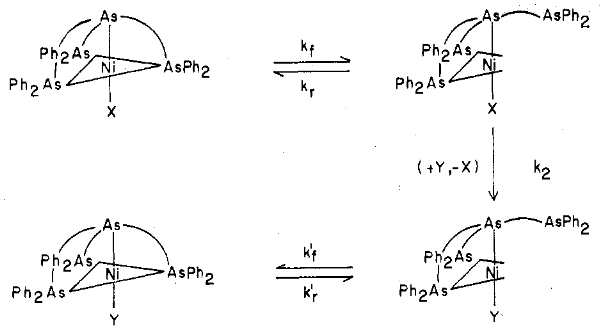

Figure 5. Mechanistic pathway for ligand replacement involving the partial tetradentate ligand dissociation in forming a four-coordinate intermediate.

By assuming occurrence of (i) a rapid preequilibrium that is the partial tetradentate ligand dissociation involving one terminal arsenic donor group, (ii) a steady-state concentration of the four-coordinate intermediate, and (iii) a rate-determining bimolecular step between the four-coordinate intermediate formed in the first step and the entering nucleophile, we obtain the rate law given by eq 12 and 13. For $k_r \gg k_2$

$$\frac{-\mathrm{d}[\mathrm{NiX(QAS)^+}]}{\mathrm{d}t} = \frac{(k_f/k_r)k_2[\mathrm{NiX(QAS)^+}][\mathrm{Y^-}]}{1 + (k_2/k_r)[\mathrm{Y^-}]} \qquad (12)$$

$$k = \frac{(k_f/k_r)k_2}{1 + (k_2/k_r)[\mathrm{Y^-}]} \qquad (13)$$

this rate law would yield linear plots of pseudo-first-order rate constants vs. the entering ligand concentrations that pass through the origin. This rate law theoretically differs from the previous one at higher concentrations of entering ligand. Limited by solubilities, the maximum entering ligand concentration used did not allow a distinction between the two mechanisms to be made.

Although the evidence gathered in this investigation was not conclusive of a singular mechanism, it did suggest that an associative step is involved in the mechanism of ligand replacement. The observation of Morgan and Tobe[8] that Qas displaces QAS from $\mathrm{PtBr(QAS)^+}$ is certainly consistent with our observations that $\mathrm{NiCl(QAS)^+}$ undergoes decomposition in the absence of strongly nucleophilic ligands and that the strong nucleophile $\mathrm{CN^-}$ promotes decomposition of $\mathrm{Ni(CN)(QAS)^+}$. The trialkylarsine $(\mathrm{C_2H_5})_3\mathrm{As}$ has an n°_{Pt} equal to 7.54 compared to 6.75 for $\mathrm{Ph_3As}$ and 7.0 for $\mathrm{CN^-}$. The n°_{Pt} value for Qas is expected to be greater than that of QAS. Therefore, both Qas and $\mathrm{CN^-}$ would be predicted to displace QAS because of the greater nucleophilic character. The fact that complete tetradentate ligand dissociation occurs suggests, but is not conclusive of, a mechanism for monodentate ligand replacement via partial tetradentate ligand dissociation. The latter mechanism is particularly attractive because it is consistent with the prediction of Tolman that 18-electron systems favor dissociative processes.[21]

Acknowledgment. This project was supported, in part, through the acquisition of a stopped-flow spectrometer made possible by financial support received from the Research Corp.

Registry No. $[\mathrm{NiCl(QAS)}]\mathrm{ClO_4}$, 41765-69-9; $[\mathrm{NiBr(QAS)}]\mathrm{Br}$, 14239-42-0; $[\mathrm{NiI(QAS)}]\mathrm{ClO_4}$, 14523-06-9; $[\mathrm{Ni(CN)(QAS)}]\mathrm{ClO_4}$, 14238-93-8; $[\mathrm{Ni(NO_2)(QAS)}]\mathrm{ClO_4}$, 72138-06-8; $[\mathrm{Ni(PPh_3)(QAS)}](\mathrm{ClO_4})_2$, 72138-08-0; $[\mathrm{Ni(N_3)(QAS)}]\mathrm{ClO_4}$, 72152-01-3; $[\mathrm{Ni(NCS)(QAS)}]\mathrm{ClO_4}$, 14238-94-9; $[\mathrm{PtBr(QAS)}]\mathrm{Br}$, 72173-25-2; $\mathrm{NO_2^-}$, 14797-65-0; $\mathrm{I^-}$, 20461-54-5; $\mathrm{SCN^-}$, 302-04-5; $\mathrm{N_3^-}$, 14343-69-2; $\mathrm{CN^-}$, 57-12-5; $\mathrm{SC(NH_2)_2}$, 62-56-6.

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Exchange Reactions in $(\mathrm{CH_3})_3\mathrm{PPCF_3}$, Phosphinidene Analogue of a Wittig Reagent

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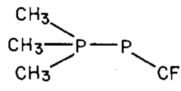
The interaction of $\mathrm{Me_3P}$ with the homocyclic phosphines $(\mathrm{CF_3P})_4$ and $(\mathrm{CF_3P})_5$ has been investigated by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy. In excess $\mathrm{Me_3P}$ the predominant exchange pathway involves the bimolecular attack of $\mathrm{Me_3P}$ on the phosphine–phosphinidene complex $\mathrm{Me_3PPCF_3}$. However, the kinetics are complicated by a side reaction which results in the production of the difluorophosphorane $\mathrm{Me_3PF_2}$.

Introduction

Main-group species with low coordination numbers play an important role in chemistry as models for reaction intermediates. They also raise interesting questions regarding structure and bonding as well as offering promise as synthetic reagents. In terms of group 5A chemistry much current emphasis has been placed on two-coordinate phosphorus and arsenic compounds. Several stable neutral molecules with this coordination number have been prepared in recent years; examples include phosphabenzene,[1] arsabenzene,[2] and compounds with P=C,[3] As=C,[4] and P=N[5] bonds. In this paper we are concerned with the rather unusual compound **1** which features both di-



1

and tetracoordinate phosphorus atoms.[6] Compound **1**, in fact, bears a striking resemblance to the classic Wittig reagents. Several years ago we noted in an NMR study[7] that the ^{19}F resonance of **1** is temperature sensitive. Enthused by the possibility that **1** represents a potential source of phosphinidene

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(RP) units, we decided to investigate the nature of the exchange process(es) more thoroughly by dynamic NMR techniques.

Experimental Section

General Procedures. Due to the moisture and/or oxygen sensitivity of the materials described herein, all manipulations were carried out in vacuo or under a blanket of dry nitrogen.

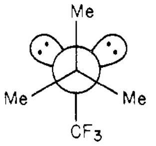
Materials. Trimethylphosphine was prepared by the method of Martin et al.[8] It was isolated as its AgI complex, which was transferred subsequently to the vacuum line. Thermolysis of the AgI complex afforded free Me_3P, which was purified by trap-to-trap distillation. (Trifluoromethyl)phosphinous diiodide was prepared as described in the literature[9] and converted to the mixture of $(CF_3P)_4$ and $(CF_3P)_5$ as described by Mahler and Burg.[10] The two cyclic phosphines can be separated by filtration followed by distillation (the pentamer) or recrystallization (the tetramer). However, we found that the NMR results were independent of whether $(CF_3P)_4$ or $(CF_3P)_5$ was used as the reagent. Accordingly, in most reactions we used a mixture of $(CF_3P)_4$ and $(CF_3P)_5$. The solvent and internal $^1H/^{19}F$ reference, α,α,α-trifluorotoluene ($C_6H_5CF_3$), was stirred over CaH_2 for several hours prior to fractional distillation in vacuo.

NMR Spectroscopy. Variable-temperature ^1H and ^{19}F spectra were measured on Varian A-60 and Varian HA-100 instruments, respectively. Both spectrometers were equipped with variable-temperature accessories. Probe temperatures down to −60 °C were measured by means of a calibrated copper–constantan thermocouple. The ^{13}C and ^{31}P NMR spectra were measured on a Bruker WH-90 spectrometer operating in the FT mode at spectrometer frequencies of 22.6 and 36.4 MHz, respectively. The ^{13}C and ^{31}P chemical shifts are cited with respect to external $(CH_3)_4Si$ and 85% H_3PO_4, respectively. In both cases, nuclei that are deshielded with respect to the reference are assigned positive chemical shift values.

Sample Preparation. All samples were prepared in 5 or 8 mm o.d. NMR tubes which were glassblown to Teflon/glass stopcocks. In a typical procedure, 17.6 mg of $(CF_3P)_4$ (0.176 mmol of CF_3P units) and 0.88 mmol of Me_3P were condensed into the base of the NMR tube at −196 °C. The NMR tube was removed from the vacuum line and allowed to warm to room temperature with gentle agitation. The resulting colorless solution was then cooled to −78 °C. After two more freeze–thaw cycles, a sufficient quantity of α,α,α-trifluorotoluene or CH_3CN was added in vacuo to obtain the desired concentration of Me_3PPCF_3. Finally, the NMR tube was cooled to −196 °C, sealed, and allowed to assume ambient temperature slowly.

Results and Discussion

NMR Parameters for Me_3PPCF_3 (1). A summary of ^1H, ^{13}C, ^{19}F, and ^{31}P NMR data pertaining to the ground state of **1** is presented in Table I. Some ^{19}F and ^{31}P NMR data have been published previously.[6] Limited coupling constant sign information[11] is also available. The ground-state geometry of **1** is not known; however, the most likely structure, viewed down the P–P bond, is



The ^{31}P NMR chemical shifts of uncoordinated Me_3P and the Me_3P component of **1** are −62.4[12] and +12.7 ppm, respectively. The difference in these numbers (+75.1 ppm) represents the coordination chemical shift, $\Delta\delta$. Very similar $\Delta\delta$ values have been observed when Me_3P is coordinated to oxygen (+98.6 ppm),[13] sulfur (+93.3 ppm),[14] or borane (+60.6 ppm).[15] From this standpoint then, the CF_3P unit appears to play the role of a normal Lewis acid.

Table I. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR Data for $Me_3P \rightarrow PCF_3$ (1) in the Presence of Excess Me_3P under Slow-Exchange Conditions

nucleus obsd	chem shift[a, b]	multiplicity[c]	coupling const, Hz
$^{31}P\{^1H\}$	12.7 (P)	d of q	$J_{PP'} = -436.5$[d] $J_{PP'C'F} = +23.3$[e]
	−81.0 (P′)	d of q	$J_{P'P} = -436.3$ $J_{P'C'F} = +37.4$[e]
$^{13}C\{^1H\}$	15.7 (C)	d of d	$J_{CP} = 47.0$ $J_{CPP'} = 10.3$
	141.5 (C′)	q of d of d	$J_{C'F} = 319.1$ $J_{C'P'} = 100.0$ $J_{C'P'P} = 4.4$
^{19}F	26.7 ± 1.4[f]	d of d	$J_{FC'P'} = +37.2$ $J_{FC'P'P} = +23.6$
^1H	1.45 ± 0.1[f]	d of d	$J_{HCP} = -12.9$ $J_{HCPP'} = +3.0$

[a] P′ and C′ refer to the phosphorus and carbon nuclei in the CF_3P group of 1. [b] Values are reported relative to 85% H_3PO_4, Me_4Si, $CFCl_3$, and Me_4Si for ^{31}P, ^{13}C, ^{19}F, and ^1H NMR experiments, respectively. [c] Key: d = doublet; q = quartet. [d] The signs of some coupling constants have been previously reported.[11] [e] More accurate values may be extracted from the ^{19}F NMR data. [f] Position solvent dependent.

The increase of J_{PC} in proceeding from Me_3P ($J_{PC} = -13.6$ Hz)[16] to **1** ($J_{PC} = +47.0$ Hz)[12,18] is anticipated and is understandable on the basis of the increase of % P(3s) character accompanying the widening of the CPC bond angles from 98.6[17] to ~109 °C. The increase of $^1J_{PC}$ on coordination of a CF_3P moiety to Me_3P (+60.6 Hz)[18] is similar to values obtained when the acceptor is oxygen (+81.9 Hz),[19] sulfur (+69.7 Hz),[20] or a CH_3^+ group (+70.1 Hz).[21]

The directly bonded phosphorus–phosphorus coupling constant in **1** (−436.5 Hz) is similar in both sign and magnitude to the data which have been reported for diphosphines such as $(CF_3)_2PPMe_2$ (−256 Hz).[7,11] Indeed, **1** is an isomer of the unknown diphosphine $Me_2PP(CF_3)Me$. The only other compounds with P→P dative bonds for which J_{PP} data are available are $Me_3P \rightarrow PF_5$ (+715 Hz),[22] $Me_2PH \rightarrow PF_5$ (+723 Hz),[22] $Cl(Me_2N)_2P \rightarrow P^+(NMe_2)_2$ (±352 Hz),[23] and $(Me_2N)_3P \rightarrow P^+(NMe_2)_2$ (±340 Hz).[23] The factors which are responsible for the trends in the sign and magnitude of J_{PP} are not clear at present.

Exchange and Decomposition Reactions of Me_3PPCF_3. The ^1H and ^{19}F NMR spectra of Me_3PPCF_3 in excess Me_3P are temperature sensitive. For example (Figure 1) when the temperature of a 0.6 M solution of Me_3PPCF_3 in $C_6H_5CF_3/Me_3P$ is raised, the ^{19}F resonance changes from a doublet of doublets at ambient temperature (Table I) to a doublet at 80 °C, coalescence occurring at ~65 °C. For the ^{19}F spectra approaching the fast-exchange limit, the resulting doublet possesses the same chemical shift as the doublet of doublets in the slow-exchange limit, and the PCF coupling constant is unchanged. The ^1H NMR spectra of **1** not only exhibit temperature dependence but are also sensitive to the concentration of Me_3P (Figure 2).

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(18) Assumes the sign of J_{PC} to be positive in this compound (see ref 20).
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(21) Elser, H.; Dreeskamp, H. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 619.
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(23) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046.

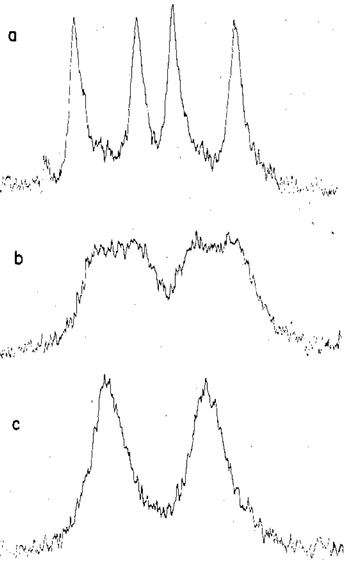


Figure 1. ^{19}F NMR spectra of a 0.6 M solution of Me_3PPCF_3 (**1**) in $Me_3P/C_6H_5CF_3$ at various temperatures: (a) 30 °C; (b) 65 °C; (c) 80 °C.

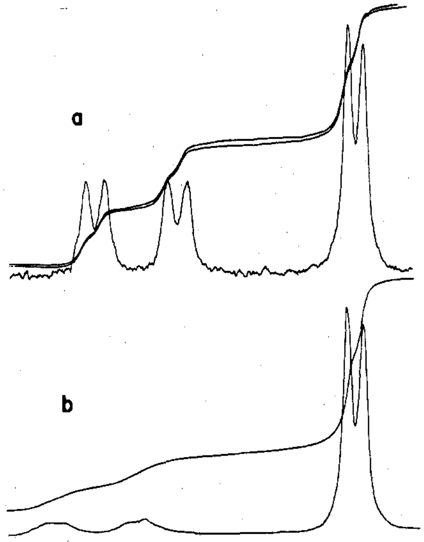


Figure 2. ^1H NMR spectra of Me_3PPCF_3 (**1**) in $C_6H_5CF_3$ with various amounts of excess Me_3P at 30 °C: (a) with 1.0 equiv of excess Me_3P; (b) with 3.0 equiv of excess Me_3P.

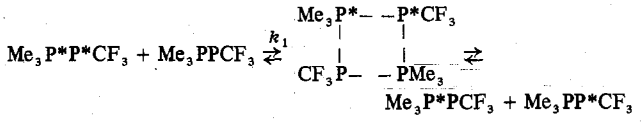
Three likely mechanisms are capable of explaining the foregoing observations:

mechanism 1

$$Me_3P^* + Me_3PPCF_3 \overset{k_1}{\rightleftarrows} Me_3P^*P(CF_3)PMe_3 \rightleftarrows Me_3P^*PCF_3 + Me_3P$$

$$1/\tau_P = K_1[PP],\quad 1/\tau_{PP} = k_1[P]$$

mechanism 2



$$Me_3P^*P^*CF_3 + Me_3PPCF_3 \overset{k_1}{\rightleftarrows} \begin{array}{ccc} Me_3P^* & - & P^*CF_3 \\ | & & | \\ CF_3P & - & PMe_3 \end{array} \rightleftarrows Me_3P^*PCF_3 + Me_3PP^*CF_3$$

$$1/\tau_P = \text{constant},\quad 1/\tau_{PP} = k_1[PP]$$

mechanism 3

$$Me_3PPCF_3 \overset{k_1}{\rightleftarrows} Me_3P + PCF_3 \overset{Me_3P^*}{\rightleftarrows} Me_3P^*PCF_3 + Me_3P$$

$$1/\tau_{PP} = \text{constant},\quad 1/\tau_P = k_1[PP]/[P]$$

Table II. Concentration Dependence for the Inverse Mean Lifetimes $(1/\tau)^{a,b}$ of Me_3PPCF_3 (PP) and Me_3P (P) (Derived from ^1H NMR Spectra Recorded at 30 °C)

c_{PP}	c_P	$1/\tau_P$	$1/\tau_{PP}$
0.59	0.59	2.0	1.9
0.84	1.24	4.1	3.8
0.29	1.78	0.63	6.6
0.59	1.78	2.2	7.2
1.19	1.83	4.1	6.0
0.21	1.95	0.63	6.6
0.59	2.37	2.7	8.4
1.22	3.65	3.8	11.6
0.62	3.72	1.2	13.2

[a] In s^{-1} units. [b] Uncertainties in $1/\tau$ are $\pm 0.3\ s^{-1}$ for values greater than $8.0\ s^{-1}$ and $\pm 0.2\ s^{-1}$ for smaller values.

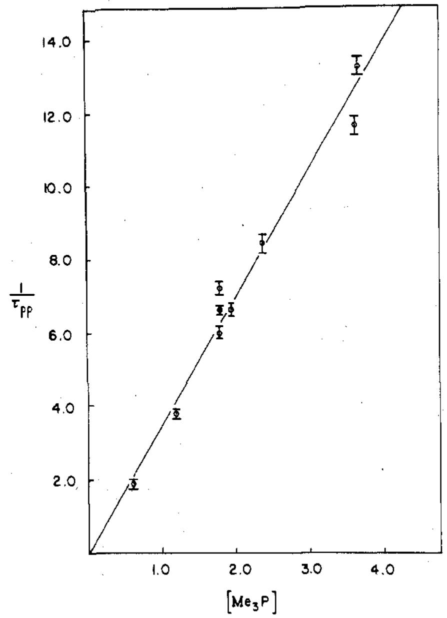
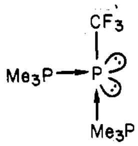


Figure 3. Dependence of the inverse mean lifetime of Me_3PPCF_3, $1/\tau_{PP}$, on the concentration of Me_3P.

Mechanism 1 involves an associative rate-determining step in which Me_3P attacks **1** to afford a pentacoordinate transition state the geometry of which would be



according to standard ligand electronegativity criteria.

For this mechanism the inverse mean lifetimes of the free base $(1/\tau_P)$ and the complex $(1/\tau_{PP})$ would be dependent on the concentrations of complex and base, respectively, as indicated above.

Mechanism 2 also involves an associatve process; however, in this case, two molecules of **1** combine to form a presumed four-centered transition state. As contrasted with the kinetics of mechanism 1, the inverse mean lifetime of Me_3P would be expected to be independent of reagent concentrations, while $1/\tau_{PP}$ would be dependent upon the concentration of **1**.

Mechanism 3 is one in which the rate-controlling feature is the scission of the $P \rightarrow P$ bond of **1** to afford Me_3P and free (trifluoromethyl)phosphinidene. Consequently, $1/\tau_{PP}$ should show no dependence on [**1**] or $[Me_3P]$. By contrast, $1/\tau_P$ should vary as the quotient of the concentrations of complex and Me_3P present in solution.

Thus, in principle, distinction between the three mechanisms can be made on the basis of ambient-temperature (30 °C) ^1H

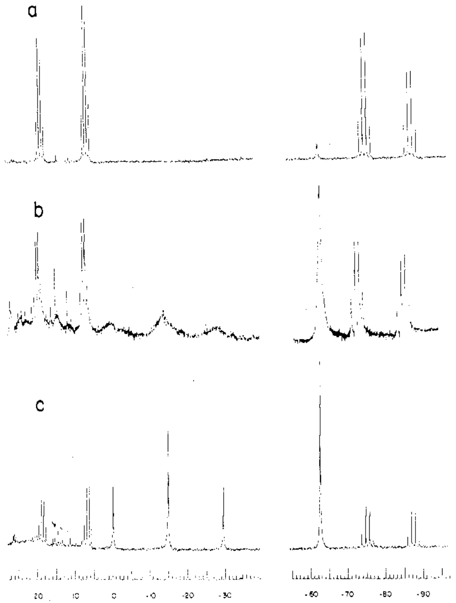


Figure 4. ^{31}P NMR spectra of Me_3PPCF_3 (**1**) in Me_3P/CH_3CN after heating for various times and temperatures: (a) no heating, 30 °C; (b) 1 h, 90 °C; (c) next day, 30 °C.

NMR concentration dependence studies. The experimental concentration dependence studies (Table II) eliminate mechanisms 2 and 3 because, as illustrated in Figure 3, $1/\tau_{PP}$ is dependent upon [P]. The concentration dependence data clearly favor mechanism 1. However, it is important to note that the range of temperatures and concentrations which we could study was severely limited by the thermal instability of **1**. The kinetics are, in fact, complicated by existence of at least one side reaction. Thus, when solutions of **1** containing an excess Me_3P are heated to temperatures in excess of 80 °C the $^{31}P\{^1H\}$ resonance of **1** diminishes in intensity, while that of Me_3P increases and a new set of peaks, a triplet, appears centered at 14.5 ppm (Figure 4). This triplet resonance, $J_{PF} = 533$ Hz, corresponds to that of Me_3PF_2.[24] Inferentially, the Me_3PF_2 is produced by fluorination of Me_3P by the CF_3 groups. Obviously, this fluorination could proceed inter- or intramolecularly. If it were an intramolecular process, the β transfer of two fluorine ligands from carbon to phosphorus would result in equimolar quantities of Me_3PF_2 and $F{-}C{\equiv}P$.[25] However, examination of the integrated areas of the Me_3P and Me_3PF_2 ^{31}P resonances suggests that the thermal decomposition of **1** in CD_3CN solution is more complicated since the overall conversion of **1** to Me_3P and Me_3PF_2 favors the former when a high concentration of Me_3P is already present in solution and the latter when very slight excess Me_3P is present initially.

Finally, equilibria of the general type

$$n\mathrm{Me_3PPCF_3} \rightleftarrows n\mathrm{Me_3P} + (1/n)(\mathrm{CF_3P})_n \quad (n = 4, 5)$$

were considered. However, neither $(CF_3P)_4$ nor $(CF_3P)_5$ was detectable in $^{31}P\{^1H\}$ NMR experiments at 80 °C or below.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant CHE76-10331) and the Robert A. Welch Foundation for generous financial support.

Registry No. **1**, 33576-11-3; $(CF_3P)_4$, 393-02-2; $(CF_3P)_5$, 745-23-3; PMe_3, 594-09-2.

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(24) See, for example: Seel, F.; Bassler, H. J. *Z. Anorg. Allg. Chem.* **1976**, *423*, 67.

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Reduction of Oxygen by Ruthenium(II) Ammines

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The reduction of O_2 to H_2O_2 by a series of ruthenium(II) ammines has been studied in aqueous acidic solution at 25.0 °C and 0.1 M ionic strength in noncomplexing media. The rate law is $-d[\mathrm{Ru(II)}]/dt = 2k_1[\mathrm{Ru(II)}][O_2]$, with $k_1 = 1.08 \times 10^{-1}$, 1.38×10^{-1}, 3.03×10^{-2}, and 7.73×10^{-3} $M^{-1}\ s^{-1}$ for $[\mathrm{Ru(NH_3)_5isn}]^{2+}$ (isn = isonicotinamide), *cis*-$[\mathrm{Ru(NH_3)_4isn(H_2O)}]^{2+}$, *trans*-$[\mathrm{Ru(NH_3)_4isn(H_2O)}]^{2+}$, and $[\mathrm{Ru(NH_3)_4phen}]^{2+}$, respectively. The reaction of $[\mathrm{Ru(NH_3)_5isn}]^{2+}$ is inhibited by $[\mathrm{Ru(NH_3)_5isn}]^{3+}$, and the inhibition increases with decreasing acidity. These results are accommodated by a mechanism involving outer-sphere formation of O_2^-; the Ru(III)/pH effect arises from a competition between the reaction of O_2^- with Ru(III) and the protonation of O_2^- followed by its reaction with Ru(II). The rate constants are correlated by a linear free-energy relation, (LFER), and they are consistent with the Marcus cross relation. Its application yields a self-exchange rate for the O_2/O_2^- couple of about 1×10^3 $M^{-1}\ s^{-1}$. In the presence of Cl^-, the reaction of *trans*-$[\mathrm{Ru(NH_3)_4isn(H_2O)}]^{2+}$ has two additional terms in the rate law: $-d \ln [\mathrm{Ru(II)}]/dt = 2(k_1 + k_5K_{Cl}[Cl^-] + k_6K_{Cl}[Cl^-][H^+])[O_2]$, with $k_5 = 7.84 \times 10^{-1}$ $M^{-1}\ s^{-1}$, $k_6 = 1.40 \times 10^2$ $M^{-2}\ s^{-1}$, and $K_{Cl} = 0.39$ M^{-1}. The k_5 path fits the LFER when it is treated as the autoxidation of *trans*-$[\mathrm{Ru(NH_3)_4isnCl}]^+$, and the k_6 path probably involves direct formation of HO_2 by the reaction of O_2 with $[\mathrm{Ru(NH_3)_4(isn)Cl}]^+$.

Introduction

Autoxidation reactions, particularly with metal ions as reducing agents, are currently of much interest.[1] Mechanistic studies of autoxidation of metal ions have emphasized Cu(I) complexes[2] but have also included aquo ions such as V(II),[3] Cr(II),[4] Fe(II),[5] and U(IV)[6] and miscellaneous other complexes such as $Fe(CN)_6^{4-}$[7] and $Ru(NH_3)_6^{2+}$.[8] Although these investigations have been instructive, little systematic understanding has yet developed, a result due, perhaps, to the variety

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