transport of the americium γ activity. Likewise, when the HF suspension was heated gently to 50–60 °C for approximately 1 h in the presence of KrF_2, there was no evidence for the formation of AmF_6. A similar reaction involving 95% PuO_2/5% AmO_2 powder also gave no evidence for the formation of americium hexafluoride.

Results and Discussion

The experiments described above demonstrate conclusively that not only uranium and neptunium, as previously reported,[7-10] but also plutonium substrates can be converted to volatile hexafluorides by using KrF_2. Krypton difluoride thus becomes only the *second* reported molecular agent for plutonium volatilization at room temperature or below. The experiments not only confirm that KrF_2 solutions in anhydrous HF form UF_6 and NpF_6 from lower valent solids but also demonstrate that UF_6, NpF_6, *and* PuF_6 can be produced from solid substrates by using *gaseous* KrF_2. A noteworthy feature of the KrF_2 treatments described above is that violent and unpredictable decomposition has *not* been observed, as is seen occasionally with O_2F_2.[5,6,13]

In agreement with the reports of Soviet workers[14] but in contrast to other reports,[15] our experiments indicate a surprisingly long lifetime of KrF_2 in metal and glass systems. Figure 1 illustrates the growth of PuF_6 and disappearance of KrF_2 with time in an essentially all-metal recirculating loop. The disappearance of PuF_6 after 20 h is due to decomposition onto the metal surface in the absence of KrF_2. These experiments unequivocally demonstrate the possibility of generating PuF_6 in practical process systems.

Experiment 2 demonstrates that NpF_6 is preferentially evolved when both Np and Pu substrates are present. While it is possible that the formation of NpF_6 is kinetically as well as thermodynamically favored over PuF_6, it is also clear that PuF_6 will fluorinate Np substrates. During one KrF_2 treatment, both NpF_6 and PuF_6 were observed with KrF_2 still present, but with time the NpF_6 absorbance increased while the PuF_6 and KrF_2 absorbances disappeared. This suggests that NpF_6 and PuF_6 could be formed at comparable rates and that a subsequent reaction occurs between PuF_6 and the neptunium solid to generate NpF_6 and PuF_4.

Treatment of U_3O_8 powder with a KrF_2/HF solution at room temperature provides slow but quantitative conversion to UF_6 with only traces of easily separated gaseous impurities. With highly refractory UO_2 powder derived from the crushing of fuel pellets, the conversion rate and yield were much less. Reaction rates with uranium fluoride/oxyfluoride residues arising from UF_6 treatment of an unconditioned metal storage tube, on the other hand, appear to be much faster.

Soviet workers have reported the preparation of thermally unstable AmF_6 by heating HF suspensions of AmF_4 with KrF_2.[7] However, in several experiments we were unable to identify such a species from similar treatments of americium oxides.

No attempts were made to identify actinide fluorides or oxyfluorides (e.g., MF_5, MOF_4, or MO_2F_2) in these reactions, although they very likely were formed as intermediates. Such intermediates will be the focus of further work.

The ability of KrF_2 to volatilize actinides at ambient temperature and at moderate rates could have a significant impact in the areas of actinide recovery and decontamination, among many other potential applications. The enormously longer lifetime and nonviolent reactivity of KrF_2 compared to the case of O_2F_2 should more than offset its lower reaction rate for some applications. Optimization of reaction variables (reactor design, solvent, stoichiometry, temperature, etc.) should improve the overall yield of the hexafluorides.

Acknowledgment. We are grateful to Dr. J. G. Malm, Dr. B. I. Swanson, and Dr. R. A. Penneman for many helpful discussions and encouragement throughout the course of this work. The authors are indebted for the use of the $^{243}AmO_2$ to the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, through the transplutonium element production facilities at Oak Ridge National Laboratory. We thank Bruce Neuman, Westinghouse Electric Corp., for providing the UO_2 fuel pellets.

Registry No. KrF_2, 13773-81-4; U_3O_8, 1344-59-8; PuF_4, 13709-56-3; PuF_6, 13693-06-6; NbF_6, 14521-05-2; UF_6, 7783-81-5; $^{243}AmO_2$, 53754-11-3.

---

[14] Prusakov, V. N.; Sokolov, V. B. *At. Energ.* **1971**, *3*, 990.

[15] Gunn, S. *J. Am. Chem. Soc.* **1966**, *88*, 5924; *J. Phys. Chem.* **1967**, *71*, 2934.

Contribution from the Department of Chemistry,
State University of New York at Binghamton, Binghamton, New York 13901

Photolysis of Group 6 Metal Hexacarbonyl Solutions Containing Diimine Ligands. Spectral Characterization and Reaction Kinetics of a Photoproduced Intermediate, Monodentate $M(CO)_5$(diimine)

Mark J. Schadt and Alistair J. Lees*

Received June 14, 1985

Electronic absorption spectra have been obtained immediately following the photolysis of $M(CO)_6$ solutions containing diimine ligands (1,10-phenanthroline, 2,2′-bipyridine, 1,4-diazabutadiene, or their derivatives) with the use of a microprocessor-controlled diode-array UV–visible spectrophotometer. The time-dependent spectra illustrate rapid formation of a reaction intermediate that is assigned to be $M(CO)_5L$, where L is a diimine ligand coordinated in a monodentate fashion. Monodentate $M(CO)_5L$ subsequently extrudes CO thermally via a first-order kinetic process to form stable $M(CO)_4L$. No discernable $M(CO)_5L$ intermediates were observed when L = 1,10-phenanthroline (phen) or a phen derivative consistent with the rigid coplanar nature of these ligands. In contrast, the chelation of $M(CO)_5L$ complexes, where L = 2,2′-bipyridine, 1,4-diazabutadiene, or derivatives, proceeds with considerably slower reaction rates. The rate data are interpreted in terms of the stereochemistry of the monodentate intermediate. For a given ligand, the reaction rate decreases in the sequence Mo > Cr > W, analogous to the order of CO release in $M(CO)_6$; this ordering suggests that the predominant barrier to chelation involves breaking of the M–C bond. Derived activation energy parameters indicate that the chelation reaction is enthalpy-controlled. The marked dependence of reaction rate on diimine and resulting negative activation entropy values imply that the chelation mechanism proceeds with a substantial associative component.

Introduction

The photochemistry of metal carbonyl complexes has, for a number of years, received a great deal of attention.[1] Recently, this interest has been further stimulated because of the importance of these molecules in the design of homogeneous catalytic processes and as models in mechanistic organometallic chemistry.[2-5] Despite

---

[1] For an excellent review see: Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

[2] Salomon, R. G. *Tetrahedron* **1983**, *39*, 485.

[3] Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

0020-1669/86/1325-0672$01.50/0

extensive study of the ligand photosubstitution chemistry of metal carbonyls, relatively little quantitative information exists on the reactivity of their reaction intermediates, and direct spectral evidence for such species is most often lacking.

Intermediates formed upon photolysis of the group 6 hexacarbonyls are perhaps the most investigated. Several papers have appeared in the literature concerning the structure and solution of the photogenerated $\mathrm{M(CO)_5}$ species in a rigid-glass[6-8] or matrix environment.[9-13] More recently, pulse radiolysis[14] and flash photolysis[15-18] measurements have provided structural and kinetic information for this intermediate. These results have indicated that the ground state of $\mathrm{M(CO)_5}$ is square-pyramidal and extremely reactive, reacting with $\mathrm{N_2}$, CO, solvent, and $\mathrm{M(CO)_6}$ at rates near the diffusion limit. The reaction of $\mathrm{M(CO)_5}$ with solvent impurities has also been reported.[19,20]

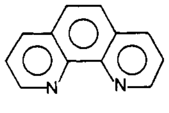
Photochemical formation of $\mathrm{M(CO)_4L}$ complexes, where M is Cr, Mo, or W and L is a bidentate ligand, is thought to proceed according to reactions 1 and 2. Evidence for the monodentate

$$\mathrm{M(CO)_6} \xrightarrow[\mathrm{L}]{h\nu} \mathrm{M(CO)_5L + CO} \tag{1}$$

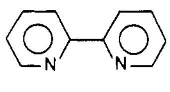
$$\mathrm{M(CO)_5L} \xrightarrow{\Delta} \mathrm{M(CO)_4L + CO} \tag{2}$$

intermediate $\mathrm{M(CO)_5L}$ was reported by Staal et al., for M = Cr or Mo and L = 1,4-diphenyl-1,4-diazabutadiene, who observed a green transient during the substitution reaction of the corresponding $\mathrm{M(CO)_5(THF)}$ (THF = tetrahydrofuran) complex with L at −60 °C.[21] This intermediate was observed to react rapidly at room temperature to form $\mathrm{M(CO)_4L}$ product. However, direct spectral evidence for the $\mathrm{M(CO)_5L}$ transient and quantitative reactivity measurements were not reported in this work. Recently though, rapid-scanning Fourier-transform infrared spectroscopy techniques have provided spectral evidence for the formation of $\mathrm{M(CO)_5L}$, where M is Cr or W and L is a 4,4′-dialkyl-2,2′-bipyridine ligand.[22] Furthermore, Connor et al. have isolated monodentate $\mathrm{M(CO)_5L}$ complexes, where M = Mo or W and L is a bidentate phosphorus or arsenic donor ligand, and determined the rate of their chelation reactions with the use of infrared spectroscopy.[23-25]

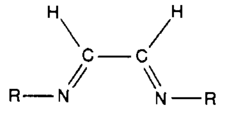
This paper reports further on our earlier communication describing monodentate reaction intermediates that are produced following photolysis of $\mathrm{W(CO)_6}$ solutions containing diimine ligands.[26] A full investigation of the group 6 hexacarbonyl complexes with three different classes of diimine ligands has been undertaken. The bidentate ligands studied here are 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), and 1,4-diazabutadiene (dab) or derivatives of these diimines. The UV–visible spectral results presented herein provide evidence for the formation of a $\mathrm{M(CO)_5L}$ complex (L is a diimine ligand that is coordinated in a monodentate fashion), which subsequently thermally extrudes CO to form $\mathrm{M(CO)_4L}$ product. Rate data and thermodynamic parameters are reported for these chelation reactions.



phen



bpy



dab

Experimental Section

Materials. The metal hexacarbonyls were purchased from Strem Chemical Co. and used without further purification. The ligands 1,10-phenanthroline (phen), 4,7-diphenyl-1,10-phenanthroline (4,7-$\mathrm{(C_6H_5)_2}$-phen), 5-nitro-1,10-phenanthroline (5-$\mathrm{NO_2}$-phen), 5-chloro-1,10-phenanthroline (5-Cl-phen), 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine [4,4′-$\mathrm{(CH_3)_2}$-bpy], and 4,4′-diphenyl-2,2′-bipyridine (4,4′-$\mathrm{(C_6H_5)_2}$-bpy) were commercially available at >99% purity and used without further purification. Starting materials, 4-*tert*-butylpyridine, cyclohexylamine, isopropylamine, *tert*-butylamine, phenylethylamine, and aqueous glyoxal (40%), were obtained in good purity from commercial sources. Spectroscopic grade benzene (J. T. Baker Chemical Co.) was further purified by absorptive filtration through Woelm basic alumina of activity grade 1 (ICN Pharmaceuticals Co., West Germany). Impurities in benzene were monitored by infrared spectroscopy on a Perkin-Elmer 283B spectrometer and by gas chromatography on a Carle Instruments Company Model 6500 gas chromatograph equipped with a polar column. All other solvents used were reagent grade. Nitrogen used in the purging experiments had been further purified to remove $\mathrm{H_2O}$ and $\mathrm{O_2}$ by passage through two 1 m × 2 cm tubes, the first containing dry $\mathrm{CaSO_4}$ and $\mathrm{P_2O_5}$ in alternating 20-cm lengths and the second containing a Cu catalyst (BASF R3-11, Chemical Dynamics Corp.). The catalyst was activated before use by heating to 120 °C while flushing with hydrogen. In this reduced form the catalyst effectively removes $\mathrm{O_2}$ from gases. *Caution*! The activated catalyst is pyrophoric.

Synthesis of Ligands. 4,4′-Di-*tert*-butyl-2,2′-bipyridine [4,4′-$\mathrm{(C_4H_9)_2}$-bpy] was prepared according to a literature proceeding for the ortho dehydration of pyridine derivatives over Raney nickel.[27] 4-*tert*-Butylpyridine (100 g) was refluxed over activated Al–Ni catalyst for 50 h. The flask contents were filtered hot and washed with hot 4-*tert*-butylpyridine. Upon cooling, a crystalline product was formed. Vacuum filtration followed by two successive recrystallizations from benzene yielded 2.3 g of colorless plates, mp 154–156 °C.

Preparation of the 1,4-disubstituted-1,4-diazabutadiene ligands was according to a previously reported method[28,29] with some modifications.

1,4-Di-*tert*-butyl-1,4-diazabutadiene [1,4-$\mathrm{(C_4H_9)_2}$-dab]. 4-*tert*-Butylamine (14.6 g, 0.2 mol) was added to a mixture of distilled water (300 mL) and acetone (50 mL) and cooled to 0 °C. Aqueous glyoxal (14.5 g, 0.1 mol) was diluted with distilled water (50 mL), cooled to 0 °C, and added dropwise to the amine solution with constant stirring. The resulting deep orange solution was kept at 0 °C for 2–3 h with occasional stirring. Vacuum filtration yielded white crystals, which were washed with cold (0 °C) water and then air-dried. The product was then dissolved in anhydrous diethyl ether and the aqueous layer discarded. Evaporation of the ether under anhydrous conditions gave 4.8 g (29% yield) of white crystals, mp 38–40 °C (lit.[29] 39–43 °C).

1,4-Diisopropyl-1,4-diazabutadiene [1,4-$\mathrm{(C_3H_7)_2}$-dab]. Isopropylamine (5.9 g, 0.1 mol) was reacted with aqueous glyoxal (7.3 g, 0.05 mol) according to the procedure described for 1,4-di-*tert*-butyl-1,4-diazabutadiene. This method gave 4.7 g (33.6% yield) of white crystalline prisms, mp 48–49 °C (lit.[29] 48–50 °C).

---

(4) Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* **1984**, *5*, 107.

(5) Henrici-Olive, G.; Olive, S. "Coordination and Catalysis"; Verlag-Chemie: New York, 1977.

(6) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *J. Am. Chem. Soc.* **1962**, *84*, 3589. *J. Am. Chem. Soc.* **1963**, *85*, 1013.

(7) Dobson, G. R. *J. Phys. Chem.* **1965**, *69*, 677.

(8) Tyler, D. R.; Petrylak, D. P. *J. Organomet. Chem.* **1981**, *212*, 389.

(9) Graham, M. A.; Rest, A. J.; Turner, J. J *J. Organomet. Chem.* **1970**, *24*, C54.

(10) Graham, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2939.

(11) Graham, M. A.; Perutz, R. N.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1972**, *34*, C34.

(12) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

(13) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 271.

(14) Flamigni, L. *Radiat. Phys. Chem.* **1979**, *13*, 133.

(15) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

(16) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381.

(17) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

(18) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1984**, *23*, 3830.

(19) Kelly, J. M.; Hermann, H.; Koerner von Gustorf, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105.

(20) Schadt, M. J.; Gresalfi, N. J.; Lees, A. J. *Inorg. Chem.* **1985**, *24*, 2942.

(21) Staal, L. H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1978**, *26*, 255.

(22) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 5784.

(23) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 347.

(24) Connor, J. A.; Hudson, G. A. *J. Organomet. Chem.* **1974**, *73*, 351.

(25) Connor, J. A.; Riley, P. I. *J. Organomet. Chem.* **1975**, *94*, 55.

(26) Schadt, M. J.; Gresalfi, N. J.; Lees, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 506.

(27) Badger, G. M.; Sasse, W. H. F. *J. Chem. Soc.* **1956**, 616.

(28) Hsieh, A. T. T.; West, B. O. *J. Organomet. Chem.* **1976**, *112*, 285.

(29) Kleigman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555.

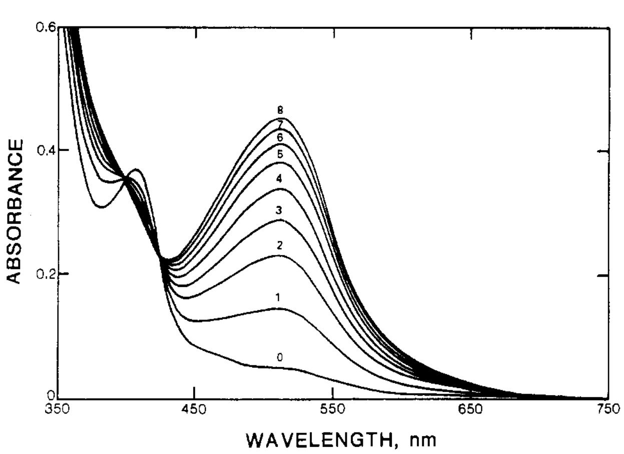


Figure 1. Absorption spectral sequence recorded following ~2-s UV irradiation of a deoxygenated solution of 5×10^{-4} M $W(CO)_6$ in benzene at 20 °C containing 10^{-2} M bpy: curve 0, initial spectrum recorded within 2 s after photolysis; curves 1–8, spectra at subsequent 15-s time intervals. The spectra illustrate the formation of $W(CO)_4(bpy)$ with its characteristic MLCT absorption maximum at 514 nm.

1,4-Dicyclohexyl-1,4-diazabutadiene [1,4-$(C_6H_{11})_2$-dab]. Cyclohexylamine (9.9 g, 0.1 mol) was added to distilled water (100 mL) at 0 °C. Aqueous glyoxal (7.3 g, 0.05 mol) was diluted with methanol (50 mL) and added dropwise to the amine solution, which was stirred constantly and maintained at 0 °C. The product formed as a white precipitate, which was isolated and purified by vacuum filtration and washed with cold (0 °C) methanol. Recrystallization from methanol gave 6.3 g (57% yield) of white plates, mp 146–148 °C (lit.[29] 145–147 °C).

1,4-Bis(phenylethyl)-1,4-diazabutadiene [1,4-$(C_8H_9)_2$-dab]. (Phenylethyl)amine (12.12 g, 0.1 mol) was diluted with acetone (50 mL) and cooled to 0 °C. Aqueous glyoxal (7.3 g, 0.05 mol) was combined with the amine solution, and a tan precipitate was collected by vacuum filtration. The product was purified by washing with cold (0 °C) acetone, giving 0.612 g (5% yield) of tan powder, mp 69–71 °C.

Synthesis of $M(CO)_4L$ Complexes (L = Diimine). Solid complexes were prepared by UV irradiation of isooctane solutions (250 mL) containing the parent hexacarbonyl (0.20 mmol) and excess diimine (0.25 mmol) with a 200-W Hg lamp. Typically the solution was irradiated for 30–45 min and then kept at 0 °C for 12 h to permit complete precipitation of $M(CO)_4L$. The product was obtained by vacuum filtration and purified by repeated washing with isooctane and, if necessary, by column chromatography on 80–200 mesh alumina (Fisher Scientific Co.). The infrared and UV–visible spectra of all the $M(CO)_4L$ complexes prepared are coincident with those obtained from products prepared by thermal routes.[30,31] All the complexes were fairly stable in the solid form and were kept in the dark under nitrogen at 0 °C.

Photolyses and Kinetic Studies. A typical experiment consisted of ~2-s UV excitation of a benzene solution (3 mL), which was 5×10^{-4} M in $M(CO)_6$ and 10^{-2} M in diimine. The solutions were deoxygenated prior to irradiation by purging with purified N_2 for 15 min. Approximately 1×10^{-4} M $M(CO)_6$ is photodissociated during the irradiation; this value was estimated from a determination of the incident light intensity from ferrioxalate actinometry[32] and the known quantum yield of $M(CO)_6$.[33] This photodissociation value was confirmed at the end of the kinetic experiment from the amount of product formed. Electronic absorption data were obtained on a microprocessor-controlled diode-array Hewlett-Packard 8450A spectrometer at each 1 nm in the 300–400-nm range and at each 2 nm in the 400–800-nm region. The initial spectrum was recorded within 4 s following photolysis, and subsequent spectra were stored on a Hewlett-Packard 82901M flexible disk drive unit at suitable intervals thereafter. The shortest acquisition time and time interval possible on this apparatus are 0.5 and 1 s, respectively.

Results and Discussion

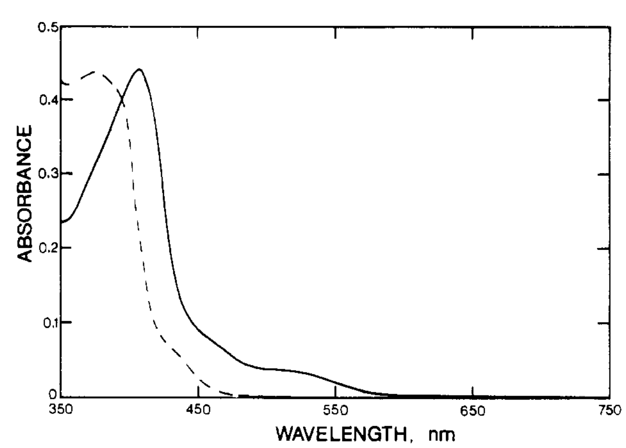


Figure 2. Difference absorption spectrum (–) obtained by subtracting spectral data of unphotolyzed solution (5×10^{-4} M $W(CO)_6$ and 10^{-2} M bpy in benzene) from curve 0 in Figure 1. This spectrum is assigned to monodentate $W(CO)_5(bpy)$. Spectral features of $W(CO)_5$(2-Phpy) (2-Phpy = 2-phenylpyridine) are included for comparison (- -). Absorptions are arbitrarily scaled to make maxima equal.

The spectral sequence obtained following ~2-s UV photolysis of a deoxygenated benzene solution at 20 °C containing 5×10^{-4} M $W(CO)_6$ and 10^{-2} M bpy is shown in Figure 1. In this experiment the initial spectrum was recorded approximately 2 s after light irradiation, and subsequent spectra were recorded at 15-s time intervals. It has been estimated that approximately 10^{-4} M $W(CO)_6$ is photodissociated (see Experimental Section). The formation of $W(CO)_4(bpy)$ as product was characterized by the growth of its intense metal-to-ligand charge-transfer (MLCT) transition at 514 nm (see Figure 1). Furthermore, this photogenerated thermal reaction appears to proceed uncomplicated by side or subsequent reactions as evidenced by the presence of sharp isosbestic points at 397 and 424 nm.

Reactions 3–5 are consistent with these spectral observations.

$$M(CO)_6 \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} M(CO)_5 + CO \tag{3}$$

$$M(CO)_5 \xrightarrow[L]{\Delta,\ \text{fast}} M(CO)_5L \tag{4}$$

$$M(CO)_5L \xrightarrow{\Delta,\ k_{obsd}} M(CO)_4L + CO \tag{5}$$

It has been previously shown that the initial photoproduct of $M(CO)_6$ (M = Cr, Mo, W) is $M(CO)_5$, which rapidly forms six-coordinate complexes with even weak donors such as N_2 or solvent at rates approaching the diffusion-controlled limit.[15-18] In the presence of a large excess of diimine it can be assumed that $M(CO)_5$ will complex rapidly. Thus, the reaction intermediate formed immediately following light excitation is thought to be a $M(CO)_5L$ species in which the normally bidentate ligand is coordinated in a monodentate fashion. Another possibility considered was that the monodentate intermediate was a coordinated solvent impurity complex. However, this seemed to be unlikely as photolyses took place in solutions of rigorously purified solvent (see Experimental Section) that contained an approximately 100-fold excess of diimine ligand. Moreover, two literature papers have appeared that report absorption data for $M(CO)_5$(impurity) species (M = Cr, Mo, or W), and these spectra are quite different from those of the monodentate complexes observed here.[19,20]

The reaction products $M(CO)_4L$ (M = Cr, Mo, and W) were isolated for each of the complexes in this study. Electronic absorption data in the 300–700-nm range and assignments for the $M(CO)_4$(diimine) complexes in benzene at 20 °C are summarized in Table I. For each complex the low-energy absorption is assigned to be a MLCT transition, whereas the higher energy components are attributed to be of d → d origin. These UV-visible spectra agree well with those of complexes of this type that have previously been prepared by thermal methods.[30,31] Each of the isolated complexes yielded a spectrum that was identical with that of the final spectrum (A_∞) recorded in the kinetic experiment.

The data storage and software facilities of the microprocessor-controlled diode-array spectrophotometer enabled subtraction

---

(30) tom Dieck, H.; Renk, I. W. *Angew. Chem.* **1970**, *82*, 805; *Chem. Ber.* **1971**, *104*, 110.
(31) Bock, H.; tom Dieck, H. *Angew. Chem.* **1966**, *78*, 549; *Chem. Ber.* **1967**, *100*, 228.
(32) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.
(33) Strohmeier, W.; von Hobe, D. *Chem. Ber.* **1961**, *94*, 761.

Table I. Electronic Absorption Spectral Data (nm) and Assignments for $M(CO)_4L$ Complexes in Benzene at 20 °C[a]

ligand (L)	$Cr(CO)_4L$	$Mo(CO)_4L$	$W(CO)_4L$
phen	330 (d → d), 410 (d → d)[b] 514 (MLCT)	337 (d → d), 400 (d → d)[b] 490 (MLCT)	340 (d → d), 396 (d → d)[b] 510 (MLCT)
4,7-$(C_6H_5)_2$-phen	333 (d → d), 410 (d → d)[b] 522 (MLCT)	339 (d → d), 395 (d → d)[b] 502 (MLCT)	349 (d → d), 388 (d → d)[b] 516 (MLCT)
5-Cl-phen	329 (d → d), 419 (d → d)[b] 534 (MLCT)	344 (d → d), 395 (d → d)[b] 502 (MLCT)	347 (d → d), 392 (d → d)[b] 520 (MLCT)
5-NO_2-phen	331 (d → d), 400 (d → d)[b] 550 (MLCT)	340 (d → d), 390 (d → d)[b] 512 (MLCT)	341 (d → d), 388 (d → d)[b] 532 (MLCT)
bpy[c]	333 (d → d), 383 (d → d)[b] 528 (MLCT)	361 (d → d), 382 (d → d)[b] 492 (MLCT)	364 (d → d), 387 (d → d)[b] 514 (MLCT)
4,4′-$(CH_3)_2$-bpy[c]	327 (d → d), 387 (d → d)[b] 516 (MLCT)	354 (d → d), 388 (d → d)[b] 482 (MLCT)	366 (d → d), 390 (d → d)[b] 500 (MLCT)
4,4′-$(C_4H_9)_2$-bpy[c]	334 (d → d), 384 (d → d)[b] 518 (MLCT)	350 (d → d), 388 (d → d)[b] 484 (MLCT)	359 (d → d), 387 (d → d)[b] 502 (MLCT)
4,4′-$(C_6H_5)_2$-bpy[c]	335 (d → d), 400 (d → d)[b] 550 (MLCT)	351 (d → d), 378 (d → d)[b] 512 (MLCT)	365 (d → d), 383 (d → d)[b] 530 (MLCT)
1,4-$(C_6H_{11})_2$-dab	390 (d → d) 562 (MLCT)	375 (d → d) 538 (MLCT)	372 (d → d) 536 (MLCT)
1,4-$(C_3H_7)_2$-dab	389 (d → d) 562 (MLCT)	373 (d → d) 538 (MLCT)	373 (d → d) 536 (MLCT)
1,4-$(C_4H_9)_2$-dab	396 (d → d) 562 (MLCT)	375 (d → d) 532 (MLCT)	375 (d → d) 540 (MLCT)
1,4-$(C_8H_9)_2$-dab[c]	395 (d → d) 564 (MLCT)	367 (d → d) 538 (MLCT)	382 (d → d) 534 (MLCT)

[a] Spectra obtained from solutions of the solid complexes. [b] Observed as a shoulder. [c] The chromium complexes of this ligand are only slightly soluble in benzene and exhibit thermal instability in room-temperature solutions. Absorption data reported were obtained within 5 s of dissolution.

Table II. Electronic Absorption Spectral Data (nm) and Assignments for $M(CO)_5L$ Complexes in Benzene at 20 °C[a,b]

ligand (L)	$Cr(CO)_5L$	$Mo(CO)_5L$	$W(CO)_5L$
bpy	402 (d → d)[c]	*d*	406 (d → d), 460 (d → d)[e]
4,4′-$(CH_3)_2$-bpy	406 (d → d)[c]	*d*	404 (d → d),[c] 462 (d → d)[e]
4,4′-$(C_4H_9)_2$-bpy	410 (d → d)[c]	*d*	402 (d → d),[c] 461 (d → d)[e]
4,4′-$(C_6H_5)_2$-bpy	404 (d → d)[c]	*d*	414 (d → d),[c] 465 (d → d)[e]
1,4-$(C_6H_{11})_2$-dab	400 (d → d)	384 (d → d)	394 (d → d), 427 (d → d)[e]
1,4-$(C_3H_7)_2$-dab	402 (d → d)	384 (d → d)	393 (d → d), 424 (d → d)[e]
1,4-$(C_4H_9)_2$-dab	410 (d → d)	380 (d → d)	385 (d → d), 425 (d → d)[e]
1,4-$(C_8H_9)_2$-dab	400 (d → d)	390 (d → d)	395 (d → d), 427 (d → d)[e]

[a] Difference spectra obtained from ~2-s UV photolysis of 5×10^{-4} M $M(CO)_6$ in benzene containing 1×10^{-2} M ligand. [b] Monodentate intermediates were not observed for any of the phenanthroline ligands. [c] An additional weak band, probably a d → d LF transition, is observed as a shoulder in the 340–360-nm range. Subtraction spectra obtained in this region contain large errors, which make assignment uncertain. [d] Intermediate not observed. [e] Observed as a shoulder.

Table III. Temperature Dependence of the First-Order Rate Constants Obtained from the Reaction of $\sim 1 \times 10^{-4}$ M $M(CO)_5L$ in Deoxygenated Benzene To Form $M(CO)_4L$ and CO[a]

ligand (L)	temp, °C	k_{obsd}, s^{-1}	
		Mo	W
bpy	10	>0.4[b]	1.09×10^{-2}
	20	>0.4[b]	3.86×10^{-2}
	30	>0.4[b]	1.33×10^{-1}
	40	>0.4[b]	3.05×10^{-1}
4,4′-$(CH_3)_2$-bpy	10	>0.4[b]	1.20×10^{-2}
	20	>0.4[b]	3.51×10^{-2}
	30	>0.4[b]	1.11×10^{-1}
	40	>0.4[b]	2.05×10^{-1}
4,4′-$(C_4H_9)_2$-bpy	10	>0.4[b]	6.39×10^{-3}
	20	>0.4[b]	1.58×10^{-2}
	30	>0.4[b]	4.74×10^{-2}
	40	>0.4[b]	1.24×10^{-1}
4,4′-$(C_6H_5)_2$-bpy	10	>0.4[b]	7.22×10^{-3}
	20	>0.4[b]	1.98×10^{-2}
	30	>0.4[b]	4.97×10^{-2}
	40	>0.4[b]	1.25×10^{-1}

[a] The $Cr(CO)_4L$ products are thermally unstable, and this leads to irreproducible chelation rate data. [b] Rate (k_{obsd}) was unobtainable on our instrumental time scale. This value represents a lower limit.

spectra to be obtained readily. Figure 2 illustrates the difference UV–visible absorption spectrum obtained by subtracting the spectral data of the unphotolyzed solution that contained $W(CO)_6$ and bpy from the data recorded immediately after photolysis. The features of this difference spectrum are characteristic of $W(CO)_5L$ complexes;[34] a comparison with the absorption spectrum of $W(CO)_5$(2-Phpy) (2-Phpy = 2-phenylpyridine) is shown in Figure 2. Consequently the absorptions of $W(CO)_5$(bpy) at 406 and 460 (sh) nm are assigned to be $^1A(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ and $^1A(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ ligand-field transitions, respectively.[34] The corresponding $^1A(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ transitions were not observable in the spectra of the chromium and molybdenum monodentate species consistent with the spin-forbidden assignment. The remaining weak absorption at 514 nm is attributed to a small amount of $W(CO)_4$(bpy) formed during the photolysis. Electronic absorption data recorded for all the monodentate intermediates observed are summarized in Table II.

Kinetic measurements have been carried out for the reaction in which $M(CO)_5$(diimine) extrudes CO to form $M(CO)_4$(diimine), eq 5. In each case the rate of this reaction was determined by monitoring the growth of the long-wavelength MLCT absorption of $M(CO)_4$(diimine) product. The growth from A_0 to A_∞ was exponential; that is, a plot of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ vs. time was linear, yielding slope = k_{obsd}. Here A_0 is defined as the initial absorbance, A_t is the absorbance at time t, and A_∞ is the final absorbance reached, all absorbance values being recorded at fixed wavelength in this region. Observed rate data were found to be unaffected by variations in the spectrophotometer acquisition time. Thus, source light from the diode-array UV–visible absorption spectrophotometer is concluded to have a negligible effect on the reaction kinetics. Reaction rates were also observed to be independent of ligand concentration over the 1×10^{-3} to 1×10^{-2} M range. Tables III and IV summarize all the first-order rate data (k_{obsd}) determined in this study. Each measurement is a mean

---

(34) (a) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105. (b) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154.

Table IV. Temperature Dependence of the First-Order Rate Constants Obtained from the Reaction of ~1 × 10^{-4} M $M(CO)_5L$ in Deoxygenated Benzene To Form $M(CO)_4L$ and CO

ligand (L)	temp, °C	k_{obsd}, s^{-1} Cr	Mo	W
1,4-$(C_6H_{11})_2$-dab	10	3.65×10^{-5}	2.13×10^{-4}	1.16×10^{-5}
	20	1.41×10^{-4}	6.50×10^{-4}	4.33×10^{-5}
	30	3.40×10^{-4}	1.73×10^{-3}	1.34×10^{-4}
	40	8.29×10^{-4}	4.05×10^{-3}	3.38×10^{-4}
1,4-$(C_3H_7)_2$-dab	10		2.14×10^{-4}	
	20	1.09×10^{-4}	6.99×10^{-4}	1.79×10^{-5}
	30	3.03×10^{-4}	1.80×10^{-3}	6.50×10^{-5}
	40	1.13×10^{-3}	5.76×10^{-3}	1.94×10^{-4}
	50	2.32×10^{-3}		5.56×10^{-4}
1,4-$(C_4H_9)_2$-dab	10	1.21×10^{-3}	2.05×10^{-3}	1.36×10^{-5}
	15		4.18×10^{-3}	
	20	2.40×10^{-3}	6.43×10^{-3}	1.05×10^{-4}
	25		1.26×10^{-2}	
	30	7.69×10^{-3}	2.38×10^{-2}	1.85×10^{-4}
	40	2.04×10^{-2}		4.63×10^{-4}
1,4-$(C_8H_9)_2$-dab[a]	10		1.54×10^{-3}	1.32×10^{-5}
	20		3.85×10^{-3}	4.11×10^{-5}
	30		9.56×10^{-3}	2.32×10^{-4}
	40		2.46×10^{-2}	9.03×10^{-4}

[a] Rate data was unobtainable for the formation of $Cr(CO)_4$[1,4-$(C_8H_9)_2$-dab] as this complex is sparingly soluble and thermally unstable.

Table V. Activation Parameters at 20 °C for the Reaction of $M(CO)_5L$ To Form $M(CO)_4L$[a]

ligand (L)	metal	ΔH^*, kcal mol^{-1}	ΔS^*, cal K^{-1} mol^{-1}
bpy	W	19.2	0.5
4,4′-$(CH_3)_2$-bpy	W	16.5	-9.0
4,4′-$(C_4H_9)_2$-bpy	W	17.0	-8.6
4,4′-$(C_6H_5)_2$-bpy	W	16.1	-11.5
1,4′-$(C_6H_{11})_2$-dab	Cr	17.5	-16.7
	Mo	16.7	-16.2
	W	19.2	-13.0
1,4-$(C_3H_7)_2$-dab	Cr	19.2	-11.2
	Mo	18.4	-10.1
	W	20.9	-8.9
1,4-$(C_4H_9)_2$-dab	Cr	16.3	-14.4
	Mo	19.8	0.6
	W	19.1	-12.4
1,4-$(C_8H_9)_2$-dab	Mo	15.6	-16.2
	W	24.7	6.2

[a] Results are obtained by using the least-square values of the data of Tables III and IV.

value of at least three kinetic experiments.

It was immediately apparent from the kinetic data that the reaction rate depended greatly on the nature of the diimine ligand. For instance, when L = 1,10-phenanthroline (phen) or a phen derivative, no discernable $M(CO)_5$(phen) intermediates (M = Cr, Mo, or W) were observed over the 10–40 °C range within 2 s after photolysis, i.e. in experiment $A_0 = A_\infty$; hence $k_{obsd} > 0.4$ s^{-1} for each of the monodentate phenanthroline complexes. This contrasts with the data for M = W and L = bpy or a substituted bpy, which yielded rate constants (k_{obsd}) at 20 °C in the 1.58×10^{-2} to 3.86×10^{-2} s^{-1} range, corresponding to half-lives of ~20 to ~45 s, respectively. When M = W and L = a dab derivative, rate constants at 20 °C ranged from 1.79×10^{-5} to 1.05×10^{-4} s^{-1}, corresponding to half-lives of ~2 to ~11 h, respectively.

Activation parameters have been calculated from Arrhenius type plots from the temperature dependence of the rate data. These results are shown in Table V; the least-squares uncertainty in the derived ΔH^* and ΔS^* values are ±2 kcal mol^{-1} and ±4 cal K^{-1} mol^{-1}, respectively. The relative magnitude of the ΔH^* and ΔS^* data indicates that the enthalpy of activation contributes more to the overall free energy than the entropy term. This conclusion is consistent with the thermodynamic results obtained for a considerably slower chelating $M(CO)_5L$ system, in which M = Cr, Mo, or W, or L = an arsine or a phospine derivative.[23-25]

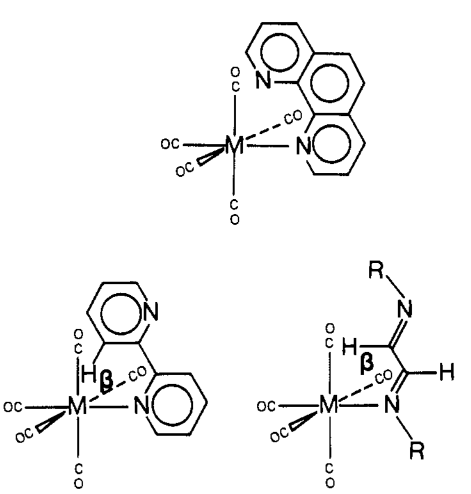


Figure 3. Stereochemistry of $M(CO)_5L$ intermediates, where L = phen, bpy, and dab.

The mechanism giving rise to CO extrusion is now considered in more detail. Presumably the mechanism involves nucleophilic attack at the metal center by the uncoordinated nitrogen atom of the diimine ligand. It has been previously established that thermal substitution of amine ligands in group 6 pentacarbonyl complexes (eq 6) follows a rate law comprising first- and second-order terms (eq 7 and 8).[35-38] The chelation reaction studied

$$M(CO)_5(\text{amine}) + L \rightarrow M(CO)_5L + \text{amine} \quad (6)$$

$$L = PR_3, AsR_3, SbR_3$$

$$\text{rate} = k_1[M(CO)_5(\text{amine})] + k_2[M(CO)_5(\text{amine})][L] \quad (7)$$

$$\text{rate} = k_{app}[M(CO)_5(\text{amine})] \quad (8)$$

here is distinct in that the entering diimine ligand is already attached to the metal center in a monodentate fashion. Experimentally the reaction rate was observed to be first-order and independent of free ligand concentration. However, this first-order kinetic behavior is intrinsic to the intramolecular process and does not indicate the nature of the mechanism. Equation 7 can, though, be reduced to eq 9. Here, k_1 and k_2 are the rate constants

$$\text{rate} = (k_1 + k_2)[M(CO)_5(\text{amine})] \quad (9)$$

representing purely dissociative (S_N1) and associative (S_N2) mechanisms, respectively.

The rate data presented in Tables III and IV reveal a rate dependence on ligand class, which follows the order phen > bpy > dab. For each of the ligand classes the rates of chelation are substantially greater than those reported for thermal substitution of either L or CO in $M(CO)_5L$ complexes in which the entering species in an amine, phosphine, phosphite, or arsenide ligand.[35-38] The more rapid chelation process is thus attributable to a substantial contribution to the CO extrusion reaction by the associating ligand when it is already coordinated in a monodentate manner. This conclusion contrasts with the dissociative (D) or dissociative interchange (I_d) mechanisms inferred for thermal substitution of amine ligands in group 6 pentacarbonyl complexes.[37,38] For a purely dissociatve type mechanism it may be anticipated that the reaction rate would be largely independent of the nature of the entering ligand. However, the marked dependence of reaction rates with diimine class leads us to reason that there is a substantial associative contribution in the overall chelation reaction. A comparison with previous data obtained by Connor et al. further illustrates this dependence on incoming nucleophile; e.g., when M = W and L = $Me_2PCH_2CH_2PMe_2$, chelation proceeds with a first-order rate constant $k_{obsd} = 3.53 \times 10^{-6}$ s^{-1} at 124 °C.[23] Although potential cis or trans effects of these monocoordinated ligands may affect the reaction rate,

---

(35) Ingemanson, C. M.; Angelici, R. J. *Inorg. Chem.* **1968**, *7*, 2646.
(36) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 1679.
(37) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.
(38) Darensbourg, D. J.; Ewen, J. A. *Inorg. Chem.* **1981**, *20*, 4168.

they are not expected to give rise to such significant differences.

The ordering of rate data (phen > bpy > dab) can be interpreted in terms of steric constraints for the coordination of diimine ligand. A comparison of the stereochemistries of the three ligand classes when they are coordinated in a monodentate fashion as pentacarbonyl complexes is shown in Figure 3. For a phen ligand the nitrogen atoms are held coplanar, resulting in rapid chelation following initial coordination and the absence of this type of monodentate intermediate in any of these experiments. On the other hand, theoretical and experimental studies on the conformation of the bpy[39-43] and dab[44,45] ligands have shown that these classes normally exist in an approximately s-trans conformation in both solid and solution phases. In order for these ligands to coordinate to the metal in a bidentate fashion, a rotation about the central carbon–carbon bond must occur. It has been estimated that an energy barrier of 5–7 kcal mol^{-1} must be overcome to produce this cis arrangement in either type of ligand.[45,46] The similarity of these rotational energy barriers do not point to an adequate explanation for the marked variation in rates observed between the three ligand classes. Instead these rate differences are thought to be brought about by a steric interaction of a β-hydrogen (β-H) (and the adjoining carbon atom) in the monodentate intermediate complex. If one refers to Figure 3, it can be seen that when L = bpy the β-CH group interacts substantially with both the carbonyl groups and the metal center of the pentacarbonyl, and this will result in significant steric crowding and electronic repulsion. Relatively large steric interaction of the β-CH in $M(CO)_5$(bpy) type complexes will aid the twisting mechanism about the C_2-C_2' bond of the ligand necessary to achieve the cis-chelation geometry. For the $M(CO)_5L$ complexes with L = dab, the β-CH is in a considerably less confined position and consequently this intermediate is much longer lived. The isolation of several monodentate dab complexes with other transition metals[46] in contrast to the absence of corresponding bpy complexes further supports this interpretation. In summary, the ability of the ligand to act as a nucleophile, when it is coordinated in a monodentate fashion, is a major contribution to the rate of the reaction.

It can be seen from Tables III and IV that, for any ligand at a given temperature, the rate of the thermal reaction of $M(CO)_5L$ to form $M(CO)_4L$ follows the order Mo > Cr > W. This order of lability is analogous to the reactivity of the parent hexacarbonyls[47] and that of the calculated M–C force constants of $M(CO)_6$ in solution.[48] Therefore, these comparisons suggest that the extrusion of CO from $M(CO)_5L$ is a major factor in controlling the rate of the overall chelation mechanism.

Thermodynamic parameters shown in Table V have indicated that the enthalpy of activation (ΔH^*) contributes more to the overall free energy than the entropy term ($T\Delta S^*$). It is informative to compare the activation enthalpy values for dissociation of CO from $M(CO)_5$(diimine) with the literature values for the release of CO from the parent hexacarbonyls. For solutions of $M(CO)_6$ at 30 °C the ΔH^* values for CO dissociation are 38–40 (Cr), 30–32 (Mo), and 39–40 kcal mol^{-1} (W), significantly greater than our data.[49-51] This lowering of the activation barrier for CO extrusion is again attributed to the associative character of the diimine ligand when it is already coordinated in a monodentate manner. However, as the energy barrier to diimine rotation has been estimated to be only 5–7 kcal mol^{-1},[47,48] it may be assumed that the predominant energy barrier to chelation consists of M–C bond breaking and that this contributes primarily to the enthalpy term. Finally, additional support for a degree of associative character in the reaction transition state is reflected by the negative ΔS^* values.

Acknowledgment. This work was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

(39) Cureton, P. H.; LeFevre, C. G.; LeFevre, R. J. W. *J. Chem. Soc.* **1963**, 1736.

(40) Cumper, C. W. M.; Ginman, R. F. A.; Vogel, A. I. *J. Chem. Soc.* **1962**, 1188.

(41) Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420.

(42) Castellano, S.; Gunther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.

(43) Spotswood, T. McL.; Tanzer, C. I. *Aust. J. Chem.* **1967**, *20*, 1227.

(44) Kliegman, J. M.; Barnes, R. K. *Tetrahedron Lett.* **1969**, 1953.

(45) Bendix, R.; Birner, P.; Birnstock, F.; Hennig, H.; Hofmann, H. *J. Mol. Struct.* **1979**, *51*, 99.

(46) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

(47) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

(48) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349.

(49) Pajaro, G.; Calderazzo, F.; Ercoli, R. *Gazz. Chim. Ital.* **1960**, *90*, 1486.

(50) Cetini, G.; Gambino, O. *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.* **1963**, *97*, 757, 1197.

(51) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082.