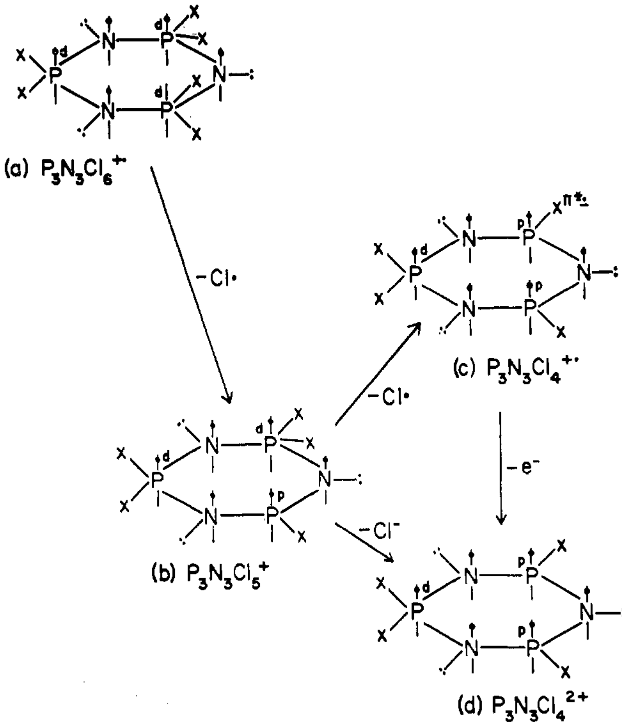

Figure 3.—Electronic configurations of gaseous P_3N_3 ions.

mechanism, previously overlooked, is that of elimination of the chloride ion. The presence of the chloride ion in the negative ion spectra of the trimer and the tetramer supports this mechanism. This ionization path is thought to be particularly important in the formation of the $P_nN_nCl_{2n-1}^+$ and $P_nN_nCl_{2m}^{2+}$ ions

$$P_nN_nCl_{2n} + e^- \longrightarrow P_nN_nCl_{2n-1}^+ + Cl^- + e^-$$
$$P_4N_4Cl_7^+ \longrightarrow P_4N_4Cl_6^{2+} + Cl^-$$

Metastable transitions in the mass spectra of bromophosphonitriles[1] provide some evidence that the ring contraction can occur by elimination of a PN unit

$$P_4N_4Cl_5^+ + \longrightarrow P_3N_3Cl_5^+ + PN$$
$$P_4N_4Cl_6^{2+} \longrightarrow P_3N_3Cl_6^{2+} + PN$$

Another reasonable fragmentation mechanism for which there is no evidence at the moment involves ring contraction with the elimination of a $PNCl_2$ fragment

$$P_4N_4Cl_7^+ \longrightarrow P_3N_3Cl_5^+ + PNCl_2$$

The presence of $PCl_3\cdot^+$, PCl_4^+, P_2Cl^+, $P_2Cl_2\cdot^+$, $P_2Cl_3^+$, $P_3N_2Cl_7^{2+}$, $P_2NCl_5\cdot^+$, $P_2NCl_5^{2+}$, $P_4\cdot^+$, and $P_3N\cdot^+$ as 2.2% of the total ions in the $P_4N_4Cl_8$ spectrum indicates bond rearrangement occurs to some extent during fragmentation. It is tempting to suggest that the ions $P_4\cdot^+$, $P_3N\cdot^+$, and $P_2N_2\cdot^+$ represent a series of structurally related ions formed by replacement of the phosphorus atoms with nitrogen atoms in the well-known P_4 tetrahedral molecule.

Experimental Section

The hexachlorotriphosphonitrile and octachlorotetraphosphonitrile were obtained from Hooker and purified by vacuum sublimation at 30–40°. The melting points were 115 and 122°, respectively.

Spectra were obtained on a CEC Model 21-104 single-focusing mass spectrometer. An ionizing voltage of 70 eV was used and the analyzer temperature and pressure were 250 ± 1° and 10^{-6} mm, respectively. Scanning was done electrically at a magnetic current of 4 A. Samples were introduced using a conventional solid inlet system.

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Kinetic Studies of Phosphite Ligand Substitution in *o*-Phenanthroline Complexes of Group VIb Metal Carbonyls

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AND CAROL M. INGEMANSON

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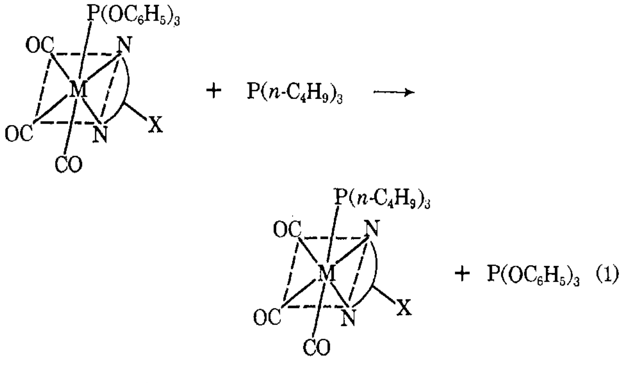
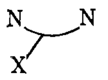
Earlier we reported kinetic studies[1,2] of the substitution reaction

$$M(CO)_4(X\text{-}o\text{-phen}) + L \longrightarrow cis\text{-}M(CO)_3(L)(X\text{-}o\text{-phen}) + CO$$

where M = Cr, Mo, or W, X = a substituted group on *o*-phenanthroline, and L = a phosphine or phosphite. For M = Cr, the kinetic data suggested that the reaction proceeded by only an SN1 mechanism, whereas both SN1 and SN2 paths appeared to operate for the analogous complexes of Mo and W. It was also observed that the rate of CO dissociation (SN1 path) increased as the basicity of X-*o*-phen increased, but the rate of CO displacement by the SN2 mechanism decreased with increasing basicity of the X-*o*-phen. In the present paper, we wish to report the results of a kinetic study of the very similar reactions



where M = Cr, Mo, or W and



is a substituted *o*-phenanthroline. The purpose of this study was to compare the rates and mechanisms of

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(1) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).

(2) J. R. Graham and R. J. Angelici, *ibid.*, **6**, 992 (1967).

$P(OC_6H_5)_3$ replacement with those observed earlier for CO substitution and also to determine whether the basicity of the X-*o*-phen group affected the rates of CO and $P(OC_6H_5)_3$ replacement in the same or in different ways.

Experimental Section

Preparation of Complexes.—The preparation[1] of the $M(CO)_4$(X-*o*-phen) complexes was effected by refluxing or irradiating with ultraviolet light an equimolar solution of $M(CO)_6$ and the desired X-*o*-phen. In general, the $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) complexes were synthesized by refluxing 0.5 g of $M(CO)_4$(X-*o*-phen) and 0.5 g of $P(OC_6H_5)_3$ in a suitable solvent.[3,4] For M = Cr or Mo, the reactants were refluxed for 20 min in 10 ml of benzene. The crystals which separated on cooling were filtered and washed with pentane. For M = W, the reactants were refluxed in 10 ml of xylene for 2 hr. The product was isolated as indicated for the Cr and Mo complexes. All complexes were identified by their infrared spectra in the C–O stretching region which exhibited three strong absorptions in the general ranges of 1930–1940, 1830–1840, and 1790–1805 cm^{-1}. The reaction products, $M(CO)_3[P(n\text{-}C_4H_9)_3]$(X-*o*-phen), were also identified by their spectra which were very similar to those of the reactant complexes. The expected lower C–O stretching frequencies of the products occurred at approximately 1890–1900, 1785–1800, and 1765–1775 cm^{-1}.

Kinetic Measurements.—The rates of reaction were determined by observing the rate of growth of a product absorption in the visible region of the spectrum. Table I shows the wavelengths of maximum absorption in this region for the reactant and product complexes. The reactions were carried out in a two-legged, foil-wrapped flask. A solution of the reactant complex was introduced into one leg and the $P(n\text{-}C_4H_9)_3$ solution into the other. The flask was purged with nitrogen gas, sealed with a serum cap, and thermostated at the desired temperature for 15 min. The solutions were thoroughly mixed by repeatedly tilting the flask. In these reaction mixtures the $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) concentration was approximately 3×10^{-4} *M*, and the $P(n\text{-}C_4H_9)_3$ concentration ranged from 1 to 8×10^{-2} *M*. Samples were withdrawn from the flask periodically with a syringe; their absorbances were measured at the wavelength of the product maximum on a Beckman DB-G spectrophotometer. An isosbestic point was observed for all reactions. Because it was difficult to obtain reliable A_∞ readings as a result of some product decomposition, the Guggenheim method was used to obtain the first-order rate constants. Hence, plots of ln $(A_t - A_{t+\tau})$, where τ was 2 or 3 half-lives, *vs.* time were used to obtain first-order rate constants. Average deviations of these constants were 5% or less. In the absence of $P(n\text{-}C_4H_9)_3$, the $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) decomposed at a rate which was approximately half that of the reaction with $P(n\text{-}C_4H_9)_3$. Addition of $P(OC_6H_5)_3$ to the complex solution diminished the rate of decomposition by a factor of approximately 6. Since the rate of reaction with $P(n\text{-}C_4H_9)_3$ was the same in the presence and absence of $P(OC_6H_5)_3$, it is assumed that any decomposition which might occur does not interfere with the reaction rate measurements.

TABLE I

MAXIMA (mμ) IN VISIBLE SPECTRA OF $M(CO)_3(L)$(X-*o*-phen) IN CHLOROBENZENE SOLVENT

	$Cr(CO)_3(L)$-(X-*o*-phen)		$Mo(CO)_3(L)$-(X-*o*-phen)		$W(CO)_3(L)$-(X-*o*-phen)	
X-*o*-phen	$P(OC_6H_5)_3$	$P(n\text{-}C_4H_9)_3$	$P(OC_6H_5)_3$	$P(n\text{-}C_4H_9)_3$	$P(OC_6H_5)_3$	$P(n\text{-}C_4H_9)_3$
5-Nitro	610	680	540	600		
4,7-Diphenyl	590	660	533	608	545	575
Unsubstituted	565	650	518	595	540	570
3,4,7,8-Tetramethyl	535	590	483	545	500	520

Results and Discussion

Like the reaction of $M(CO)_4$(X-*o*-phen) with phosphines and phosphites,[1,2] reaction 1 follows a two-term rate law

$$\text{rate} = (k_1 + k_2[P(n\text{-}C_4H_9)_3])[M(CO)_3[P(OC_6H_5)_3](\text{X-}o\text{-phen})]$$

Only for the reactions of $Mo(CO)_3[P(OC_6H_5)_3]$(*o*-phen) and $Mo(CO)_3[P(OC_6H_5)_3]$(5-NO_2-*o*-phen) were the k_2 terms large enough to be observed; even in these cases k_2 is very small. Values of k_1 and k_2 (where measurable) are given in Table II. The k_1 term implies that substitution occurs by an SN1 mechanism in which the rate-determining step involves breaking of the M–$P(OC_6H_5)_3$ bond. The k_2 term suggests an SN2 path in which the rate-determining step involves $P(n\text{-}C_4H_9)_3$ attack on the metal atom.

TABLE II

RATE CONSTANTS FOR REACTION OF $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) ACCORDING TO EQ 1 IN CHLOROBENZENE SOLVENT

	10^4k_1, sec^{-1}		
	M = Cr	M = Mo	M = W
X-*o*-phen	29.8°	29.8°	80.4°
5-Nitro (3.57)[a]	1.73 (1.10)[d]	0.75[b] (0.600)[d]	... (1.01)[d]
4,7-Diphenyl (4.84)	4.85 (2.65)	1.03 (1.09)	2.66
Unsubstituted (4.86)	4.61 (2.71)	0.76[c] (1.14)	1.79 (1.63)
3,4,7,8-Tetramethyl (6.31)	18.9 (6.12)	1.90 (2.01)	5.28 (3.76)

[a] pK_a of X-*o*-phen in parentheses: A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956). [b] $k_2 = 3.1 \times 10^{-4}$ M^{-1} sec^{-1}. [c] $k_2 = 0.322 \times 10^{-4}$ M^{-1} sec^{-1}. [d] 10^4k_1 for CO dissociation from $M(CO)_4$(X-*o*-phen), at 47.9° for M = Cr and Mo and 114.0° for W.[1,2]

For the k_1 term, the rate of dissociation of $P(OC_6H_5)_3$ from $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) is much faster than CO dissociation from the analogous $M(CO)_4$(X-*o*-phen) complex (Table II). These reactions have roughly the same rate constants when the former reactions are carried out at temperatures 20–30° lower than those of the latter. This suggests that $P(OC_6H_5)_3$ is less tightly bonded than is CO to the $M(CO)_3$(X-*o*-phen) moiety. This is supported by an equilibrium study of the reaction

$$Mo(CO)_4(o\text{-phen}) + P(OC_6H_5)_3 \rightleftharpoons Mo(CO)_3[P(OC_6H_5)_3](o\text{-phen}) + CO$$

The small value of the equilibrium constant (<0.05) also suggests that CO is more strongly bonded to Mo than is $P(OC_6H_5)_3$.[5]

Aside from the difference in rates of $P(OC_6H_5)_3$ and CO dissociation, the reactivities of the $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) and $M(CO)_4$(X-*o*-phen) complexes are remarkably similar. For example, in both sets of compounds, the rates of CO and $P(OC_6H_5)_3$ dissociation decrease with M in the order: Cr > Mo ≫ W. Also in both series, k_1 increases as the basicity of the substituted *o*-phenanthroline increases. Not only is the trend the same, but also the magnitude of change in the rate of dissociation of $P(OC_6H_5)_3$ and CO is very

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[3] L. W. Houk and G. R. Dobson, *J. Chem. Soc., A*, 317 (1966).

[4] L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966).

[5] J. R. Graham and R. J. Angelici, unpublished results.

similar (Table II). That a variation in the nature of X-*o*-phen affects the rate of M–$P(OC_6H_5)_3$ and M–CO bond breaking in the same way suggests either that these bonds are affected in much the same way by a change in X-*o*-phen or that the rates are largely determined by the extent of stabilization of the transition state by X-*o*-phen and the nature of the M–L bond is of relatively little importance. Although there is no direct evidence for it, it seems improbable that the M–$P(OC_6H_5)_3$ and M–CO bonds would be weakened to the same extent by an increase in the basicity of X-*o*-phen. If the M–$P(OC_6H_5)_3$ bond has greater σ- and less π-bond character than does the M–CO bond, the more strongly electron-donating *o*-phenanthrolines should weaken the M–$P(OC_6H_5)_3$ bond more than the M–CO bond. On the contrary, the rates of both types of complexes depend on X-*o*-phen in much the same way. It appears that the *o*-phenanthroline strongly influences the relative rate of M–L dissociation whether L is $P(OC_6H_5)_3$ or CO. This influence might be attributed to the ability of X-*o*-phen to stabilize the transition state. The faster rates of L dissociation in complexes containing the more basic X-*o*-phen groups suggests that stabilization of the transition state is greater in these cases. This stabilization may result from the greater capacity of the basic X-*o*-phen groups to provide electron density to the metal during the process of L dissociation. If the magnitude of these stabilizations is large compared to changes in the M–L bond strength, the rates of reaction will be dominated by the nature of the *o*-phenanthroline. Hence, a very large transition-state stabilization by X-*o*-phen not only accounts for the similar effects of X-*o*-phen on the rates of reaction of $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) and $M(CO)_4$(X-*o*-phen) but also accounts for the unusually fast rates of CO dissociation from $M(CO)_4$(X-*o*-phen) as compared to $M(CO)_6$.[1,6]

Finally it should be noted that the reactions of $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) proceed almost exclusively by an SN1 mechanism, whereas an SN2 mechanism carries an appreciable fraction of the reaction of $M(CO)_4$(X-*o*-phen). The diminished role of $P(n\text{-}C_4H_9)_3$ attack in the present reactions may be attributed to the steric hindrance of the $P(OC_6H_5)_3$ group in the complex. Taken together with the faster rate of $P(OC_6H_5)_3$ dissociation, the rate of $P(n\text{-}C_4H_9)_3$ attack thus becomes very small compared to the rate of $P(OC_6H_5)_3$ dissociation. Only for the complexes $Mo(CO)_3[P(OC_6H_5)_3]$(5-NO_2-*o*-phen) and $Mo(CO)_3[P(OC_6H_5)_3]$(*o*-phen) were k_2 terms established in the rate law. As noted earlier[2] for the $Mo(CO)_4$(X-*o*-phen) complexes, nucleophilic attack occurs more rapidly on the complex bearing the less basic 5-NO_2-*o*-phen ligand than on that containing *o*-phen. It should be emphasized that the k_2 values in the present study are small, and their absence in the $W(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) reactions could be caused by a small change in the activation parameters of the SN1 or SN2 paths.

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An Outer-Sphere Charge-Transfer Transition in Tris(ethylenediamine)ruthenium(III) Iodide

By Sr. Helen Elsbernd[1] and James K. Beattie

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Charge-transfer bands in the electronic spectra of coordination compounds are of two types. The more common is due to the transfer of an electron from a ligand to the central metal atom, or *vice versa*. The other involves groups outside the inner coordination sphere of the metal. Few examples of the latter have been reported. The intense ultraviolet bands that appear in the solution spectra of hexaamminecobalt(III)[2–4] and hexaamminechromium(III)[4] complex ions upon addition of halide, thiocyanate, and other anions have been attributed to charge transfer from the anion to the complex cation. Similar outer-sphere charge-transfer transitions have been suggested to account for the spectra observed for a series of salts of $Cr(bipy)_2Cl_2^+$ and $Cr(phen)_2Cl_2^+$ with various anions.[5]

We wish to report that both the salt and the ion pair of iodide with $Ru(en)_3^{3+}$ are striking examples of this outer-sphere charge-transfer phenomenon. The charge-transfer transition is of sufficiently low energy that the absorption occurs as a well-defined band in the visible region of the spectrum. This results in a highly unusual situation with the charge-transfer transition of considerably lower energy than the first d–d transition of the complex.

Experimental Section

Materials.—$[Ru(en)_3]I_3$ was prepared and recrystallized by the method of Meyer.[6] In this procedure $[Ru(en)_3]ZnCl_4$ was oxidized with iodine and dark purple crystals were obtained by the addition of a sodium iodide solution. *Anal.* Calcd for $C_6H_{24}N_6I_3Ru$: C, 10.89; H, 3.65; N, 12.69; I, 57.50. Found: C, 10.94; H, 3.66; N, 12.36; I, 56.42.

The formulation of the product as $[Ru(en)_3]I_3$ was further checked by an ion-exchange technique. Under oxygen-free conditions a solution of known concentration was added to a Dowex 50W-X8 cation-exchange column in the hydrogen form. The eluent was titrated with sodium hydroxide and the charge per ruthenium atom was determined to be +3. All of the iodine present was found to be ionic iodide by titrating the acidified eluent solution with silver nitrate.

Crystals of $[Rh(en)_3]I_3$ doped with $[Ru(en)_3]I_3$ were obtained

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