Table I. Kinetic Data for the Disappearance of $Ru_3(CO)_{10}(NO)_2$ by Phosphine Substitution in Cyclohexane Solution

Temp, °C	$10^3[L]$, *M*	$10^4[Ru_3(CO)_{10}(NO)_2]_0$, *M*	10^5k_{obsd},[a] sec^{-1}
		$L = (C_6H_5)_3P$	
22.1	1.6	1.6	9.7 (4)
22.1	4.0	4.0	9.6 (2)
22.1	8.0	4.0	10.1 (2)
22.1	16.0	4.0	9.8 (3)
22.1	32.0	4.0	10.1 (2)
22.1	80.0	4.0	10.1 (3)
10.1	16.0	4.0	1.27 (3)
15.9	16.0	4.0	3.52 (12)
28.1	16.0	4.0	26.4 (5)
		$L = CH_3(C_6H_5)_2P$	
22.1	16.0	4.0	9.6 (2)
22.1	32.0	4.0	10.7 (2)
22.1	80.0	4.0	10.1 (2)

[a] Least-squares standard deviation in the least significant digit is in parentheses.

cleaved to monomeric species such as $Ru(CO)_3L_2$;[7] however, the rate of the primary substitution reaction remains essentially the same and is hence independent of the nature as well as of the concentration of entering ligand. This evidence, along with the observation of inhibition by carbon monoxide, supports a dissociative mechanism

$$Ru_3(CO)_{10}(NO)_2 \xrightarrow{k_1} Ru_3(CO)_9(NO)_2 + CO \quad \text{(slow)}$$

$$Ru_3(CO)_9(NO)_2 + L \rightarrow \text{products} \quad \text{(fast)}$$

The rates for both substitution steps with triphenylphosphine and the activation parameters for the first step and related reactions are given in Table II. Comparison with the values reported for first-order substitution[9] and exchange[10] on $Ru_3(CO)_{12}$ (also in Table II) shows that the data are quite consistent with the operation of dissociative mechanisms in both cases. The Ru–C bond broken in the rate-determining step of the reaction appears to be somewhat weaker in **1** than in $Ru_3(CO)_{12}$, resulting in a slightly smaller $\Delta H^{\ddagger}$ and a slightly faster rate of substitution.

The bridging nitrosyl ligands present in **1** in place of the terminal carbonyl ligands in $Ru_3(CO)_{12}$ have no substantial effect on the mechanism of the substitution reaction. They do not serve as "electron wells" and cause **1** to show a relative preference for a second-order rate law. The roughly octahedral geometry around the ruthenium atoms in **1** is important in this respect, since the mononuclear nitrosyl complexes where second-order terms have been shown to be important[1,2] can have less crowded associative transition states.

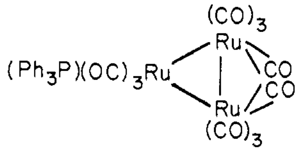
The nitrosyl bridges in **1** also do not produce a rate enhancement of the magnitude which results from the introduction of carbonyl bridges into molecules of this sort. A striking example of the latter effect is provided by the comparison between nonbridged $Ir_4(CO)_{12}$ and its bridged periodic analog $Rh_4(CO)_{12}$. At room temperature the substitution rate of the latter is at least 10^7 times faster, far too great an increase to be explained by metal-carbon bond strength differences. Presumably carbonyl-bridged complexes can undergo substitution by some mechanism other than a purely dissociative one—a mechanism not available to the nitrosyl-bridged **1**.

The observation of a rate constant for the second substitution on $Ru_3(CO)_{10}(NO)_2$ ($\mathbf{2} + L \rightarrow \mathbf{3}$) comparable to that of the first ($\mathbf{1} + L \rightarrow \mathbf{2}$) is worthy of comment because only *one* rate constant is observed for trisubstitution on $Ru_3(CO)_{12}$ (no mono- or disubstituted cluster can be isolated or detected).[9] It would appear that a "long-range" effect is at work across the $Ru_3(CO)_{12}$ cluster. Monosubstitution must produce some change in the reactivity of the initially unsubstituted ruthenium atoms, perhaps by inducing transient formation of a labile (see above) carbonyl-bridged structure such as

Table II. Rate Constants and Activation Parameters for the Substitution of Ruthenium Carbonyl Clusters at 22.1°

Compd	Entering ligand	10^5k_1,[a] sec^{-1}	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[a] eu
$Ru_3(CO)_{10}(NO)_2$	$(C_6H_5)_3P$	10.0 (2) 7 (1)[b]	27.9 (5)	18 (2)
$Ru_3(CO)_{12}$	$(C_6H_5)_3P$	0.09[c,d]	32 (2)[d]	23 (4)[d]
$Ru_3(CO)_{12}$	CO	0.09[c,e]	32 (1)[e]	21[e]

[a] Numbers in parentheses are the least-squares standard deviations in the least significant digit. [b] Approximate first-order rate constant observed for the disappearance of an intermediate. [c] Extrapolated from higher temperature data. [d] Data of Candlin and Shortland.[9] [e] Data of Cetini, Gambino, Sappa, and Vaglio.[10]



Registry No. $Ru_3(CO)_{10}(NO)_2$, 36583-24-1; $(C_6H_5)_3P$, 603-35-0; $CH_3(C_6H_5)_2P$, 1486-28-8; $Ru_3(CO)_8((C_6H_5)_3P)_2\cdot(NO)_2\cdot C_6H_6$, 36631-36-4.

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High-Pressure Interaction of Phosphorus Trifluoride with Oxygen, Sulfur, Selenium, and Tellurium[1]

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The use of high pressures (4000 atm) in the synthesis of volatile inorganic substances has not received the general acceptance that this technique has received in organic synthesis and mechanistic studies.[2-6] This communication further demonstrates[7,8] the versatility of combining the

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techniques of the familiar vacuum line with the reaction-enhancing technique of elevated pressures. The reactions studied are selected from those reactions in which it is reasonable to expect the volume of the products or the volume of the transition state (reacting molecules and surrounding solvent) to be less than the volume of the reactants. This decrease in volume will shift the equilibrium to favor the formation of products as the pressure is increased. In addition it has been shown that the rate constant for a single-step reaction will change according to the expression

$$(\partial \ln k/\partial P)_T = -\Delta V^*/RT \qquad (1)$$

where the activation volume (ΔV^*) represents the difference in the partial molar volumes of the transition state and the reactants.[3] Therefore when the volume of the activated state is less than the volume of the reactants ΔV^* will be negative and the rate constant will increase.

Experimental Section

Apparatus. All work was carried out in a borosilicate glass vacuum system constructed with glass–Teflon valves (Fisher & Porter Co., Warminster, Pa.; Model 795-005-0004). High pressures were generated using a gas pressure booster manufactured by High Pressure Equipment Co., Erie, Pa. The samples were contained in sealed ampoules made from 3-mm diameter thin-walled gold tubing which were placed in a high pressure microreactor (Autoclave Engineers, Erie, Pa.)[8] and nitrogen gas was used to generate the desired pressure. At the end of a reaction period the microreactor was cooled to −196° before releasing the pressure. The frozen ampoule was placed in an opening device attached to the vacuum line and water and other condensable materials on the surface of the gold tubing were removed before opening. The volatile materials were then transferred directly into the vacuum line. Spectra were recorded on a Beckman Model IR-10 double-beam grating spectrophotometer. Volatile materials were confined in a 10-cm cell fitted with KBr or AgCl windows sealed with rubber O rings at reduced pressure. Mass spectra were taken at 70-eV electron energies on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 150°.

Materials. The following commercial reagents were used without any or with minor purification: O_2, Mg, Se, and Te. Phosphorus trifluoride was purified by distilling the sample through a trap cooled to −95° to remove impurities of low volatility and then retaining the material which stopped in a trap cooled to −130° (mol wt: calcd, 87.9; found, 87.8; confirmed by infrared[9] and mass[10] spectra). PF_5 was purified by passage through a trap cooled to −130° and collected in a trap cooled to −160° (mol wt: calcd, 126.0; found, 124.9; confirmed by infrared[9] and mass[10] spectra).

Synthesis of OPF_3 at High Pressure. PF_3 (64.9 mg, 0.738 mmol) was condensed into a gold tube. The vacuum line and manometer were purged with O_2, and then O_2 (32 mg, 2 mmol) was condensed into the Au tube with the PF_3. The tube was sealed and held at 4000 atm and 300° for 12 hr. The ampoule was opened and the excess O_2 was removed by pumping the volatile material through two −196° traps. There was 99% recovery of the volatile material with an 86% conversion to OPF_3 and 24% unreacted PF_3 calculated from a mixed molecular weight measurement. OPF_3 and PF_3 were identified by infrared[9] and confirmed by mass spectra.[10]

Synthesis of $[F_2P(O)]_2O$ at High Pressure. PF_3 (88.0 mg, 1.00 mmol) was condensed into an Au tube which contained Mg (24 mg, 1.0 mg-atom). The vacuum line and manometer were purged with O_2, and then O_2 (48 mg, 1.5 mmol) was condensed into the gold tube. The tube was sealed and held at 4000 atm and 300° for 12 hr. The ampoule was opened and the excess O_2 was removed by pumping the volatile material through two −196° traps. The material was distilled through a −63.5° trap and collected in a −196° trap. The material stopping at −63.5° was $[F_2P(O)]_2O$ (63.8 mg, 0.343 mmol) identified by infrared spectrum[11] and confirmed by mass spectrum ($P_2O_3F_4^+$, 60%; $P_2O_3F_3^+$, 20%; POF_2^+, 100%); the yield was 68.6% based on the PF_3 employed. The other trap contained OPF_3 (32.6 mg, 0.314 mmol).[9,10]

Synthesis of SPF_3 at High Pressure. PF_3 (77.0 mg, 0.875 mmol) was condensed into an Au tube containing S (320 mg, 10 g-atoms). The tube was sealed and held at 4000 atm for 12 hr. The ampoule was opened and the volatile material was trapped at −196°. There was 96% recovery of the volatile materials with a 96% conversion to SPF_3 and 4% unreacted PF_3 calculated from a mixed molecular weight measurement. SPF_3 and PF_3 were identified by infrared[12] and confirmed by mass spectra.[13]

Additional experimental results are summarized in Table I. The purity of the volatile products and reagents was determined by molecular weight, infrared spectrum, and mass spectrum.

Table I. Interactions of PF_3[a]

Reactant	PF_3, mmol	Reactant, mmol	Products,[b] mmol
		1 Atmosphere	
O_2	1.00	1.50	[1.00]
S	1.00	1.00	[1.00]
Se	1.00	1.00	[1.00]
		4000 Atmospheres	
O_2	0.738	1.00	[0.106], OPF_3 (0.632)
S	0.875	1.00	[0.036], SPF_3 (0.839)
Se	1.102	1.00	[0.670], $SePF_3$ (0.45)
Te	1.433	1.00	[1.431]
		4000 Atmospheres with Mg (1 mmol)	
O_2	1.00	1.50	OPF_3 (0.314), $[F_2P(O)]_2O$ (0.343)
S	1.07	1.00	[0.19], SPF_3 (0.877)
OPF_3	0.00	1.59	OPF_3 (0.901), $[F_2P(O)]_2O$ (0.32)

[a] All reactions were carried out for 17 hr at 300° and all products were identified by infrared spectrum and confirmed by mass spectrum except as noted in text. [b] [mmol of unreacted PF_3].

Results and Discussion

It has been reported that PF_3 was readily oxidized at low temperatures and atmospheric pressure by F_2, Cl_2, and Br_2;[14] however, the analogous reaction has not been reported for O_2, S, Se, or Te. The combination reaction between PF_3 and a group VI nonmetal element according to the equation

$$PF_3 + X \rightarrow XPF_3 \qquad (2)$$

where $X = {}^1\!/_2O_2$, S, Se, Te, should be pressure favored since the volume of the system is reduced as the reaction proceeds.[5] Indeed in this study it has been found that PF_3 is readily oxidized when combined at 300° and elevated pressures with O_2, S, and Se.

When PF_3 and tellurium were combined at 4000 atm and 300° for 12 hr, the PF_3 was quantitatively recovered. At 500° the tellurium reacted with the gold tubing forming a gray-black alloy.

With selenium a 50% conversion of PF_3 to $SePF_3$ was obtained at 4000 atm and 300°. This light-sensitive material which decomposed to red amorphous selenium and PF_3 at room temperature could be manipulated for short periods of time in the vacuum system and a mass spectrum was obtained (monoisotopic pattern: $SePF_3^+$ (100%), $SePF_2^+$ (13.3%), SeP^+ (1.9%), PF_3^+ (21.6%), Se^+ (26.7%), PF_2^+ (56.8%), PF^+ (12.1%), P^+ (2.6%));[15] however an infrared spectrum was not obtained due to extremely rapid decomposition when the sample was placed in the spectrometer light path.

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Sulfur reacted readily with PF_3 to give a 50% yield of SPF_3 at 800 atm and 300°. When the pressure was increased to 4000 atm, an almost quantitative conversion was obtained. The usefulness of high pressure to retard thermal decomposition is demonstrated by this work since Thorpe and Rodger, who carried out the first synthesis of SPF_3 from P_4S_{10} and PbF_2, found that this substance decomposed to sulfur and PF_3 at 300°.[16] Since the decomposition reaction requires an increase in volume as the reaction progresses, the decomposition would not be favored at high pressure.

The literature contains many references to the synthesis of OPF_3, including the low-pressure synthesis from O_2 and PF_3 in an electric discharge.[17] At pressures greater than 800 atm within 12 hr at 300°, PF_3 is converted to OPF_3 in approximately 90% yields. When the pressure is increased to 4000 atm, the yield is approximately the same, however, no reaction takes place at 4000 atm and 25°.

Phosphorus trifluoride and oxygen in the presence of magnesium at 4000 atm and 300° readily forms $[F_2P(O)]_2O$. This product is most likely formed by the reaction of OPF_3 and magnesium oxide. The magnesium oxide formation is not pressure dependent; however, as discussed earlier, the synthesis of OPF_3 requires high pressure.

$$2Mg + O_2 \rightarrow 2MgO \tag{3}$$

$$2PF_3 + O_2 \rightarrow 2OPF_3 \tag{4}$$

$$MgO + 2OPF_3 \rightarrow MgF_2 + P_2O_3F_4 \tag{5}$$

Magnesium and OPF_3 do not undergo reaction under similar conditions, and only traces of $P_2O_3F_4$ have been observed when these substances were combined. This is most likely due to a thin oxide film on the metal.[18]

The analogous reaction with sulfur, SPF_3, and magnesium does not take place.

Registry No. OPF_3, 13478-20-1; $[F_2PO]_2O$, 14456-60-1; SPF_3, 2404-52-6; PF_3, 7783-55-3; O_2, 7782-44-7; S, 7704-34-9; Se, 7782-49-2; Te, 13494-80-9; $SePF_3$, 26083-30-7.

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Kinetics of Interaction of Nickel(II) with 2-(2-Aminoethyl)pyridine

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The reactivity of ligands containing nitrogen donor atoms toward transition metal ions in oxidation state II, particularly nickel(II), has been examined thoroughly.[2] When the ligand taking part in metal complex formation is uncharged, the mechanism of the formation process is in most cases well understood irrespective of the ligand dentate number. However, the nature of the variation of reaction rates encountered[2-4] when nickel(II) reacts with protonated ligands precludes the application of any simple unifying mechanistic scheme in this situation.

As a consequence, a study has been undertaken of the kinetics of reaction of nickel ions with certain mixed aromatic and aliphatic amines[5] which exist as a mixture of protonated and unprotonated forms in the neutral to weak acidic pH range. From these results and others, the importance in the complex formation process of ligand charge and chelate ring size, besides metal-ligand affinity, may be assessed. 2-(2-Aminoethyl)pyridine, AEP, reacts with nickel ions, and thermodynamic quantities for the formation of the six-membered chelate ring 1:1 and 1:2 complexes have been obtained.[6] This communication is concerned with the kinetics and mechanism of the 1:1 Ni(II)-AEP complex formation.

Experimental Section

Materials. 2-(2-Aminoethyl)pyridine (Aldrich) was distilled under vacuum and dissolved in absolute ethanol. Dry hydrogen chloride was bubbled through the stirred solution. The resulting precipitate was isolated under a nitrogen blanket and washed thoroughly with absolute ethanol. *Anal.* Calcd for $C_7H_{10}N_2\cdot 2HCl$: C, 43.06; H, 6.20; N, 14.37. Found: C, 42.66; H, 6.25; N, 14.41. Reagent grade nickel nitrate was used as a source of nickel ions. The concentration of stock nickel solutions was estimated complexometrically. Other materials used were reagent grade commercial products.

Proton Dissociation Constants. Ligand solutions were titrated potentiometrically with standard sodium hydroxide solution to yield in separate determinations the two proton dissociation constants. The ionic strength of 0.1 *M* was achieved by addition of the appropriate amount of sodium perchlorate, and the measurements were made at 25°. The results obtained, pK_{a_1} of 3.82 ± 0.02 and pK_{a_2} of 9.65 ± 0.02, are consistent with values available by interpolation of literature data.[6]

Kinetics. The nickel complex of AEP has a higher absorbance than a mixture of the protonated and neutral forms of AEP in the ultraviolet region. Wavelengths used for monitoring complex formation in a Durrum-Gibson stopped-flow spectrophotometer were 275 nm (cacodylate buffer) and 288 nm (2,6-lutidine buffer). Reactions were run under pseudo-first-order conditions with nickel ion concentrations in the range 13-80-fold excess to ensure that only the 1:1 complex is formed. For most kinetic determinations both metal ion and ligand solutions were maintained at a desired pH with a buffering agent and the ionic strength of each solution was made up to 0.1 *M* with sodium perchlorate. A few measurements were made at pH just above 7. For these, in order to minimize any possible complication from precipitation of nickel hydroxide, the ligand solution was buffered with 0.02 *M* lutidine buffer (a concentration twice that used in experiments below pH 7) and mixed with unbuffered nickel ion solution below pH 7. The pH of the resulting mixture (total ionic strength of 0.1 *M*) was measured and is assumed to be obtained virtually within the mixing time of the stopped-flow instrument. Visual observation of the mixed solution and appropriate blank runs confirm that in the time after mixing in which kinetic measurements are made, about 10 sec, there is no apparent interference from formation of insoluble material. Oscilloscope traces yielded excellent first-order rate plots, linear for 3-4 half-lives. The pseudo-first-order rate constants were divided by the total nickel ion concentration to yield the second-order complex formation rate con-

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