to write the following order of increasing *trans*-influence: $PEt_3 < PBu_3 < P(OBu)_3 < P(OEt)_3 \sim PPh_3 < P(OPh)_3$. The complex *trans*-$[Ru(NH_3)_4(PEt_3)(P(OEt)_3)](PF_6)_2$ has been isolated and characterized by microanalysis, electronic and voltammetric spectra. The aquation of this complex provides additional support to the generalizations about the influence of π bonding on the *trans*-influence of phosphanes.

Introduction

Despite the relevance of phosphines and phosphites in catalysis, there have been few attempts to compare the *trans*-effect and *trans*-influence of these ligands for a homologous series [1–4]. These studies [4–6] are restricted mainly to the effects of phosphanes on bond lengths, stretching frequencies and coupling constants of ligands on the *trans*-position on the coordination sphere and, in a few cases, to the measurement of displacement equilibria.

Unfortunately the few data available [3–6] refer to systems where the metal center is surrounded by different kinds of ligands, a situation which does not permit any reliable conclusion.

In our laboratory we are studying the chemistry of phosphanes when coordinated to a metal center using rutheniumammines as probes [7–10]. Complexes of the type *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$, where P(III) is a phosphane, are very convenient for these studies. Since the ammonias are innocent ligands [11], such complex ions allow us to study the effects provoked by the systematic substitution of different P(III) ligands on the site *trans* to them in the coordination sphere.

This paper deals with the comparison of the *trans*-effect and *trans*-influence of phosphites and phosphanes. We define the *trans*-effect of P(III) as the second-order specific rate (k_1) of the substitution of water on the coordination sphere of *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ for pz. The *trans*-influence, of P(III), is defined as the weakening of the Ru(II)–pz bond in terms of ΔG_{eq} for the *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$–pz reaction.

Experimental

Equipment

The UV–Vis spectra and slow kinetics measurements were obtained on a VARIAN 634 M or Cary 14 spectrophotometer.

An Aminco-Morrow spectrophotometer was employed for the fast kinetic measurements.

Cyclic voltammograms were obtained using an electrochemical system consisting of Potentiostat/Galvanostat (model-173), Programmer (model-175) and a Recorder (model-RE0074), all obtained from Princeton Applied Research Corporation (PARC). Glassy carbon, platinum wire and SCE electrodes were employed as working, auxiliary and reference electrodes, respectively.

In all the experiments the ionic strength was kept at 0.10 M ($NaCF_3COO$) and the temperature stabilized at (25.0 ± 0.1) °C using a Superohm thermostat. All the manipulations were carried out under argon employing standard techniques [12].

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Chemicals

Doubly distilled water was used throughout. Acetone, ethanol and ether were purified according to the literature [13].

$RuCl_3 \cdot xH_2O$, isonicotinamide (isn), pyrazine (pz), phosphites ($P(OR)_3$) and phosphines (PR_3) ligands were purchased from Aldrich and used without further purification.

From $RuCl_3 \cdot xH_2O$, $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_5(H_2O)](PF_6)_2$, *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](PF_6)_2$, *trans*-$[Ru(NH_3)_4(PEt_3)_2](PF_6)_2$, *trans*-$[Ru(NH_3)_4(P(OBu)_3)_2](PF_6)_2$ and *trans*-$[Ru(NH_3)_4(PPh_3(H_2O)](PF_6)_2$ were prepared as described in the literature [7, 9, 10, 14]. All these complexes were characterized by comparing the UV–Vis and voltammetric spectra with those reported in the literature [7, 9, 10, 14]. The ions *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$, where P(III) = PEt_3, $P(OBu)_3$, PBu_3, PPh_3 and $P(OPh)_3$ were generated in solution by aquation of the corresponding bisphosphite and bisphosphino complexes.

The compounds *trans*-$[Ru(NH_3)_4(P(OPh)_3)_2](PF_6)_2$, *trans*-$[Ru(NH_3)_4(PBu_3)_2](PF_6)_2$ and *trans*-$[Ru(NH_3)_4(P(OEt)_3)(PEt_3)](PF_6)_2$ were prepared as follows.

I. trans-[Ru(NH$_3$)$_4$(P(OPh)$_3$)$_2$](PF$_6$)$_2$

200 mg of $[Ru(NH_3)_5(H_2O)](PF_6)_2$ were dissolved on 15 ml of dry purified acetone, previously degassed for 30–40 min. Using syringe techniques 2.0 ml of $P(OPh)_3$, already degassed, were added to the reaction flask. After 30–40 min at room temperature (23–27 °C), the solvent and the excess of phosphite were eliminated by rotoevaporation. A white solid was obtained. It was dissolved in the minimum amount of acetone and reprecipitated by adding 5–10 ml of cold and degassed dry ether, then filtered and washed with ether, and finally dried and stored under vacuum while protected from light. The yield was better than 80%. No significant decomposition was found to occur over a one month period, as judged by the CV and UV–Vis spectra.

II. trans-[Ru(NH$_3$)$_4$(PBu$_3$)$_2$](PF$_6$)$_2$

200 mg of $[Ru(NH_3)_4(H_2O)](PF_6)_2$ were dissolved in 15 ml of dry purified acetone, previously degassed in an argon atmosphere of 30–40 min. Using the syringe techniques 2.0 ml of PBu_3, already degassed, were added to the reaction flask. After 30–40 min at room temperature (23–27 °C), the solvent and the excess of phosphine were eliminated by rotoevaporation. A white solid was obtained. It was dissolved in the minimum amount of absolute ethanol and reprecipitated by adding 200–250 ml of cold and degassed dry ether. The solution was allowed to cool in the refrigerator for 16 h to improve the yield, which was better than 60%. The precipitate was filtered, washed with ether, and then dried and stored in a vacuum desiccator protected from light. As judged from the CV and UV–Vis spectra, no decomposition of the diphosphine compound was observed within a one week period.

III. trans-[Ru(NH$_3$)$_4$(P(OEt)$_3$)(PEt$_3$)](PF$_6$)$_2$

100–130 mg of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)](PF_6)_2$ were dissolved on 15–20 ml of dry purified acetone, previously degassed in an argon atmosphere for 30–40 min. Using the syringe techniques 1.5 ml of PEt_3 were added to the Ru(II) solution. After 20 min the solvent and excess of phosphine were rotoevaporated. The yellow residue was dissolved in the minimum volume of degassed acetone and reprecipitated adding cold and degassed dry ether. The pale yellow solid was filtered in a glovebag washed with ether, dried and stored under vacuum. Yield: better than 70%. According to the CV and UV–Vis spectra the compound is stable for more than one month when stored under vacuum and in the absence of light.

The analyses (Table I) were performed by the staff of the Microanalytical Laboratory at Stanford University and of the Instituto de Quimica of Universidade de São Paulo.

Methods

The aquation of the complex ion *trans*-$[Ru(NH_3)_4(P(OEt)_3)(PEt)_3]^{2+}$ was studied in the presence of large excess of isonicotinamide, isn. A weighed amount (5–6 mg) of solid *trans*-$[Ru(NH_3)_4(P(OEt)_3)(PEt_3)](PF_6)_2$ was dissolved in 100 ml of 0.6 M isn aqueous solution previously degassed (at the desired hydrogen ion concentration, temperature and ionic strength). About 30 ml of this solution was transferred through Teflon tubing to a 10 cm

TABLE I. Analytical Data and Formal Potentials for the Ruthenium–Phosphane Complexes

Complex	C(%)		H(%)		N(%)		$E^{\circ\prime}$ (V)[a, b]
	Calc.	Found	Calc.	Found	Calc.	Found	
trans-$[Ru(NH_3)_4(P(OPh)_3)_2](PF_6)_2$	40.01	37.76	3.89	3.87	5.19	5.34	[c]
trans-$[Ru(NH_3)_4(PBu_3)_2](PF_6)_2$	33.37	33.28	7.64	7.68	6.48	6.84	0.47
trans-$[Ru(NH_3)_4(P(OEt)_3)(PEt_3)](PF_6)_2$	19.38	20.26	5.65	4.98	7.53	7.45	0.56

[a] μ = 0.10 ($NaCF_3COO/CF_3COOH$); (25.0 ± 0.1) °C; $C_{H^+} = 1.0 \times 10^{-3}$ M. [b] *vs.* SCE; uncertainty of ±0.01 V. [c] This complex undergoes fast aquation.

path length quartz cell, (previously flushed with argon), sealed with a serum cap. The progress of the reaction was monitored at 365 nm. Pseudo-first-order rate constants (k_{obs}) were determined graphically from plots of $\ln(A_\infty - A_t)$ *versus* t, where A_∞ was the final absorbance value and A_t the absorbance at time t.

The substitution reactions were performed under pseudo-first-order conditions (excess of pz). The reactions between *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ and pyrazine were monitored following the increase of absorbance in the region of spectra of the MLCT bands of the pyrazine derivatives.

The kinetic data were according to the relation

$$k_{obs} = k_1[pz] + k_{-1}$$

The k_{obs} values were obtained from $\ln(A_\infty - A_t)$ *versus* t plots. Values of k_1 and k_{-1} were calculated from the slope and intercept of plots of k_{obs} *versus* [pz]. K_{eq} was calculated from the ratio k_1/k_{-1}.

The rate constants were reproducible to within ±6%, and each value is a mean of at least three independent determinations. The $\ln(A_\infty - A_t)$ *versus* t plots were linear for at least four half-lives.

TABLE II. Substitution in *trans*-$[Ru(NH_3)_4(P(OR)_3)(H_2O)]^{2+}$ by Pyrazine[a]

$P(OR)_3$	[pz] (M)	$10 \times k_{obs}$[b] (s^{-1})
$P(OPh)_3$[c]	0.0251	0.462
	0.0503	0.495
	0.0754	0.533
	0.101	0.578
	0.151	0.619
	0.201	0.680
	0.251	0.715
$P(OBu)_3$	0.0200	5.24
	0.0300	6.30
	0.0400	7.27
	0.0500	8.25
	0.0600	9.18
	0.0800	10.5
	0.100	11.9
	0.150	14.9
	0.200	16.3
	0.300	18.1

[a] $\mu = 0.10$ ($NaCF_3COO/CF_3COOH$); (25.0 ± 0.1) °C; $C_{H^+} \sim 1.0 \times 10^{-3}$ M; $C_{Ru(II)} \sim 5.0 \times 10^{-4}$ M. [b] Each value is a mean of at least four independent determinations agreeing within 6%. [c] 10% acetone.

TABLE III. Substitution in *trans*-$[Ru(NH_3)_4(PR_3)(H_2O)]^{2+}$ by Pyrazine[a]

PR_3	[pz] (M)	k_{obs}[b] (s^{-1})
PPh_3[c]	0.0500	0.110
	0.100	0.180
	0.200	0.280
	0.250	0.390
	0.300	0.430
	0.350	0.460
	0.400	0.500
	0.450	0.530
PBu_3[d]	0.0100	0.840
	0.0150	1.04
	0.0200	1.19
	0.0250	1.37
	0.0300	1.54
	0.0400	1.90
	0.0500	2.25
	0.0600	2.54
	0.0800	3.16
	0.100	3.70
	0.150	4.02
	0.200	5.83
PEt_3	0.0100	0.960
	0.0150	1.21
	0.0200	1.47
	0.0250	1.72
	0.0300	1.98
	0.0350	2.23
	0.0400	2.49
	0.0450	2.74
	0.0500	3.00
	0.0600	3.35
	0.0800	4.02
	0.100	4.54
	0.120	5.07
	0.150	5.60

[a] $\mu = 0.10$($NaCF_3COO/CF_3COOH$); (25.0 ± 0.1) °C; $C_{H^+} \sim 1.0 \times 10^{-3}$ M; $C_{Ru(II)} \sim 5.0 \times 10^{-4}$ M. [b] Each value is a mean of at least four independent determinations agreeing within 6%. [c] 10% acetone. [d] 7.5% EtOH.

Results and Discussion

The kinetic data for the substitution reaction

$$trans\text{-}[Ru(NH_3)_4P(III)(H_2O)]^{2+} + pz \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4P(III)pz]^{2+} + H_2O$$

are shown in Table II and III. All these reactions exhibit the same kinetic pattern already described for the substitution reactions of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ and related complex ions with electrophilic reagents [7, 9, 10]. Under pseudo-first-order conditions the rate is dependent of the concentration of pz at low concentrations but exhibits departure from linearity at ligand concentrations higher than 0.1 M. This behavior is consistent with the model for a dissociative activation process [7, 15, 16].

Since the mechanism is assumed to be governed by a dissociative path [7, 9, 10], the rate for the substitution of the water molecule on the coordination sphere by pz should express a relative order of the *trans*-effect of the phosphorous ligands on

TABLE IV. Data[a] on Substitution Reactions of *trans*-$[Ru(NH_3)_4(P(III))(H_2O)]^{2+}$ with Pyrazine, Formal Potentials for the Aquo–Phosphane Complexes, Phosphane Ligands Cone Angles, UV–Vis Bands Maxima and the Molar Absorptivities for the Aquo–Phosphane and the Pyrazine Derivatives Complexes

P(III)	k_1 ($M^{-1}\ s^{-1}$)	$10 \times k_{-1}$ (s^{-1})	K_{eq} (M^{-1})	$E^{\circ\prime}$ [a, b] (V)	θ [c] (°)	λ (nm) (ε ($M^{-1}\ cm^{-1}$))[a, d]	λ (nm) (ε ($M^{-1}\ cm^{-1}$))[a, e]
$P(OPh)_3$	0.15	0.42	3.6	0.66	128	316 (7.8×10^2)	330 (2.2×10^3)
PPh_3	1.2	0.60[f]	19	0.53	145	386 (7.3×10^2)	393 (3.0×10^3)
		0.39[g]	30				
$P(OEt)_3$[h]	3.8	2.0	20	0.46	109	316 (6.5×10^2)	365 (4.2×10^3)
$P(OBu)_3$	9.8	3.3	30	0.43	115	316 (5.4×10^2)	365 (4.0×10^3)
PBu_3	34	5.1	68	0.30	132	355 (6.2×10^2)	417 (3.9×10^3)
PEt_3	51	4.5	1.1×10^2	0.33	132	344 (6.4×10^2)	419 (4.5×10^3)

[a] $\mu = 0.10(NaCF_3COO/CF_3COOH)$; (25.0 ± 0.1) °C; $C_{H^+} = 1.0 \times 10^{-3}$ M. [b] For the *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{3+/2+}$ complex ions; *vs.* SCE, uncertainty of ±0.01 V. [c] Data from ref. 17. [d] For the *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ complex ions. [e] For the MLCT bands of *trans*-$[Ru(NH_3)_4P(III)(pz)]^{2+}$ complex ions. [f] From k_{obs} *vs.* [pz] plots. [g] By aquation of *trans*-$[Ru(NH_3)_4(PPh_3)(pz)]^{2+}$. [b] Data from ref. 7.

the *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ complexes. From the kinetic data of Table IV the following order of increasing *trans*-effect can be written: $P(OPh)_3 < PPh_3 < P(OEt)_3 < P(OBu)_3 < PBu_3 < PEt_3$. As indicated by the sequence, the phosphines are stronger *trans* labilizing agents than the corresponding phosphites.

Steric and electronic effects are operative in such systems. No direct relationship can be established between the cone angle parameter [17] (θ) of the ligand and its *trans*-effect for all the series. However comparison of each phosphite with the analogous phosphine molecule shows that phosphites, with smaller cone angles than the corresponding phosphines, undergo slower anation.

The phosphanes are biphilic ligands and therefore a synergism exists between the σ and π components of the Ru(II)–P(III) bond. Except for PEt_3, a trend is observed for all the series: the better the σ base character of the P(III) ligand, the faster the complex ion *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ substitutes the water molecule. In contrast, the stronger the π acid character of the phosphanes, the slower the substitution.

The *trans*-influence of P(III) in the *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ complex ions is related to the weakening of the bond Ru(II)–pz in terms of ΔG_{eq}. Since the affinity of the metal center for pz is $K_{eq} = k_1/k_{-1}$, the following relative order of increasing *trans*-influence of P(III) is assessed on the basis of $1/K_{eq}$ data (see Table IV): $PEt_3 < PEt_3 < P(OBu)_3 < P(OEt)_3 \sim PPh_3 < P(OPh)_3$.

Contrary to what is observed for the *trans*-effect sequence, the phosphites exhibit a stronger *trans*-influence than the corresponding phosphines. The larger the cone angle, the greater one would expect to be the steric strain created by the phosphane at the coordination sphere of the metal center and therefore stronger its *trans*-influence [17]. However, as observed for the *trans*-effect series below, the *trans*-influence sequence does not follow the same tendency of increasing the ligand cone angle. In fact phosphites with smaller cone angles than those of the homologous phosphines exhibit a stronger *trans*-influence.

For the *trans*-influence a straightforward relationship seems to come out of an analysis of the electronic effects. The *trans*-influence sequence follows the same order as the π acidity increase of the phosphanes. The stronger the π acceptor ability of the P(III), the greater will be the competition for the $4d_\pi$ electrons of Ru(II) between P(III) and pz along the axis P(III)–Ru(II)–pz weakening the Ru(II)–pz bond. These observations are in agreement with the well established [18] strong π acid and very weak σ base characters of the pyrazine molecule.

The validity of the generalization about the relevance of π bonding on the *trans*-influence of phosphanes has additional support from the aquation data of the complex *trans*-$[Ru(NH_3)_4(P(OEt)_3)(PEt_3)]^{2+}$. This study allows a direct comparison of the *trans*-influence of triethyl phosphite and triethyl phosphine. Dealing with such small molecules permits an assessment of the electronic effect influence on the mutual destabilization of these phosphanes.

As judged from cyclic voltammetric and electronic spectra data of the final solution the aquation

$$\textit{trans-}[Ru(NH_3)_4(P(OEt)_3)(PEt_3)]^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans-}[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+} + PEt_3$$

proceeds at the specific rate $2.2 \pm 0.2 \times 10^{-5}\ s^{-1}$ ($C_{H^+} = 1.0 \times 10^{-3}$ CF_3COOH, $\mu = 0.10$ $NaCF_3COO$, (25.0 ± 0.1) °C). In acidic media the final product exhibits the spectral characteristics [7] of the *trans*-$[Ru(NH_3)_4(P(OEt)_3(H_2O)]^{2+}$ ions: $E^{\circ\prime} = (0.46 \pm 0.01)$ V *versus* SCE, $\lambda_{max} = 316$ nm, $\epsilon = (6.4 \pm 0.1) \times$

10^2 M^{-1} cm^{-1}. The complex ion *trans*-$[Ru(NH_3)_4(PEt_3)(H_2O)]^{2+}$ has the following characteristics: $E^{\circ\prime} = (0.33 \pm 0.01)$ *versus* SCE, $\lambda_{max} = 344$ nm, $\epsilon = (6.4 \pm 0.2) \times 10^2$ M^{-1} cm^{-1}. If the aquation is performed in the presence of pz, only the characteristic band at 365 nm for the *trans*-$[Ru(NH_3)_4(P(OEt)_3)(pz)]^{2+}$ is observed.

It is well accepted [8] that the more positive is the value of $E^{\circ\prime}$ for the Ru(III)/Ru(II) couples on *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{3+/2+}$ complexes, the stronger is the stabilization of Ru(II) relative to Ru(III), due to the back-bonding Ru(II)–P(III).

Since phosphites are stronger π acids than phosphines, their complexes exhibit more positive $E^{\circ\prime}$ values than the corresponding phosphine complexes (Table IV).

An interesting trend has been also observed relating *trans*-effect and *trans*-influence respectively with $E^{\circ\prime}$ for the Ru(III)/Ru(II) couples on the complexes *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{3+/2+}$.

As $E^{\circ\prime}$ becomes more positive, the slower is the rate for the substitution of the water molecule on the coordination sphere of the complex and the smaller the *trans*-effect of L. This could be understood assuming that through the π back-bonding interaction Ru(II)–P(III), the metal center exhibits the same character as Ru(III) and therefore reacts slower [19]. The more positive the $E^{\circ\prime}$ value, the less available will be the $4d_{\pi}$ electrons of the Ru(II) center to interact with the incoming ligand. In any case pz is a stronger π acid, and by consequence the *trans*-influence of the P(III) ligand is stronger. Further work on this area is in progress at our laboratory and will be reported later.

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References

1 C. Masters, 'Homogeneous Transition-Metal Catalysis', Chapman and Hall, London, 1981.

2 J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, California, 1980.

3 L. H. Pignolet, 'Homogeneous Catalysis with Metal Phosphine Complexes', Plenum, New York, 1983.

4 J. Halpern, *Phosphorus Sulfur, 18*, 307 (1983).

5 L. G. Marzilli, P. J. Toscano, J. H. Ramsden, L. Randaccio and N. B. Pahor, in E. C. Alyea and D. W. Meek (eds.), 'Catalytic Aspects of Metal Phosphine Complexes', American Chemical Society, Washington, D.C., 1982, pp. 85–99.

6 P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1556 (1970).

7 D. W. Franco and H. Taube, *Inorg. Chem., 17*, 571 (1978).

8 D. W. Franco, *Inorg. Chim. Acta, 48*, 1 (1981), and refs. therein.

9 J. C. Nascimento Filho and D. W. Franco, *Inorg. Chim. Acta, 113*, 55 (1986).

10 J. M. de Rezende and D. W. Franco, *XVIII Congresso Nazionale Di Chimica Inorganica*, Como, Italy, 1985, pp. 549–552.

11 C. K. Jorgensen, *Struct. Bonding (Berlin), 1*, 234 (1966).

12 D. F. Shriver, 'The Manipulation of Air-Sensitive Compound', McGraw-Hill, New York, 1969.

13 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon, Oxford, 1983.

14 C. G. Kuehn and H. Taube, *J. Am. Chem. Soc., 98*, 689 (1976).

15 J. H. Espenson, 'Chemical Kinetics and Reaction Mechanism', McGraw-Hill, New York, 1981.

16 J. D. Atwood, 'Inorganic and Organometallic Reaction Mechanism', Brooks/Cole, Monterey, 1985.

17 C. A. Tolman, *Chem. Rev., 77*, 313 (1977).

18 (a) P. C. Ford, De F. P. Rudd, R. Gaunder and H. Taube, *J. Am. Chem. Soc., 90*, 1187 (1968); (b) A. M. Zwickel and C. Creutz, *Inorg. Chem., 10*, 2395 (1971).

19 S. S. Isied and H. Taube, *Inorg. Chem., 15*, 3070 (1976).