

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF TURIN, TURIN, ITALY

Acetylenic Derivatives of Metal Carbonyls.

II. Carbon Monoxide Exchange with $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ Complexes

BY G. CETINI, O. GAMBINO, P. L. STANGHELLINI, AND G. A. VAGLIO

Received August 2, 1966

Exchange reactions of CO with some carbonyl compounds such as $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ in *n*-heptane solution were studied. The kinetic order and activation energies for exchange were determined. The rate constants are discussed in relation with the CO stretching frequencies and Taft's polar constants σ^* of R, R'. Results show an unusual relation between the nature of the Co-CO bond and the exchange rate.

Introduction

A kinetic study of CO exchange in metal carbonyl derivatives is an important method for investigating the significance of some factors with respect to the stabilities of the compounds, especially the M-CO bond.

The rates of substitution reactions may not be as satisfactory because they can be affected not only by the nature of the metal-ligand bond in the initial compound but also by the properties of the compound which is produced as a result of the reaction.

It was therefore decided to make a detailed and systematic study both of the substitution reactions (these now form the subject of another paper¹) and of the exchange reactions in a series of compounds of the type $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ which are derived from $\text{Co}_2(\text{CO})_8$ by its reaction¹⁻⁴ with various acetylene derivatives $\text{R}-\text{C}\equiv\text{C}-\text{R}'$. The following carbonyl compounds have been studied: $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CF}_3)_2$, $\text{Co}_2(\text{CO})_6\text{C}_2(\text{C}_6\text{H}_5)_2$, $\text{Co}_2(\text{CO})_6\text{C}_2(\text{COOCH}_3)_2$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{CH}_3\text{C}_6\text{H}_5$, $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_3)_2$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{HC}_6\text{H}_5$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}-\text{CH}_3$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$, and $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_2\text{Cl})_2$. A kinetic study of the CO exchange with $\text{Co}_2(\text{CO})_6\text{C}_2(\text{C}_6\text{H}_5)_2$ was reported previously by Keeley and Johnson⁵ and by Basolo and Wojcicki.⁶

The presence of different groups R and R' in the acetylene derivatives enables one to obtain a gradual change of the σ - and π -bonding abilities of the ligand and allows one therefore to study the influence which these ligands may have on the rates of exchange of the CO groups. These changes in R and R' also result in changes in the C-O stretching frequencies and were determined by examining the infrared spectra of the compounds.

The kinetic data are discussed in terms of the donor-acceptor capacities of the coordinated acetylene derivatives.

Experimental Section

Compounds and Solvents.—All compounds used were prepared and purified according to the methods described in the literature.¹⁻⁴

Their purity was checked by thin layer chromatography, infrared spectrophotometry, and combustion analysis. *n*-Heptane was purified by refluxing over sodium followed by fractional distillation.

The ¹⁴CO used in the experiments was supplied by the Radiochemical Centre of Amersham and was suitably diluted with inactive CO of a very high standard of purity, which had been previously dried by calcium chloride and silica gel columns. The argon used was purified in the same way.

Apparatus.—The apparatus used for the study of the exchange reaction between the carbonyl derivatives and the ¹⁴CO consisted of a simple vacuum line to which reaction ampoules, similar to one described by Cetini and co-workers,⁸ can be connected. The volume of the ampoules was measured separately and for each experiment a series of ampoules of constant volume was used. (In the case of variations in excess of 1% the necessary corrections were made.)

The experiments were carried out as follows: equal volumes of the metal carbonyl solutions in *n*-heptane were pipetted in the ampoules: these were connected to the line and after saturation by slow bubbling of CO for standard times radiocarbon monoxide (or mixtures of ¹⁴CO and argon in known compositions) was added and the ampoules were sealed. They were then placed in a thermostated bath ($\pm 0.1^\circ$) and kept in a state of continuous agitation.

At various times the ampoules were removed and their contents analyzed. Measurements of activity at equilibrium time were carried out on ampoules left in the thermostat for periods equivalent to 8-10 half-exchange times or on ampoules kept at higher temperatures for suitably long times.

Control experiments were also carried out in which the carbonyl compound, after labeling with radioactive CO, was exchanged. For each compound, infrared spectra in the carbonyl stretching region (2000-2100 cm^{-1}) were determined during the course of the kinetic study and compared with solutions of the same compound at the same concentration; in no case was any decomposition of the compound discovered. Light was excluded in all experiments. The solubility of CO at the temperature at which the ampoules were filled (25°) is reported in the literature.⁹ Solubility at other temperatures was determined in our laboratory.

Measurement of Specific Activity.—Measurements of the specific activity of the gas phase and the solution of each ampoule were taken. Specific gas activity was determined by separate measurements of the mass and the activity of the CO. The gas was passed with He flow through a gas chromatograph

(1) G. Cetini, O. Gambino, R. Rossetti, and E. Sappa, unpublished work.

(2) H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **78**, 120 (1956).

(3) U. Krücker and W. Hübel, *Ber.*, **94**, 2829 (1961).

(4) J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *Chem. Ind. (London)*, 1137 (1960).

(5) D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).

(6) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961).

(7) M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964).

(8) G. Cetini, R. Ercoli, O. Gambino, and G. Vaglio, *Atti Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.*, **99**, 1123 (1964-1965).

(9) J. C. Gjaldbek, *Acta Chem. Scand.*, **7**, 623 (1952).

TABLE I
 RATES OF CO EXCHANGE WITH $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ IN *n*-HEPTANE AT 40.0°

R	R'	$\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$, mM	$(\text{CO})_t^a$, mM	$(\text{CO})_t^b$, mmoles	$t_{1/2}$, hr	10^7R , M sec ⁻¹	10^6k , sec ⁻¹
$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	8.22	8.50	1.05	7.2	8.9	10.9
CH_3	CH_3	8.22	8.50	0.867	11.7	5.18	6.32
		8.22	4.12	0.457	8.75	5.21	6.34
CH_3	C_6H_5	8.22	8.50	1.02	13.7	4.64	5.66
C_6H_5	C_6H_5	8.22	8.50	1.05	14.25	4.54	5.54
		12.31	4.05	0.495	8.75	6.50	5.30
		4.32	4.10	0.498	13.4	2.40	5.51
H	C_6H_5	8.22	8.50	0.99	21.5	2.95	3.58
		8.22	4.80	0.605	16.75	3.11	3.77
H	CH_3	8.22	8.50	0.93	21.2	2.57	3.56
		8.22	3.95	0.450	16.5	2.72	3.28
H	H	8.22	8.50	0.928	62.5	1.00	1.21
		13.15	4.45	0.485	34.4	1.69	1.29
CH_2Cl	CH_2Cl	7.94	8.50	0.98	83.8	0.735	0.93
COOCH_3	COOCH_3	8.22	8.50	0.97	299.5	0.208	0.255
CF_3	CF_3	8.22	8.50	0.890	1020	0.060	0.073
		8.22	3.72	0.484	750	0.063	0.076

^a Dissolved CO. ^b Total CO in each ampoule.

column packed with molecular sieves. On exit it was suitably mixed with argon and passed into an ionization flow chamber.

The apparatus consists of a Model Erba chromatograph, with thermal conductivity detectors, and a Nuclear Chicago Corp. ionization flow chamber and Model 6000 electrometer. The determination of the specific activity of the solution was carried out by a Tricarb Model 314 EX liquid scintillation spectrometer of the Packard Instrument Co.

The scintillator used was a toluene solution of 2,5-diphenyl-oxazole (PPO) (4 g/l.) and 1,4-di[2-(5-phenyloxazolyl)]benzene (POPOP) (0.05 g/l.).

Infrared spectra were recorded using a Beckman Model IR7 double-beam spectrophotometer with sodium chloride optics.

Treatment of the Data.—In all the experiments linear plots of $\log(1 - F)$ vs. time were obtained and thus all the reactions studied follow McKay's equation.¹⁰ F , the exchange fraction, is given by $(A_0 - A_t)/(A_0 - A_\infty)$ for measurements made on the initially labeled compounds and A'_t/A'_∞ for measurements made on the initially inactive compound, where A_0 , A_t , and A_∞ represent the specific activities at time 0, at time t , and at equilibrium time of initially labeled compound, and A'_t and A'_∞ represent the specific activities at time t and at equilibrium time of initially inactive compound.

The rate of exchange is calculated by the equation

$$R = \frac{0.693}{t_{1/2}} \frac{x[\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'][\text{CO}]_t}{x[\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'] + [\text{CO}]_t}$$

where x is the number of exchangeable CO groups in the carbonyl derivative and $[\text{CO}]_t$ is the total molar concentration of CO expressed as though all the CO was in solution.

The orders of reaction a and b with respect to the two reagents are calculated and also the specific reaction rate on the basis of the relationship

$$R = k[\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}']^a[\text{CO}]^b$$

Results

In some preliminary experiments the correspondence between the experimental and the theoretical values of A_∞ and A'_∞ , calculated on the basis of the exchange of all six carbonyl groups, was determined. It was found that under our conditions all six CO groups are equivalent.

The kinetic order of exchange was determined in experiments conducted at 40.0° on the following com-

plexes: $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{HCH}_3$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{HC}_6\text{H}_5$, $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_3)_2$, $\text{Co}_2(\text{CO})_6\text{C}_2(\text{C}_6\text{H}_5)_2$, and $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CF}_3)_2$. The data show a first-order dependence on the carbonyl concentration and no dependence on CO concentration.

The influence of the two substituents R and R' on the exchange rate was determined by measuring the rate constants of the different complexes at a temperature of 40.0°. It will be noted that the rate constants decrease in the following order: $(\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2)_2 > (\text{CH}_3)_2 > \text{CH}_3\text{C}_6\text{H}_5 > (\text{C}_6\text{H}_5)_2 > \text{HC}_6\text{H}_5 > \text{HCH}_3 > \text{H}_2 > (\text{CH}_2\text{Cl})_2 > (\text{COOCH}_3)_2 > (\text{CF}_3)_2$. The results are tabulated in Table I. Experimental values with complex concentration 8.22 mM (for $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_2\text{Cl})_2$ 7.94 mM) and CO concentration 8.50 mM are represented in Figure 1. The effect of the temperature on k is determined by experiments carried out in the range 32.0–60.4°. From these data the activation energies and entropies are calculated. The results are given in Table II.

 TABLE II
 DATA ON THE CO EXCHANGE REACTION WITH
 $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ IN *n*-HEPTANE

	Temp, °C	10^6k , sec ⁻¹	E_a , kcal mole ⁻¹	ΔS^\ddagger , cal mole ⁻¹ deg ⁻¹
$\text{Co}_2(\text{CO})_6\text{C}_2(\text{C}_6\text{H}_5)_2$	32.0	1.58		
	40.0	5.45		
	48.0	18.5	29.9	15.4
$\text{Co}_2(\text{CO})_6\text{C}_2\text{HC}_6\text{H}_5$	32.0	1.00		
	40.0	3.68		
	48.0	12.2	30.4	16.2
$\text{Co}_2(\text{CO})_6\text{C}_2(\text{CF}_3)_2$	40.0	0.0745		
	50.0	0.396		
	60.4	2.06	33.8	19.2

Discussion

The first observation that can be made about the series of carbonyls examined is that there are regular variations in the rate constant k in relation to the groups R and R'. It can be seen for example that CO

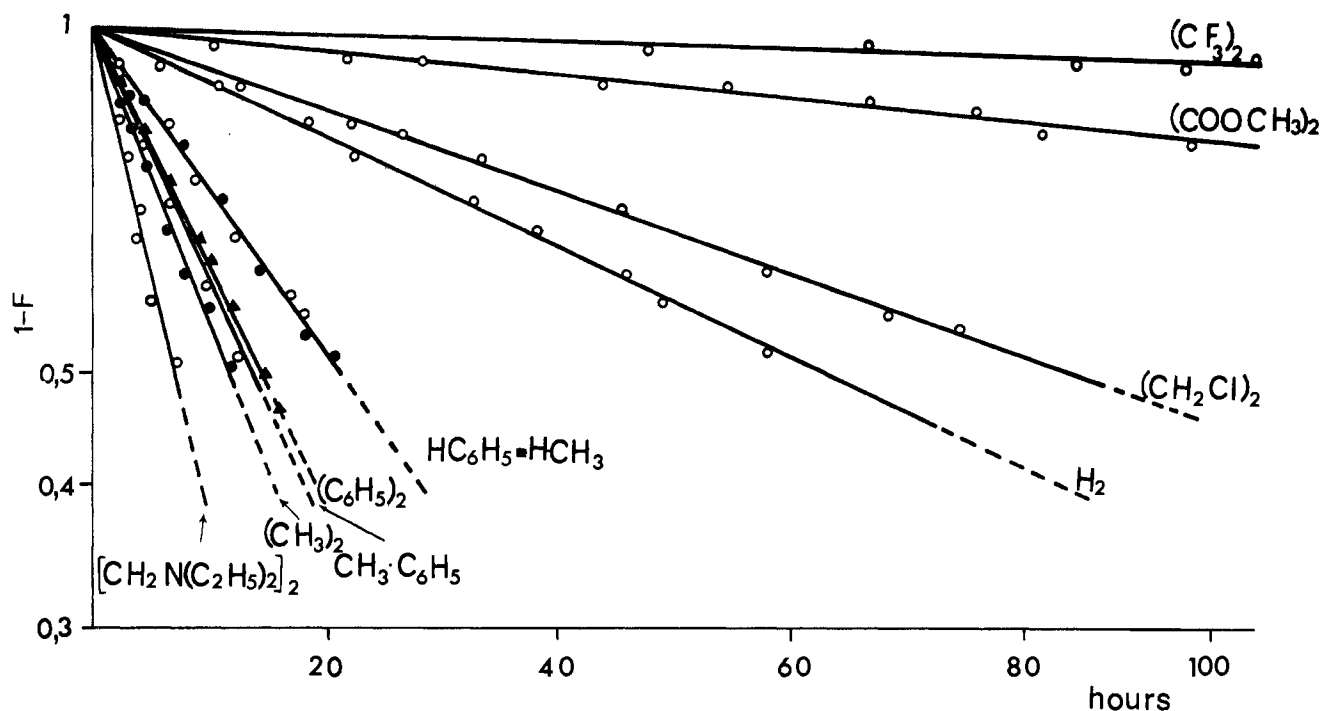


Figure 1.

TABLE III

	k , $\nu_{\text{C-O}}$, AND $\sigma^*_{\text{R}} + \sigma^*_{\text{R}'}$ VALUES FOR VARIOUS $\text{Co}_2(\text{CO})_8\text{C}_2\text{RR}'$ COMPOUNDS INVESTIGATED										
R	$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	CH_3	CH_3	C_6H_5	H	H	H	CH_2Cl	COOCH_3	CF_3	
R'	$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	CH_3	C_6H_5	C_6H_5	C_6H_5	CH_3	H	CH_2Cl	COOCH_3	CF_3	
$10^6 k$, sec^{-1}	10.9	6.3	5.66	5.45	3.67	3.42	1.24	0.93	0.255	0.0745	
$\nu_{\text{C-O}}$ in											
<i>n</i> -heptane, cm^{-1}	2088.5	2090.0	2091.0	2090.5	2094.5	2094.5	2099.5	2102.5	2112.0	2122.5	
$\sigma^*_{\text{R}} + \sigma^*_{\text{R}'}$		0.000	0.600	1.200	1.090	0.490	0.980	2.100	4.00	5.8 ^a	

^a $\sigma^*_{\text{CF}_3}$ is calculated by extrapolation from the series CH_3 , CH_2F , CHF_2 (see ref 7).

exchange is more favored by the CH_3 group than by the C_6H_5 group and more by the latter than by H. This is established by the constant decrease of k in the series $(\text{CH}_2)_2 > \text{HCH}_3 > \text{H}_2$; $(\text{C}_6\text{H}_5)_2 > \text{HC}_6\text{H}_5 > \text{H}_2$; $(\text{CH}_3)_2 > \text{CH}_3\text{C}_6\text{H}_5 \cong (\text{C}_6\text{H}_5)_2$. The effect is larger for the first series than it is for the last.

The CO stretching frequencies also show a gradual variation of $\nu_{\text{C-O}}$ with changes in the groups R, R' (see Table III). The Ingold-Taft polar constants σ^{*11} of these groups show a linear correlation with the values of $\nu_{\text{C-O}}$ ¹² (Figure 2). This is in accord with the earlier observations of Bigorgne⁷ and his hypothesis that, since the σ^* values are related to the inductive effect of the groups, the shifts in frequencies can be mainly attributed to this effect.

The possibility of a mesomeric effect, superposed on the inductive effect and of opposite sign, cannot be excluded. Perhaps the mesomeric effect, which can generally be ignored in view of the dominant inductive effect, is responsible for the behavior of the C_6H_5 group being analogous to that of the CH_3 group.

An examination of the $\nu_{\text{C-O}}$ shift in the different compounds reveals that an increase in electronegativity

(11) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, New York, N. Y., 1956, p 619.

(12) We have reported the highest CO stretching frequencies of each compound. All the characteristic $\nu_{\text{C-O}}$, however, follow a similar relationship.

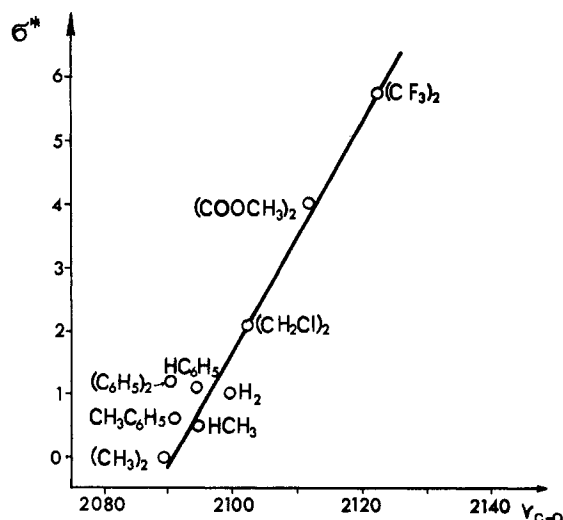


Figure 2.

of the group shifts these frequencies to higher values. Thus, in going from $(\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2)$ to $(\text{CF}_3)_2$, the order of the C-O bond increases, which suggests that the order of the Co-CO bond decreases.

We have related the rate constant k with the values of $\nu_{\text{C-O}}$ (Figure 3) and have observed that $\log k$ decreases linearly with increasing $\nu_{\text{C-O}}$.

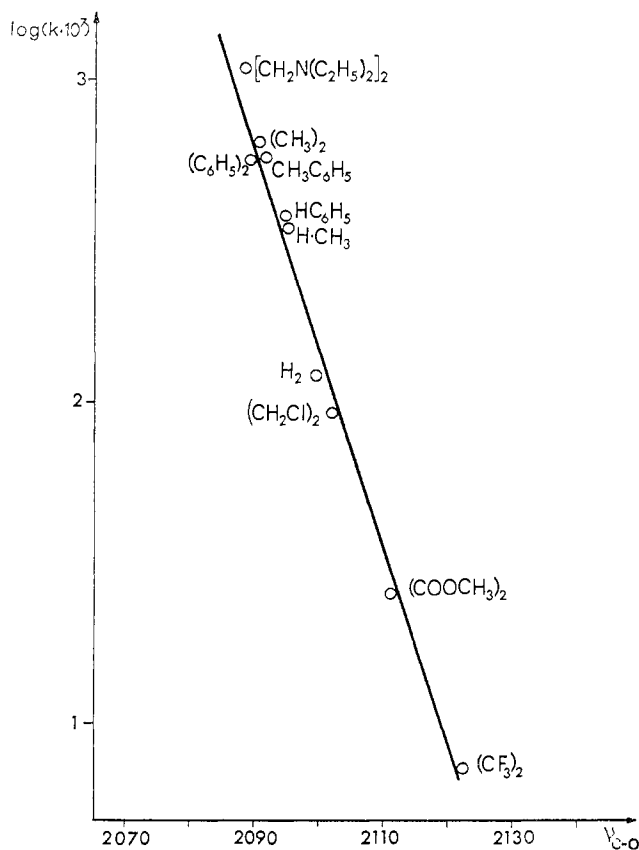


Figure 3.

Since our results show that the reaction is first order in carbonyl compound and zero order in carbon monoxide, the rate-determining step should be the dissociation of a CO group from the carbonyl. This is in agreement with the values of the activation energies and entropies which are typical for such a process.

One would therefore expect to find a behavior completely opposite to that observed, *i.e.*, a rate constant increasing in the direction $(\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2)_2 \rightarrow (\text{CF}_3)_2$, this being the direction in which the Co-CO bond decreases.

A possible explanation of this result, from the kinetic point of view, follows if we assume that the reaction occurs by loosening, in the first stage, of the acetylene-Co bond. This stage is followed by the isotopic exchange in the activated complex *via* addition of ^{14}CO , splitting of CO groups, and rearrangement of the molecule for re-formation of the acetylene-Co bond. In fact, derivatives of these acetylenic compounds with a greater number of CO groups are already known.^{13,14}

Therefore the over-all rate of exchange reaction decreases with the increasing strength of the acetylene-Co bond, strictly related to the increase of the electron-acceptor power of the acetylene groups. We necessarily conclude that casual factors must be excluded but also that such dependence must be explained with respect to the structure and the nature of such compounds. Exactly the opposite correlation was reported earlier¹⁵ as well as one similar to that reported here.¹⁶

Acknowledgment.—This work was carried out under the auspices and with the financial support of the Italian Consiglio Nazionale delle Ricerche (C.N.R.). Stimulating discussions with Professors F. Basolo and F. Calderazzo are gratefully acknowledged.

(13) H. W. Sternberg, J. G. Shukys, C. D. Donne, R. Markby, R. A. Friedel, and I. Wender, *J. Am. Chem. Soc.*, **81**, 2339 (1959).

(14) D. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

(15) A. T. Brault, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, **3**, 770 (1964).

(16) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586, 5590 (1965).