thylcyclohexane.[13] While the observed equatorial preference of methyl groups in these chelated piperazine rings seems certain, the calculated conformer energy difference must be viewed only as approximate since the observed peak ratios may not be truly equilibrium values. Equilibrium of the chelated ppz ring systems requires Pt–N bond breaking and then ring equlibration with subsequent ring closure. Although all samples were prepared by heating an aqueous solution of reactants at 80–90 °C, there is no guarantee that equilibrium has been established for the substituents on the chelated piperazine ring.

Acknowledgment. The generous financial support of the Research Corp. is gratefully acknowledged. The support of the Fairfield University Research Committee, which contributed funds to cover costs for NMR spectral services at Yale University, is also appreciated. This project could not have been completed without the assistance of those who helped to provide the NMR spectra cited above: Peter Demou, Paul Okarma, and Mark Murcko of Yale University and Professor Elie Abushanab of the University of Rhode Island. Also the National Institutes of Health, which subsidized the costs for outside academic users at the Southern New England High Field NMR Facility at Yale, is gratefully acknowledged. J.E.S. also appreciates the financial support of Fairfield University, which allowed him to discuss this work at the C. N. Reilley Memorial Symposium organized for the 36th Southeastern Regional ACS Meeting in Raleigh, NC, during Oct 1984.

Registry No. [Pt(bpy)(1,2-en)]·2Cl, 34409-74-0; [Pt(bpy)(1,3-pn)·2Cl, 96729-08-7; [Pt(bpy)(ppz)]·2Cl, 106267-47-4; [Pt(bpy)(2-Meppz)]·2Cl major isomer, 106252-63-5; [Pt(bpy)(2-Meppz)]·2Cl minor isomer, 106294-70-6; [Pt(bpy)(*cis*-2,6-Me_2ppz)]·2Cl, 106295-66-3; [Pt(bpy)(*trans*-2,5-Me_2ppz)]·2Cl, 106252-64-6; [Pt(bpy)(*cis*-2,5-Me_2ppz)]·2Cl, 106294-71-7; [Pt(bpy)(1,4-dithn)]·2Cl, 39174-46-4; [Pt(bpy)(thiomorph)]·2Cl, 106252-65-7; Pt(bpy)Cl_2, 13965-31-6.

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Kinetics and Reactivity of M(CO)₅L Intermediates Produced by the Photolysis of Group 6 Metal Hexacarbonyl Solutions Containing Diimine Ligands

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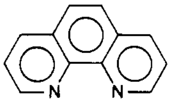
The photochemistry of metal carbonyls has been the subject of considerable interest for a number of years.[1] Despite extensive ligand photosubstitution studies, quantitative measurements regarding the reactivity of photogenerated organometallic intermediates are often lacking. This information, however, has important applications in the areas of systematic organometallic synthesis and the design of homogeneous catalytic processes.[2]

Recently, we have investigated the kinetics and mechanism of chelation reactions that occur following the photolysis of $M(CO)_6$ (M = Cr, Mo, W) solutions containing diimine or dipyridyl ligands.[3] These studies have provided UV–visible spectral evidence for the formation of a $M(CO)_5L$ intermediate in which the normally bidentate ligand L is coordinated in a monodentate fashion. It was also shown that the photoproduced $M(CO)_5L$ intermediate proceeds to form the stable $M(CO)_4L$ product via a thermal ring closure process. These steps are illustrated in eq 1 and 2.

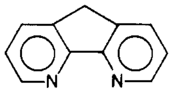
$$M(CO)_6 \xrightarrow[L]{h\nu} M(CO)_5L + CO \qquad (1)$$

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

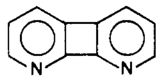
This paper is concerned with the kinetic and mechanistic behavior of a series of photoproduced monodentate $M(CO)_5L$ species, where M = Cr, Mo, or W and L = 1,10-phenanthroline (phen), 4,5-diazafluorene (daf), or 1,8-diazabiphenylene (dabp).



1,10-phenanthroline (phen)



4,5-diazafluorene (daf)



1,8-diazabiphenylene (dabp)

Although these three diimine ligands are closely related structurally, it has been found that their corresponding $M(CO)_5L$ derivatives undergo substantially different chelation behavior.

Experimental Section

Materials. The parent metal hexacarbonyls were purchased from Strem Chemical Co. and were used without further purification. Spectroscopic grade chloroform was obtained from Aldrich Chemical Co., as was spectroscopic grade toluene, which was dried by being refluxed over P_2O_5 (Fisher Scientific Co.) and subsequently distilled. Spectroscopic grade benzene (J. T. Baker Chemical Co.) was further purified by absorptive filtration through Woelm basic alumina of activity grade 1 obtained from ICN Biomedicals, Inc. Spectroscopic grade methylcyclohexane (J. T. Baker Chemical Co.) was purified by reflux and distillation from sodium benzophenone ketyl. High-purity (>99.9999%) nitrogen, used for deoxygenating, was further purified by passage through two 1 m × 2 cm tubes; the first contained dry $CaSO_4$ (W. A. Hammond Drierite Co.) and P_2O_5 in alternating 20 cm lengths, the second contained a Cu catalyst (Chemical Dynamics Corp., BASJ R-3-11). The catalyst was activated before use by heating to 120 °C while flushing with a steady stream of hydrogen. In this reduced form, the catalyst removes trace amounts of H_2O and O_2. *Caution!* The activated catalyst is pyrophoric. All other solvents were reagent grade. The ligand phen is commercially available in good purity (Aldrich Chemical Co.) and was used without further purification. The daf ligand was obtained from Prof. W. R. Cherry (Louisiana State University). The dabp ligand was obtained from Prof. J. A. H. MacBride (Sunderland Polytechnic, Sunderland, U.K.).

Synthesis of $M(CO)_4L$ Complexes. Solid $M(CO)_4L$ complexes (L = phen, daf) were prepared by UV irradiation with a 200-W medium-pressure Hg lamp of a continuously N_2-purged hexanes solution (200 mL) that contained the parent hexacarbonyl (0.1 mmol) and a slight excess of ligand (0.13 mmol). Nitrogen purging was maintained throughout the course of the reaction to avoid oxidation of the complex. Typical photolysis time was 30–40 min. Following irradiation, the solution was cooled in an ice bath to aid the precipitation of $M(CO)_4L$. The product was isolated by vacuum filtration and washed with hexanes to remove unreacted starting materials. If necessary, the product was further purified by column chromatography on 80–200-mesh alumina (Fisher Scientific Co.). The complexes are reasonably stable, and were kept in the dark under nitrogen at 278 K.

Synthesis of $M(CO)_5L$ (L = dabp) Complexes. The isolated M-$(CO)_5$(dabp) complexes were prepared by prior generation of the corresponding tetrahydrofuran (THF) adduct, $M(CO)_5$(THF). A tetra-

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Table I. Electronic Absorption Data and Assignments for the Low-Energy Features of $M(CO)_5L$ and $M(CO)_4L$ Complexes in Benzene at 293 K

complex	band maxima, nm
$Cr(CO)_5(daf)^a$	412 (d → d)
$Mo(CO)_5(daf)^a$	390 (d → d)
$W(CO)_5(daf)^a$	399 (d → d)
$Cr(CO)_5(dabp)^b$	391 (d → d)
$Mo(CO)_5(dabp)^b$	382 (d → d)
$W(CO)_5(dabp)^b$	385 (d → d)
$Cr(CO)_4(phen)^b$	420 (d → d),^{c} 519 (MLCT)
$Mo(CO)_4(phen)^b$	395 (d → d),^{c} 490 (MLCT)
$W(CO)_4(phen)^b$	396 (d → d),^{c} 510 (MLCT)
$Cr(CO)_4(daf)^b$	404 (d → d),^{c} 516 (MLCT)
$Mo(CO)_4(daf)^b$	388 (d → d),^{c} 478 (MLCT)
$W(CO)_4(daf)^b$	397 (d → d),^{c} 494 (MLCT)

[a] Difference spectra obtained from photolysis of a benzene solution containing 5×10^{-4} M $M(CO)_6$ and 10^{-2} M ligand. [b] Spectra recorded from solutions of the solid complexes. [c] Observed as a shoulder.

hydrofuran solution (200 mL) of the parent hexacarbonyl (2 mmol) was deoxygenated by continuous nitrogen purging and then irradiated with a 200-W medium-pressure Hg lamp for 60 min. When the irradiation was completed, an approximately 20% excess amount of dabp was added to the reaction vessel in the dark. The tetrahydrofuran was removed by rotary evaporation and the resultant complex redissolved in hexanes and purified by chromatography on a 7-cm alumina column; both these steps were carried out in low light conditions to minimize photoreaction. Washing with hexanes removed the unreacted hexacarbonyl complex from the column, while elution with benzene yielded the $M(CO)_5L$ complex. Further purification steps included repeated hexanes washings and sublimation of the unreacted metal hexacarbonyl from the product at 303 K and 10^{-3} Torr. The product complexes were obtained in 60% yield and stored in the dark under nitrogen at 278 K.

Photolysis Studies. A typical experiment consisted of a 2-s irradiation with the 313-nm line of a medium-pressure 200-W Hg lamp of a benzene solution (3 mL) containing 5×10^{-4} M $M(CO)_6$ and 10^{-2} M ligand at 298 K. The solutions were purged with nitrogen for 15 min prior to irradiation. Approximately 10^{-4} M $M(CO)_6$ is photodissociated during this irradiation time as is estimated from the incident light intensity (ferrioxalate actinometry[4]) and the reported quantum yield of $M(CO)_6$.[5] The temperature was controlled to ±0.2 K by a Lauda K2-R circulating bath.

In the case of L = phen, photolysis samples were prepared in either a 9:1 (v/v) methylcyclohexane:toluene glass at 100 K or a toluene solution at 180 K. Typically, a 10^{-4} M $M(CO)_6$ solution containing 10^{-2} M phen was used for these studies. These solutions were degassed prior to use by four freeze-pump-thaw cycles. The temperature of these samples was controlled by an Oxford Instruments variable liquid-nitrogen cryostat (Model DN1704K), which maintains temperatures to ±0.1 K throughout the 77–500 K region.

Physical Measurements. Electronic absorption spectra were obtained on a diode-array Hewlett-Packard 8450A UV-visible spectrophotometer. The reported band maxima are considered accurate to the specified resolution of this instrument which is 1 nm in the 200–400-nm region and 2 nm in the 400–800-nm region. Spectra were recorded throughout the reaction and stored on a Hewlett-Packard 82901M flexible disk drive unit. Difference absorption spectra were obtained by subtracting the spectrum recorded before photolysis from that recorded immediately after. Infrared spectra were recorded on a Perkin-Elmer Model 283B spectrophotometer. All complexes were recorded as chloroform solutions in a 1-mm path length NaCl cell.

Results and Discussion

Electronic absorption data obtained from all the complexes in this study are summarized in Table I.

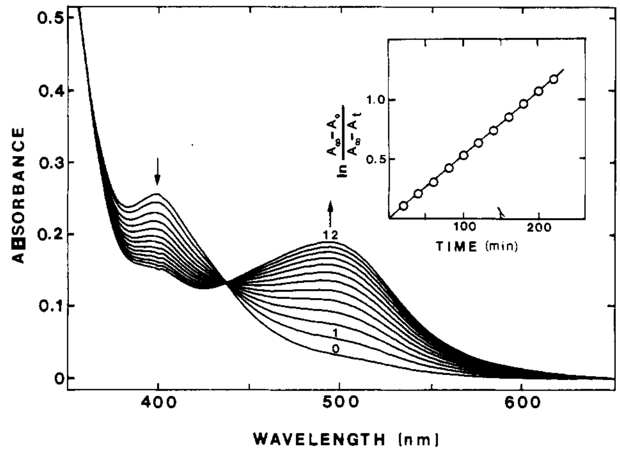

Figure 1. Electronic absorption spectral sequence recorded at 293 K following 2-s irradiation of a deoxygenated benzene solution containing 5×10^{-4} M $W(CO)_6$ and 10^{-2} M daf: curve 0, initial spectrum recorded within 2-s after photolysis; curves 1–12, subsequent spectra at 20-min intervals. The inset depicts the time-dependent behavior of absorption at 494 nm.

Table II. Observed Rate Constant Data and Derived Activation Energy Parameters for the Reaction of Photoproduced $M(CO)_5(daf)$ To Form $M(CO)_4(daf)$ and CO

M	temp, K	k_{obsd}, s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal K^{-1} mol^{-1}
Cr	283	$(2.00 \pm 0.14) \times 10^{-4}$	19.1 (±1.3)	−7.5 (±4.5)
	293	$(1.20 \pm 0.08) \times 10^{-3}$		
	303	$(2.30 \pm 0.16) \times 10^{-3}$		
	313	$(6.60 \pm 0.45) \times 10^{-3}$		
Mo	288	$(4.02 \pm 0.27) \times 10^{-2}$	21.6 (±1.5)	10.3 (±5.0)
	293	$(8.24 \pm 0.56) \times 10^{-2}$		
	298	$(1.48 \pm 0.10) \times 10^{-1}$		
	303	$(2.68 \pm 0.18) \times 10^{-1}$		
W	283	$(1.67 \pm 0.11) \times 10^{-5}$	21.1 (±1.4)	−5.6 (±5.0)
	293	$(8.80 \pm 0.60) \times 10^{-5}$		
	303	$(1.72 \pm 0.12) \times 10^{-4}$		
	313	$(8.60 \pm 0.58) \times 10^{-4}$		

As noted in an earlier paper,[3c] photolysis of $M(CO)_6$ solutions at room temperature in the presence of excess phen ligand results in rapid formation of the corresponding $M(CO)_4(phen)$ products. In the present study we have further endeavored to detect the presence of a $M(CO)_5(phen)$ intermediate via photolysis of the parent hexacarbonyl complex in low-temperature 9:1 (v/v) methylcyclohexane:toluene glasses at 150 K or in toluene solutions at 180 K. In either medium no UV–vis spectral evidence has been obtained for the prior formation of a monodentate coordinated species involving phen. When the glass is warmed or measurements are performed directly following photolysis in low-temperature fluid conditions, the spectral features of $M(CO)_4(phen)$ (see Table I) are immediately observed.

Figure 1 depicts the spectral sequence observed following 2-s irradiation with a 200-W Hg lamp of a 5×10^{-4} M $W(CO)_6$ solution in benzene containing 10^{-2} M daf at 293 K. In this experiment the initial spectrum was recorded within 2-s after light irradiation and subsequent spectra were acquired at 20-min intervals. The formation of the reaction product, $W(CO)_4(daf)$, was observed by monitoring the growth of its intense metal-to-ligand charge-transfer (MLCT) absorption centered at 494 nm. A sharp isosbestic point at 438 nm indicates that this reaction proceeds uncomplicated by side or subsequent reactions. The initially photoproduced species is therefore attributed to monodentate $W(CO)_5(daf)$, and its absorption maximum at 399 nm is assigned to the $^1A(e^4b_2^2) \rightarrow {}^1E(e^3b_2^1a^1)$ transition characteristically observed from $M(CO)_5L$-type compounds.[6]

The rate of this chelation reaction (eq 2) has been determined by monitoring the kinetics of the growth of the long-wavelength MLCT absorption representing the $M(CO)_4(daf)$ product. The growth of A_0 to A_∞ is exponential, and plots of $\ln (A_\infty - A_0)/(A_\infty - A_t)$ vs. time exhibited linearity with correlation coefficients typically greater than 0.99 (see Figure 1 inset). Here A_0 is defined

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as the initial absorbance of the solution, A_t is the absorbances at varying time throughout reaction, and A_∞ is the final absorbance. All absorbance values were recorded at a fixed wavelength in the MLCT region. The slope of the plotted line is equal to the reaction rate constant k_{obsd}. Reaction rates were determined to be independent of ligand concentration over the 10^{-3}–10^{-1} M range. Rate data have been obtained at several temperatures, and these are listed in Table II. Activation parameters calculated from Arrhenius-type plots are also shown in Table II.

Rate data for dissociation of CO from M(CO)$_5$(daf) follows the order Mo > Cr > W, which is congruent with that previously established for the reactivity of the parent hexacarbonyls[7] and that of the calculated M–C force constants of M(CO)$_6$ in solution.[8] It is also noted that the observed reaction rates are considerably greater than values previously reported for CO or L dissociation in M(CO)$_5$L complexes in which the entering species is an amine, phosphine, phosphite, or arsenide ligand.[9] This rate increase is attributed to a substantial contribution to the CO dissociation reaction when the associating ligand is already attached to the metal center in a monodentate manner. These results are in agreement with those previously reported for M(CO)$_5$L complexes, where M = Cr or Mo, and L = a series of bidentate sulfur ligands.[10] In contrast, a number of M(CO)$_5$L complexes, where L = a bidentate phosphorus or arsenic ligand, have been shown to undergo chelation via a largely dissociative-type mechanism.[11]

Activation energy parameters indicate that the M(CO)$_5$(daf) chelation process is largely enthalpy controlled. Furthermore, it is notable that the positive ΔS^* value obtained for the reaction of Mo(CO)$_5$(daf) suggests an increased amount of dissociative character in the transition state consistent with that reported for thermal substitution reactions of other Mo carbonyl complexes.[7,12]

The reaction product W(CO)$_4$(daf) was isolated. Anal. Calcd for W(CO)$_4$(daf): C, 38.8; H, 1.74; N, 6.04. Found: C, 39.3; H, 1.92; N, 5.45. Infrared bands (in chloroform) at 2011, 1897, 1877, and 1832 cm^{-1} are consistent with the C_{2v} arrangement of the CO groups in the complex.[13] The bands are assigned as A_1^{1a}, B_1, A_1^{1b}, and B_2, respectively.

Photolysis of M(CO)$_6$ solutions at 293 K containing dabp in benzene results in the formation of species having absorption maxima in the 385–391-nm region. As noted above, this absorption is typical of M(CO)$_5$L species and is therefore assigned as a $^1A(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a^1)$ transition. However, an important difference is reported here. The M(CO)$_5$(dabp) photoproduct does not further react thermally to form the corresponding bidentate product, but instead it is stable and remains in solution. Thus, it appears for the M(CO)$_5$(dabp) complex that one of the ligand nitrogen atoms coordinates with the metal center, while the other nitrogen atom remains free.

The M(CO)$_5$(dabp) complexes have been isolated as solid complexes following prior formation of the tetrahydrofuran adduct (see Experimental Section). The infrared spectrum of W(CO)$_5$(dabp) has been recorded in chloroform and indicates four bands in the CO region centered at 2069, 1981, 1932, and 1900 cm^{-1}, consistent with the C_{4v} arrangement of the CO ligands. These bands correspond to the A_1^1, B_2, E_1, and A_1^2 modes, respectively.[13b,c] However, the intensity of the normally forbidden B_2 mode is enhanced, indicating that the CO ligands are somewhat distorted from ideal C_{4v} group symmetry. Anal. Calcd for W(CO)$_5$(dabp): C, 37.7; H, 1.27; N, 5.86. Found: C, 38.2; H, 1.42; N, 6.03.

This study has demonstrated the vast difference in coordination abilities of a closely related group of diimine ligands. The rapid bidentate coordination of phen, proceeding with no observable monodentate species, is significantly altered by the removal of a bridging C–H group to form daf. Apparently, the methylene bridge in daf distorts the bipyridine portion of the molecule so as to reduce the N–metal overlap, and this leads to a relatively slow chelation process. Removal of the remaining methylene bridge of daf to form dabp has further reduced the coordination abilities of the second nitrogen, so the M(CO)$_5$(dabp) complexes remain as the stable products. This observation may also be interpreted in terms of a reduction of the N–metal overlap in the M(CO)$_5$(dabp) complex. Furthermore, the relatively low basicity of the dabp ligand (pK_a 1.92)[14] compared to phen (pK_a 4.84)[15] may also be contributing to the lack of chelation in the M(CO)$_5$(dabp) complexes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are also indebted to Drs. Cherry and MacBride for supplying the daf and dabp ligands used in this study.

Registry No. Cr(CO)$_5$(daf), 106213-19-8; Mo(CO)$_5$(daf), 106213-20-1; W(CO)$_5$(daf), 106213-21-2; Cr(CO)$_5$(dabp), 106213-22-3; Mo(CO)$_5$(dabp), 106213-23-4; W(CO)$_5$(dabp), 106213-24-5; Cr(CO)$_4$(phen), 14168-63-9; Mo(CO)$_4$(phen), 15740-78-0; W(CO)$_4$(phen), 14729-20-5; Cr(CO)$_4$(daf), 106213-25-6; Mo(CO)$_4$(daf), 106213-26-7; W(CO)$_4$(daf), 106213-27-8; Cr(CO)$_6$, 13007-92-6; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0.

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Preparation of Sulfheme Derivatives from Reconstituted Myoglobins Lacking Heme Vinyl Substituents

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Sulfmyoglobin is a green form of myoglobin in which the heme prosthetic group is modified by reduction of one of the pyrrole rings and incorporation of one sulfur atom into the macrocycle.[1,2] The structure of the resulting prosthetic group is that of a sulfur-containing chlorin,[3] although the identity of the reduced pyrrole ring is unknown, and several different models for the nature of sulfur attachment have been suggested.[4,5] On the basis of nuclear magnetic resonance (NMR) studies, Timkovich and Vavra have recently concluded that either heme ring A or B is probably modified in the formation of sulfmyoglobin.[6] This conclusion

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