This isomer possesses *nonequivalent* platinum ions and contains the structural elements of both the $D_{2h}$ isomer (nitrogens trans to a bridging OH group) and the $C_s$ and $C_2$ isomers (nitrogens atoms trans to bridging and terminal OH groups). If the chemical shifts for the two platinum ions in the $C_1$ isomer are intermediate between those of the $D_{2h}$ and $C_s$ ($C_2$) isomers, a second-order pattern of the type found at ~+1947 ppm would be expected for the compound. An alternative assignment, based on the NMR properties of the hydrogen peroxide oxidation products of *cis*-$[Pt^{II}(^{15}NH_3)_2(\mu\text{-OH})]_2^{+2}$,[28] is that the weak doublet of doublets at +1977 ppm and a triplet centered at ~+1947 ppm are *both* due to the nonequivalent platinum ions of the $C_1$ isomer. However, in the case of the ethylamine compounds, this assignment seems less favorable since it does not account for one of the isomers, $C_s$ ($C_2$), and it requires that the chemical shift of one of the platinums of $C_1$ be the same as the platinum ions of $C_s$ ($C_2$) but that the other platinum of $C_1$ be significantly different from the platinum ions found in $D_{2h}$. Clearly, a definitive assignment will require additional information and most likely an X-ray structural analysis of one or more of the minor products produced in the reaction.

(28) Appleton, T. G., personal communication.

Although a fifth isomer having $C_i$ symmetry is theoretically possible, its formation would involve breaking and re-forming *both* $\mu$-OH linkages of the four-membered Pt Pt ring. Its presence, as well as other possible structures having trans ethylamine ligands (inconsistent with the coupling data[26]), is considered unlikely.

In summary, the oxidation of a bis($\mu$-hydroxo)-bridged Pt(II) dimer with hydrogen peroxide is described. Platinum-195 NMR spectroscopy and earlier X-ray structural data[10] indicated that the oxidation yields as a major product a $D_{2h}$-symmetry Pt(IV) dinuclear complex having a bis($\mu$-hydroxo) bridge. However, NMR spectra showed that lower symmetry, dinuclear, bis($\mu$-hydroxo)-bridged products are also produced, indicating that at least in part the reaction occurs through an open-ring intermediate that allows isomerization to occur.

**Acknowledgment.** We wish to acknowledge the American Cancer Society (Grant 296) and the Bristol Myers Co. for support of this research. We are also grateful to the Johnson Matthey Co. for supplying the platinum salts used in the syntheses. The knowledgeable comments made by Dr. Trevor Appleton concerning the results of the study are also greatly appreciated.

# Notes

Contribution from the Department of Chemistry, Fairfield University, Fairfield, Connecticut 06430

## Stereochemical Preferences of Methyl-Substituted Piperazines Chelated to Platinum(II)

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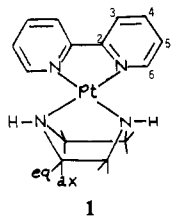
Chelated ligands can endow a metal complex with an ability to discriminate in its further reactions with other substrates. Such selectivity can arise from the conformational preferences of the chelated ligand, i.e. from the stereochemical disposition of substituents on the chelate rings.

Piperazine is an interesting diamine molecule that has been recognized as a chelating agent for some time.[1,2] Early workers saw that chelation would cast the normally chair conformation of the free piperazine ligand into a boat conformation anchored by the metal ion binding. X-ray crystallography has shown this to occur.[3]

Little is known about the stereochemical preferences of methyl substituents on the carbon skeleton of chelated piperazine ligands. We have prepared a series of methyl-substituted piperazine (ppz) complexes of the type **1** to study these preferences. The chelated




**1**

boat moiety has axial and equatorial substituents, two of which are designated on **1**, ax and eq, respectively.

(1) Mann, F. G.; Watson, H. R. *J. Chem. Soc.* **1958**, 2772.
(2) Allen, D. W.; Mann, F. G. *J. Chem. Soc. A* **1970**, 999.
(3) Hassel, O.; Pedersen, B. F. *Proc. Chem. Soc., London* **1959**, 394.

### Experimental Section

**Diamines.** All ligands were purchased from commercial sources (Aldrich Chemical Co.) and used without further purification. The commercial sample of 2,5-dimethylpiperazine (2,5-$Me_2$ppz) was trans-rich (80–90%). To get the cis isomer of 2,5-$Me_2$ppz, the initial amine mixture was converted to the dihydrochloride derivative and recrystallized from 95% ethanol. The *trans*-dihydrochloride is less soluble and is easily removed; an 80% cis-enriched sample was obtained after several recrystallizations. The NMR spectrum of the *cis*-dihydrochloride in $D_2O$ shows a methyl doublet at 1.42 ppm (vs. external $Me_4Si$), 0.07 ppm downfield from that of the *trans*-dihydrochloride isomer. However, eventually the 80:20 cis–trans mixture could not be purified further by fractional removal of the less soluble *trans*-dihydrochloride. At this stage 4.0 g of the 80:20 cis–trans dihydrochloride mixture was converted to an *N,N'*-dibenzoyl derivative.[4] The cis–trans derivative mixture was recrystallized from 95% ethanol several times to yield 0.7 g (10% yield) of white solid *N,N'*-dibenzoyl-*cis*-2,5-dimethylpiperazine, mp 148.5–152 °C (lit.[4] 147–148.5 °C). This solid was converted to the dihydrochloride by heating in 2 M HCl; after the solution was cooled, the solid benzoic acid was filtered off and the solution evaporated to give solid dihydrochloride. The cis amine was liberated in 5 M NaOH and ether extracted for reaction with $Pt(bpy)Cl_2$ (bpy = 2,2'-bipyridine).

**Platinum Complexes.** $Pt(bpy)Cl_2$ was reacted with the appropriate ligands in water at 80–90 °C as described earlier.[5]

**NMR Spectra.** Samples for NMR analysis were prepared in $D_2O$ as described earlier.[5] $^{13}C$ NMR spectra were obtained on a Varian CFT-20 spectrometer at the University of Rhode Island through the generosity of Professor Elie Abushanab of the School of Pharmacy. The NMR spectra of the *cis*-2,5-$Me_2$ppz ligand and its platinum complex were obtained at Yale University on a JEOL FX-90 ($^1H$ and $^{13}C$) spectrometer and on a Bruker WM-250 ($^1H$) spectrometer. $^{13}C$ spectra are referenced vs. internal dioxane, which has been found to have a shift of 67.73 ppm from $Me_4Si$ sealed in an external capillary.[5]

### Results

Carbon-13 NMR spectra which were used to characterize the complexes are summarized in Table I. All data are consistent with the formulation of a 1:1 mixed complex with both ligands being bound in a bidentate fashion. Some of the carbon resonances exhibit coupling to the $^{195}Pt$ nucleus (natural abundance 33%).

(4) Ishiguro, T.; Kitamura, E.; Matsumura, M. *J. Pharm. Soc. Jpn.* **1957**, 77, 1051.
(5) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007.

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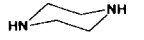
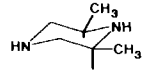
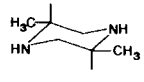
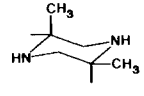
**Table I.** Carbon-13 NMR Chemical Shifts[a] and $J_{^{195}Pt^{13}C}$[b] Data

| complex[e] | diamine structure | bpy carbons | | | | | aliphatic ring carbons | | | | Me carbons |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_2$ | $C_6$ | $C_4$ | $C_5$ | $C_3$ | | | | | |
| Pt(bpy)(1,2-en)$^{2+}$ | $NH_2CH_2$-$CH_2NH_2$ | 156.93[a] (32)[b] | 151.62 (32) | 142.97 (6) | 129.52 (34) | 125.19 (27) | 48.33 (0) | | | | |
| Pt(bpy)(1,3-pn)$^{2+}$ | $NH_2CH_2CH_2$-$CH_2NH_2$ | 157.09 (34) | 148.92 (30) | 143.17 (6) | 129.04 (33) | 125.35 (27) | 42.69 (25) | 28.37 (40) | | | |
| Pt(bpy)(ppz)$^{2+}$ |  | 157.01 (~27) | 153.63 (43) | 143.18 (7) | 129.56 (38) | 125.02 (27) | 51.98 (9) | | | | |
| Pt(bpy)(2-Meppz)$^{2+}$ |  | | | | | | | | | | |
| major isomer | | 156.79 (29) | 153.94 (43.8) | 143.40 (*c*) | 130.08 (34) | 125.15 (26) | 60.23 (*c*) | 60.10 (*c*) | 52.79 (9) | 51.50 (7) | 22.46 (0) |
| | | 156.60 (30) | | | 129.99 (38) | 124.53 (26) | | | | | |
| minor isomer | | 156.45 (*d*) | *d* | *d* | *d* | *d* | 58.58 (*d*) | 57.78 (*d*) | 52.55 | 45.36 (12) | 15.58 (24) |
| | | 156.36 (*d*) | | | | | | | | | |
| Pt(bpy)(*cis*-2,6-$Me_2$ppz) |  | 157.56 (*d*) | 153.57 (42) | 143.12 | 129.73 (37) | 125.33 (26) | 60.54 (10) | 59.13 (9) | | | 22.36 (0) |
| | | 157.26 (*d*) | 153.46 (44) | *c* | 129.53 (39) | 125.09 (27) | | | | | |
| Pt(bpy)(*trans*-2,5-$Me_2$ppz) |  | 157.09 (31) | 153.66 (42) | 143.21 (*c*) | 129.75 (38) | 125.21 (24) | 60.31 (9) | 59.05 (17) | 56.85 (8) | 53.19 (10) | 22.51 (0) |
| | | 156.82 (31) | 153.57 (43) | | | 125.06 (25) | | | | | 15.68 (27) |
| Pt(bpy)(*cis*-2,5-$Me_2$ppz) |  | 157.28 (*d*) | 153.38 (43) | 143.09 (*c*) | 129.60 (38) | 125.16 (27) | 60.25 (10) | 59.38 (10) | | | 21.89 (0) |
| Pt(bpy)(1,4-dithn)$^{2+}$ |  | 157.07 (*d*) | 155.48 (43) | 144.27 (6) | 130.08 (37) | 125.56 (26) | 38.63 (0) | | | | |
| Pt(bpy)(thiomorph)$^{2+}$ |  | 156.91 (*d*) | 155.73 (44) | 143.95 (7) | 129.98 (40) | 125.24 (27) | 54.46 (10) | 36.38 (14) | | | |
| | | | 152.59 (41) | 143.41 (7) | 129.69 (37) | | | | | | |

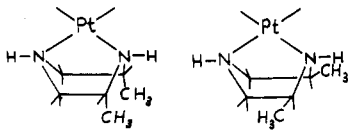
[a] $^{13}C$ shifts are given in ppm vs. external $Me_4Si$; shifts were measured vs. internal dioxane, which is 67.73 ppm downfield from external $Me_4Si$. [b] Coupling constants (in parentheses) are given in Hz. [c] Platinum coupling present but too small (<6 Hz) to be resolved from major peak. [d] Signals either too weak to be seen or lost due to overlap with another signal. [e] Abbreviations: 1,2-en, 1,2-diaminoethane; 1,3-pn, 1,3-diaminopropane; ppz, piperazine; bpy, 2,2′-bipyridine; 1,4-dithn, 1,4-dithiane; thiomorph, thiomorpholine.

The spectral parameters for the bipyridine ring carbons are similar to those found earlier[5,6] in mixed 1,2- and 1,3-diamine–bipyridine platinum(II) chelates. Exemplary data from these earlier studies are included in Table I. One noteworthy feature of the piperazine chelate data lies in the position of the bpy $C_6$ chemical shifts, found at ~153.5 ppm for all chelates; similar 1,2- and 1,3-diamine complexes showed $C_6$ resonances at ~151.5 and ~149 ppm, respectively.[5,6] Data for the two thiane complexes given in Table I seem to indicate that the coordination of sulfur renders the bpy $C_6$ resonance at lower field, ~155.5 ppm. The chemical shifts for the other four carbons of the bpy ring in these molecules are not significantly different from those found earlier in 1,2- and 1,3-diamine complexes. Two other noteworthy variations from data on the 1,2- and 1,3-diamine chelates are found in $J_{PtC}$ data for bpy $C_6$ and $C_5$, where values of 43 and 38 Hz are observed for the piperazine chelates vs. values of 32 and 33 Hz for those comparable 1,2- and 1,3-diamine complexes studied earlier.[5,6]

The $^{13}C$ resonances of the chelated aliphatic diamine ring carbons (50–60 ppm) are easily distinguishable from the methyl carbon resonances (15–25 ppm). Since the ring carbon resonances provide little diagnostic value, no attempt was made to assign them unambiguously. Certainly the typical 7–8 ppm downfield shift[7] (vs. the unsubstituted piperazine chelate) due to methyl substitution is visible for the $\alpha$ and $\beta$ carbons in the substituted complexes. Ring carbons generally showed platinum couplings of 9–10 Hz, although somewhat larger values are seen in a few cases. Multipath coupling effects[8,9] are probably responsible for the diminished Pt–C coupling for these ppz carbons as was seen earlier for chelated ethylenediamine units.[9] Methyl substituents were found to exhibit either no discernable platinum–carbon coupling or a $^3J_{PtC}$ value of 25 Hz; those methyl carbons that show no platinum satellites occurred at ~22.4 ppm while the methyl groups that are significantly coupled to the platinum nucleus resonate further upfield at ~15.6 ppm.

## Discussion

The platinum complex of *cis*-2,6-$Me_2$ppz (all abbreviations are found in Table I) exhibits a carbon-13 NMR spectrum whose aliphatic resonances indicate that both methyl groups are structurally identical, as is expected from the configuration of the precursor amine. Two stereoisomers are possible for the chelated ppz ring, based on the methyl group of orientation:



2 3

In **2**, the methyl groups are diaxial on the boat ppz ring, placing them parallel to the plane of the square-planar complex. In **3**, the methyl groups have assumed a diequatorial orientation on the chelated boat piperazine ring and are perpendicular to the main plane of the complex.

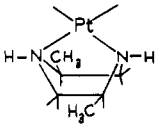
$^3J_{PtC}$ data in other amine complexes have been shown[5,6,7,10] to exhibit a Karplus-type dependence on the vicinal PtNCC dihedral angle, and this information allows one to assign structure **3** to the compound isolated. The PtNCC dihedral angle for an axial methyl substituent on the chelated boat ppz ring, as estimated from models, should be ~160°, while an equatorial methyl carbon on the boat ppz ring is estimated to have a dihedral angle near 90°. The lack of any visible $^3J_{PtC}$ for the methyl carbon resonance at 22.36 ppm strongly indicates a diequatorial orientation of the methyl groups on the boat ppz ring in this complex, **3**.

The chelation of *trans*-2,5-$Me_2$ppz requires one methyl group to be in an axial environment and one to be in an equatorial orientation. The $^3J_{PtC}$ data for the methyl carbons confirm such a situation. The methyl resonance at 22.51 ppm shows no visible $^3J_{PtC}$ and corresponds to the ppz ring equatorial methyl group; it is noteworthy that the chemical shift of the methyl carbon in the *cis*-2,6-$Me_2$ppz chelate, also equatorial in orientation, is 22.36 ppm. The axial methyl carbon in the *trans*-2,5-$Me_2$ppz chelate occurs at 15.68 ppm and exhibits a $^3J_{PtC}$ value of 27 Hz in agreement with dihedral angle predictions. This nearly 7 ppm upfield shift for an axial methyl group on a six-membered ring relative to an equatorial counterpart is comparable in magnitude to what has been seen in chair ring systems.[11]

When the 2-Meppz ligand chelates the platinum(II) metal ion, the major product exhibits a methyl peak at 22.46 ppm with no $^3J_{PtC}$ being visible. Both the chemical shift and coupling constant data compellingly suggest an equatorial ring orientation for the methyl group in the major product. In the same solution spectral evidence is available for a minor product, abundance ~9% of the major isomer. The aliphatic $^{13}C$ resonances of this minor isomer were identified; however, not all the bpy ring carbons were resolved probably due to overlap with corresponding peaks in the major isomer. Of diagnostic importance is the fact that the minor species has a methyl $^{13}C$ resonance at 15.58 ppm with a $^3J_{PtC}$ value of 24 Hz. The correspondence of these data with those established for a known axial methyl group orientation in the *trans*-2,5-$Me_2$ppz complex indicates an axial ppz ring orientation of the substituent in this minor isomer. An alternative explanation of the spectrum attributing the minor isomer to monodentate 2-Meppz ligation has been ruled out by observing no pH dependence of the peaks attributed to the minor isomer in the pH range 2–8. Amine protonation is known to lead to substantial protonation shifts of $^{13}C$ resonances $\alpha$ and $\beta$ to the basic site.[12]

The highly preferred equatorial ring orientation in the Pt(bpy)(2-Meppz)$^{2+}$ complex could be explained by the sterically crowded situation that occurs in the methyl axial conformer. In a boat ring each axial substituent suffers from an eclipsing 1,2-interaction and an additional 1,3-axial interaction much like that formed in a chair conformation of six-membered rings. The equatorial substituents point above and below the plane of the square-planar complex; there being no axial ligands attached to the metal ion, these substituents would seem to be less sterically constrained.

The chelation of *cis*-2,5-dimethylpiperazine yields a product with a methyl resonance at 21.89 ppm showing no coupling to the platinum-195 nucleus. This product is assigned structure **4**,



4

wherein both methyl groups are equatorially disposed on the boat ppz ring. The other possible isomeric product, having diaxial methyl substituents, would be expected to exhibit a methyl resonance at ~16 ppm, but no resonance is seen in this region of the $^{13}C$ NMR spectrum. Thus **4** appears to be the exclusive product obtained, exhibiting the same pronounced preference as was found for 2-Meppz chelation.

All of the complexes studied show a pronounced preference for the methyl substituent to occupy an equatorial position on the boat piperazine ring in these chelates. The approximate 11:1 preference of the equatorial orientation over the axial ones for [Pt(bpy)(2-Meppz)]$^{2+}$ would correspond to a free energy difference at 300 K of 1.4 kcal/mol; this number is comparable to the accepted $\Delta G°$ value of 1.7 kcal/mol for the axial–equatorial difference in me-

(6) Sarneski, J. E.; Erickson, L. E.; Reilley, C. N. *Inorg. Chem.* **1981**, *20*, 2137.
(7) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1978**, *17*, 1701.
(8) Contreras, R. H.; Scuseria, G. E. *Org. Magn. Reson.* **1984**, *22*, 411.
(9) Sarneski, J. E.; Erickson, L. E.; Reilley, C. N. *J. Magn. Reson.* **1980**, *37*, 155.
(10) Bagger, S. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 467.
(11) Anet, F. A. L.; Bradley, C. H.; Buchanan, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 258.
(12) Sarneski, J. E.; Surprenant, H. L.; Molen, F. K.; Reilley, C. N. *Anal. Chem.* **1975**, *47*, 2116.

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-$Me_2$ppz)]·2Cl, 106295-66-3; [Pt(bpy)(*trans*-2,5-$Me_2$ppz)]·2Cl, 106252-64-6; [Pt(bpy)(*cis*-2,5-$Me_2$ppz)]·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.

(13) Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.

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

# 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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*Received August 19, 1986*

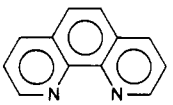
The photochemistry of metal carbonyls has been the subject of considerable interest for a number of years.[1] Despite extensive ligand photosubstitution studies, quantitative measurements regarding the reactivity of photogenerated organometallic intermediates are often lacking. This information, however, 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.

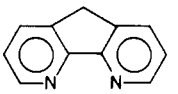
$$M(CO)_6 \xrightarrow[L]{h\nu} M(CO)_5L + CO \quad (1)$$

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

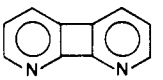
This paper is concerned with the kinetic and mechanistic behavior of a series of photoproduced monodentate $M(CO)_5L$ species, where M = Cr, Mo, or W and L = 1,10-phenanthroline (phen), 4,5-diazafluorene (daf), or 1,8-diazabiphenylene (dabp).




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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