(15) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); see also R. E. Connick and D. Fiat, *ibid.*, **44**, 4103 (1966).
(16) J. Neely and R. Connick, *J. Am. Chem. Soc.*, **92**, 3476 (1970).
(17) M. Eigen and G. Wilkins, *Adv. Chem. Ser.*, No. **49**, 55 (1965).
(18) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **13**, 107 (1970).
(19) B. Perlmutter-Hayman and R. Shinar, *Int. J. Chem. Kinet.*, **9**, 1 (1977).
(20) M. C. Rose and J. E. Stuehr, *J. Am. Chem. Soc.*, **94**, 5532 (1972).
(21) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold, New York, N.Y., 1950, p 485.

**Table I.** Comparative Magnetic Moments ($\mu_B$)

| | | | |
|---|---|---|---|
| Ni(cyclen)Cl$_2$ | 3.06 | Ni(tbcyclen)(NO$_3$)$_2$[7] | 3.20 |
| Ni(cyclen)Br$_2$ | 3.16 | Ni(cyclam)Cl$_2$[11] | 3.09 |
| Ni(cyclen)(NO$_3$)$_2$ | 3.15 | Ni(tbcyclen)Cl$_2$[7] | 3.70 |

**Table II.** Electronic Spectral Data for Nickel(II) Complexes of Cyclen and Tbcyclen

| Complex | Medium | nm ($\lambda$) |
|---|---|---|
| Ni(cyclen)(NO$_3$)$_2$ | Solid | 870, 545, 350 |
| | CH$_3$CN | 900 (33), 545 (28), 355 (45) |
| | C$_2$H$_5$OH | 900 (30), 545 (25), 350 (45) |
| | CH$_3$OH | 920 (28), 555 (19), 355 (29) |
| | H$_2$O | 950 (27), 560 (10), 360 (13), 300 sh (16) |
| Ni(tbcyclen)(NO$_3$)$_2$·$^1/_2$H$_2$O[7] | Solid | 1025, 600, 380 |
| | H$_2$O | 650 (24), 480 (215), 400 sh (53) |
| | CH$_3$OH | 1025 (25), 850 sh (5), 610 (30), 348 (70) |
| Ni(cyclen)Br$_2$·$^1/_2$C$_2$H$_5$OH | Solid | 945 br, 590, 375 |
| | CH$_3$OH | 945 (20), 545 (12), 340 (19) |
| Ni(cyclen)Cl$_2$ | Solid | 950 br, 585, 375 |
| Ni(tbcyclen)Cl$_2$·$^1/_2$H$_2$O[7] | Solid | 710, 440 |
| | H$_2$O | 650 (150), 480 (320), 400 sh (120) |
| | CH$_3$OH | 1560 sh (2.5), 1460 (5), 1090 (10), 715 (100), 440 (245) |
| | C$_2$H$_5$OH | 710 (295), 440 (315) |
| | CH$_3$CN | 710 (164), 440 (345) |
| Ni(tbcyclen)ClClO$_4$·H$_2$O[7] | Solid | 710, 440 |

## A Comparative Study of Steric Effects of Nickel(II) Complexes Containing 12-Membered Macrocyclic Ligands

Richard Smierciak, Joe Passariello, and Elliott L. Blinn*

Substitution on the nitrogen atoms on a polyamine ligand has been shown to have a major effect on the stoichiometry, the geometry, and the electronic configuration of nickel(II) complexes.[1,2] For example, by employing diamine ligands, one to three bidentate ligands will coordinate to the nickel(II) depending on the bulkiness of the groups substituted on the nitrogen atoms. Square-planar, octahedral, and tetrahedral geometries have been observed for nickel(II) complexes as a function of the organic groups on the donor atoms and the counteranions.

We have made a comparative study on the effect of N substitution on 12-membered saturated cyclic tetradentate ligands coordinated to nickel(II). Because these are cyclic tetradentate ligands it is unlikely that substitution will alter the stoichiometry of the nickel(II) complexes. The expected nickel(II) to ligand ratio should be one to one. (The nickel(II) complexes of 1,4,7,10-tetrathiocyclododecane and 1,4,7,10-tetrathiacyclotridecane are exceptions and they form complexes with a nickel(II) to ligand ratio of two to three.[3]) A 12-membered cyclic tetradentate ligand should not coordinate coplanar with the nickel(II)[3-5] and therefore square-planar or trans octahedral geometries are not likely. A tetrahedral geometry is also unlikely because the small 12-membered cyclic ligand cannot span the large tetrahedron bond angles. Therefore, unlike saturated linear tetradentate ligands or larger saturated cyclic tetradentate ligands, the geometrical options available to the nickel(II) ion bonded to 12-membered saturated cyclic ligands are more limited. It is for these reasons we would like to compare the chemistry of nickel(II) complexes of 1,4,7,10-tetraazacyclododecane, cyclen,[6] with the nickel(II) compounds of 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane, tbcyclen.[6] The complexes of tbcyclen have been reported earlier;[7] those containing cyclen are first reported here.

We have observed that all the nickel(II)- or cobalt(II)-tbcyclen complexes containing monodentate counteranions have a trigonal-bipyramidal geometry, [M(tbcyclen)X]Y (where X is chloride, bromide, and thiocyanate, and Y is chloride, bromide, or perchlorate). However, complexes containing a planar, weak field counteranion such as nitrate or oxalate have a cis octahedral geometry.[7,8]

The five-coordinate geometry of all the nickel(II) complexes is believed to be due to the large benzyl groups limiting the space around the nickel(II) to only five donor atoms. To attain a six-coordinate complex, the counteranion must be a small weak field planar bidentate ligand. The tbcyclen bonded to the nickel(II) in a six-coordinate geometry has an unusually low $Dq$ value for a tetradentate ligand. The $Dq$ value for [Ni(tbcyclen)NO$_3$]NO$_3$ is 973 cm$^{-1}$ and this value is between that found for Ni(H$_2$O)$_6^{2+}$ and Ni(NH$_3$)$_6^{2+}$.[7] This low $Dq$

value was attributed both to the small size of the macrocycle imposing strained metal-to-donor bonds and to the steric strain imposed by the four benzyl groups.

We have prepared a variety of nickel(II)–cyclen complexes of the type Ni(cyclen)X$_2$ where X = Cl, Br, or NO$_3$. These complexes are purple in the solid state and in solution. In contrast all the nickel(II)–tbcyclen complexes which have a six-coordinate geometry are blue while the nickel(II)–tbcyclen complexes which have a five-coordinate geometry are green. All the Ni(cyclen)X$_2$ complexes have magnetic moments in the 3.06–3.20 $\mu_B$ range (Table I). (In contrast, the magnetic moment of [Ni(tbcyclen)Cl]Cl is 3.7 $\mu_B$.[7]) These magnetic moments for the Ni(cyclen)X$_2$ complexes are within the range expected for nickel(II) in a six-coordinate geometry.[1] Also, the electronic spectra of all these complexes in the solid state and in solution are typical of six-coordinate nickel(II) (Table II). Therefore it can be concluded that the benzyl groups on the tbcyclen are responsible for the five-coordinate geometry of nickel(II)–tbcyclen complexes.

In the infrared spectra of Ni(cyclen)(NO$_3$)$_2$ the absorption peaks at 810, 1260, and 1490 cm$^{-1}$ can be assigned to bidentate nitrate while the bands at 830 and 1325 cm$^{-1}$ can be assigned to ionic nitrate.[9,10] These assignments confirm the similar assignments made on Ni(tbcyclen)(NO$_3$)$_2$.[7] The bidentate nitrate indicates that the cyclen and tbcyclen must be in a folded configuration around the nickel(II). The N–H stretching frequencies also suggest that all the nickel(II)–cyclen complexes are in a cis configuration. There are several N–H stretches between 3300 and 3100 cm$^{-1}$ in contrast to Ni-(cyclam)Cl$_2$ (cyclam is 1,4,8,11-tetraazacyclotetradecane) which has only one N–H stretch at 3145 cm$^{-1}$.[11] Since the cyclam coordinates coplanar with the nickel(II) all the hydrogens bonded to nitrogens are in essentially the same environment. In contrast, the cyclen is coordinated to the nickel(II) in a folded manner and therefore all the hydrogens bonded to the nitrogen are not in identical environments.

**Table III.** Comparative Conductance Data

| Compd | $CH_3OH^a$ | $H_2O^a$ |
|---|---|---|
| Ni(cyclen)(NO$_3$)$_2$ | 122 | 198 |
| Ni(cyclen)Br$_2\cdot^1/_2C_2H_5OH$ | 122 | 209 |
| Ni(tbcyclen)(NO$_3$)$_2$ | 59 | 168 |
| Ni(tbcyclen)Cl$_2$ | 59 | 193 |
| Ni(cyclam)Cl$_2$[11] | 106 | 247 |
| Ni(cyclam)Br$_2$[11] | 112 | 245 |

$^a$ Concentration = 1 × 10$^{-3}$ M. Units $\Omega^{-1}$ cm$^2$ equiv$^{-1}$.

These observed N–H stretching frequencies are also relatively broad for the complexes Ni(cyclen)Cl$_2$ and Ni(cyclen)Br$_2\cdot$ $^1/_2C_2H_5OH$. Intramolecular hydrogen bonding might be responsible for the broad N–H peaks.

The electronic spectra of all the complexes prepared are also consistent with a cis octahedral geometry. There is no indication of any splitting in the lowest energy band, $v_1$, for all the nickel(II)–cyclen complexes studied in the solid state or in solution. Such a splitting is expected if the nickel(II)–cyclen complexes had a trans octahedral geometry. However, the electronic spectra of the nickel(II)–cyclen complexes look very similar to the spectra of [Ni(en)$_3$](ClO$_4$)$_2$ and [cis-Ni-(en)$_2$(OH$_2$)$_2$](B(C$_6$H$_5$)$_4$)$_2$.[12]

The conductivity data (Table III) suggest that all the complexes prepared in this study are two to one electrolytes in water and are one to one electrolytes in methanol. Therefore it appears that both halides are displaced from the nickel(II) by water and only one halide is displaced by the weaker ligand methanol. However, it was surprising that the compounds which are nonionic in the solid state (Ni(cyclam)Cl$_2$,[11] Ni-(cyclen)Br$_2$, and Ni(cyclen)Cl$_2$) have higher conductivities at 1 × 10$^{-3}$ M concentration in methanol than the compounds which are ionic in the solid state ([Ni(tbcyclen)Cl]Cl and [Ni(tbcyclen)NO$_3$]NO$_3$) (Table III).[7] The lower mobilities of the large cations [Ni(tbcyclen)X]$^+$ vs. [Ni(cyclam)X]$^+$ or [Ni(cyclen)X]$^+$ in solution are a logical explanation. However, there are other additional explanations. The Ni(cyclam)X$_2$[11] and the Ni(CT)X$_2$ (CT is 2,4,4,9,11,11-hexamethyl-1,5,8,12-tetraazacyclotetradecane)[13] are paramagnetic complexes and both their geometries in the solid state are that of a tetragonally distorted octahedron. However, in water these complexes are square planar.[12] Since water is a stronger ligand than Cl$^-$ and Br$^-$ it would be expected that water should displace the coordinated halides and bond to the nickel(II). It has been postulated that Ni(cyclam)$^{2+}$ and Ni(CT)$^{2+}$ are hydrophobic cations that cause water molecules to be less available for bonding to the nickel(II). Such hydrophobic cations cause an increase in hydrogen bonding in the bulk solvent and thereby decrease the activity of the water.[13] The Ni(tbcyclen)$^{2+}$ should be as hydrophobic a cation as the Ni(cyclam)$^{2+}$ and the Ni(CT)$^{2+}$ cations. However, it is unlikely that Ni(tbcyclen)$^{2+}$ could reduce its coordination number and attain either a square-planar geometry or a tetrahedral geometry.[4] The electronic spectra of all complexes listed in Table II confirm that a square-planar or tetrahedral geometry is not attained in any solvent. The conductivity differences between the Ni(II)–tbcyclen and the Ni–cyclen complexes can be explained by noting that the former complexes must function more as a solvent structuring solute than the Ni(II)–cyclen complexes. Since CH$_3$OH can hydrogen bond in an analogous manner to that of water,[12] it can be assumed that Ni(II)–tbcyclen will be less solvated that the Ni(II)–cyclen complexes. The work necessary to keep the ions from pairing is a function of the charges on the cation and anion, $Z_1$ and $Z_2$, the dielectric constant, $\epsilon$, and the distance between ions in the ion pair, $r$. The less solvated the cation the smaller will be the $r$ value and as a result more ion pairing is expected.

$$w = Z_1Z_2e^2/r\epsilon$$

Therefore in methanol there is more ion pairing for the Ni-(II)–tbcyclen complexes than the Ni(II)–cyclen complexes. However, water has a greater dielectric constant than methanol and a greater solvating ability than methanol and as a result the difference in the degree of ion association in water compared to methanol is not as obvious. Nevertheless, the molar conductivities of the Ni(II)–tbcyclen complexes are generally lower than those of the Ni(II)–cyclen complexes.

Finally, an explanation for the anomalously weak field strength of the ligand tbcyclen can be obtained by a comparison of the electronic spectra of Ni(cyclen)X$_2$ and Ni-(tbcyclen)(NO$_3$)$_2$ complexes. The $Dq$ value for all the Ni-(II)–cyclen complexes is greater than Ni(tbcyclen)(NO$_3$)$_2$ (1080–1150 cm$^{-1}$ vs. 975 cm$^{-1}$). The range of $Dq$ values for the Ni(II)–cyclen complexes is within the values observed for nickel(II) complexes of trien and other polyamine ligands.[13,14] Therefore the unusually low $Dq$ value of the [Ni(tbcyclen)-NO$_3$]NO$_3$ must be due primarily to steric strain and not to any inherent property of a 12-membered ring. Kodoma and Kimura[15] also noted that Cu(II)–cyclen complexes exhibited both the thermodynamic and kinetic macrocyclic effects despite the fact that cyclen is sterically more constrained than the larger macrocyclic ligands.

**Experimental Section**

**Physical Measurements.** The physical methods employed in this study have been reported.[7]

**Synthesis of Nitrato(1,4,7,10-tetraazacyclododecane)nickel(II) Nitrate.** One gram (0.0034 mol) of Ni(NO$_3$)$_2\cdot$6H$_2$O was added to 100 mL of absolute ethanol in a 150-mL beaker. This solution was brought to boiling and to it was slowly added a 0.5 g (0.0029 mol) of solid cyclen[16] with rapid stirring. The solution changed from a green to a bluish green color. The volume of this solution was reduced to less than 20 mL by boiling and purple crystals formed upon refrigeration after several hours. These crystals were filtered, purified by recrystallization with absolute ethanol, and dried. Anal. Calcd for Ni(C$_8$H$_{20}$N$_4$)(NO$_3$)$_2$: N, 23.68; H, 5.68; C, 27.06. Found: N, 23.83; H, 5.71; C, 27.88.

**Synthesis of Chloro(1,4,7,10-tetraazacyclododecane)nickel(II) Chloride.** Five-tenths of a gram (2.19 × 10$^{-3}$ mol) of cyclen[16] was added to 100 mL of absolute ethanol and the solution was allowed to boil. To this boiling colorless solution was added, with rapid stirring, a yellow-green solution of 0.7 g (2.94 × 10$^{-3}$ mol) of NiCl$_2\cdot$6H$_2$O dissolved in approximately 10 mL of absolute ethanol. Upon the addition of NiCl$_2\cdot$6H$_2$O the resulting solution immediately turned light blue. The solution was allowed to evaporate at room temperature to dryness. The bluish material was recrystallized using 30 mL of 75% ethanol–25% *tert*-butyl alcohol mixture. The product was then filtered and dried. Anal. Calcd for Ni(C$_8$H$_{20}$N$_4$)Cl$_2$: N, 18.56; H, 6.68; C, 31.83. Found: N, 18.39; H, 6.53; C, 31.99.

**Synthesis of Bromo(1,4,7,10-tetraazacyclododecane)nickel(II) Bromide–Hemiethanol.** A light yellow-green solution containing 0.80 g (1.25 × 10$^{-2}$ mol) of [(C$_2$H$_5$)$_4$N]$_2$NiBr$_4$ dissolved in 50 mL of absolute ethanol in a 150-mL graduated beaker was allowed to boil. To [(C$_2$H$_5$)$_4$N]$_2$NiBr$_4$ was added 0.2 g (1.16 × 10$^{-3}$ mol) of cyclen[16] slowly as a solid. The mixture was stirred rapidly as the cyclen was added. Upon the addition of solid cyclen, the yellow-green solution immediately turned to a cloudy blue. The volume of this solution was reduced to 30 mL by boiling. The solution was then refrigerated for 30 min and filtered, and the blue solid was washed with 10 mL of absolute alcohol and 10 mL of ether and dried. Anal. Calcd for Ni(C$_6$H$_{12}$N$_4$)Br$_2\cdot^1/_2C_2H_5OH$: N, 13.54; H, 5.60; C, 26.12. Found: N, 13.37; H, 5.71; C, 25.66.

**Registry No.** Ni(cyclen)Cl₂, 63598-05-0; Ni(cyclen)Br₂, 63527-99-1; Ni(cyclen)(NO₃)₂, 63528-01-8; [(C₂H₅)₄N]₂NiBr₄, 1185-60-0.

## References and Notes

(1) L. Sacconi, *Transition Met. Chem.*, **4**, 244 (1968).
(2) E. V. Uhlig, *Coord. Chem. Rev.*, **10**, 227 (1973).
(3) W. R. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970).
(4) L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974).
(5) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).
(6) The abbreviations cyclen and tbcyclen have been generally used in the chemical literature; however, a more systematic abbreviation would be [12]aneN₄ and Bzyl₄[12]aneN₄.
(7) G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, **11**, 1145 (1972).
(8) C. M. Sarter and E. L. Blinn, *Inorg. Chem.*, **12**, 3083 (1976).
(9) B. K. Bayhs and J. C. Bailer, *Inorg. Chem.*, **9**, 641 (1970).
(10) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 806 (1965).
(11) B. Bosnick, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1109 (1965).
(12) D. H. Busch, *Werner Centennial, Adv. Chem. Ser.*, **No. 62** (1967).
(13) M. E. Farago, J. M. James, and W. C. G. Trew, *J. Chem. Soc. A*, 820 (1967).
(14) N. C. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1960).
(15) M. Kodama and E. Kimura, *J. Chem. Soc.*, **326**, 1891 (1975).
(16) J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, **96**, 2268 (1974).

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## Organonitrogen Derivatives of Metal Carbonyls. 11. Studies on Cyclopentadienylmetal Dicarbonyls of Molybdenum and Tungsten Containing Ligands Derived from Diphenyltriazene and Acetone Phenylhydrazone[1]

R. B. King* and K. N. Chen[2]

In 1974 the compound (CH₃)₂CNOMo(CO)₂C₅H₅ was first reported[3] as a product from the reaction of NaMo(CO)₃C₅H₅ with 2-bromo-2-nitrosopropane. A subsequent x-ray crystallography study[4,5] indicated structure I (M = Mo; R = R' = CH₃) in which the nitrogen and oxygen atoms but not the carbon atom of the R₂NCO ligand are bonded to the molybdenum atom. Subsequent preparative work[1] resulted in the discovery of far more efficient and convenient methods of preparing analogues of I from a variety of ketoximes and with



I                                        II
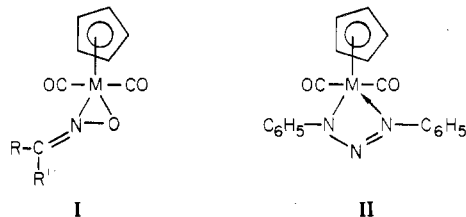
either molybdenum or tungsten as the central metal atom.

The success in preparing in reasonable yields a variety of ketoximato derivatives of the type I in which the oxime nitrogen and oxygen but not the ketone carbon are bonded to the metal raised the question as to whether analogous complexes could be prepared from other types of ketone derivatives. This paper describes the preparation and properties of the complexes [(CH₃)₂CNNC₆H₅]M(CO)₂C₅H₅ (M = Mo and W) derived from acetone phenylhydrazone. In addition, a new method for the preparation of the 1,3-diphenyltriazenido derivatives (C₆H₅)₂N₃M(CO)₂C₅H₅ (II, M = Mo and W) is reported. The molybdenum derivative II (M = Mo) has previously been prepared by a different method[6] but the

tungsten analogue II (M = W) is reported here for the first time.

## Experimental Section

Microanalyses were performed by the Atlantic Microanalytical Laboratory, Atlanta, Ga., and Galbraith Laboratories, Knoxville, Tenn. Molecular weight determinations were determined in benzene solution using a Mechrolab Model 301 vapor pressure osmometer located in the laboratory of Professor G. E. Boyd at the University of Georgia. Melting points were taken in capillaries and are uncorrected.

Infrared spectra in the ν(CO) region were taken in cyclohexane solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm⁻¹ band of polystyrene film. Proton NMR spectra (Table I) were recorded on a Varian T-60 spectrometer at 60 MHz. Carbon-13 NMR spectra (Table I) were recorded on a Jeolco PFT-100 spectrometer operating at 25.0349 MHz with proton noise decoupling and a deuterium lock using a 5 to 8 s repetition rate. Both the proton and carbon-13 NMR spectra were run in CDCl₃ solutions using tetramethylsilane as an internal standard. In the carbon-13 NMR spectra chromium(III) acetylacetonate was added in ~0.15% concentration as a shiftless relaxation reagent[7] to facilitate observation of the metal carbonyl resonances.

Dichloromethane and diethyl ether were freshly distilled over phosphorus pentoxide and calcium hydride, respectively. Pyridine was dried over solid potassium hydroxide and then freshly distilled over barium oxide. Solvents were saturated with nitrogen before use in organometallic experiments. In addition, all organometallic reactions were run in a dry nitrogen atmosphere.

**Reagents.** 1,3-Diphenyltriazene (Eastman) and the metal hexacarbonyls (Pressure Chemical Company, Pittsburgh, Pa.) were purchased from the indicated commercial sources. Acetone phenylhydrazone, bp 99–103 °C (0.5 mm) (lit.[8] bp 108–109 °C (1.6 mm)) was prepared by reaction of phenylhydrazine with excess acetone according to a published procedure.[8] The cyclopentadienylmetal tricarbonyl chlorides, C₅H₅M(CO)₃Cl (M = Mo and W), were prepared on a 0.1 mol scale by an adaptation described elsewhere[1] of the standard published method.[9]

**Preparation of [(CH₃)₂CNNC₆H₅]Mo(CO)₂C₅H₅ (III, M = Mo).** A solution of 2.3 g (15 mmol) of acetone phenylhydrazone in 300 mL of diethyl ether was treated with 7 mL of a 2.5 M hexane solution of *n*-butyllithium (17.5 mmol). The resulting deep orange solution was treated with 2.89 g (10.3 mmol) of C₅H₅Mo(CO)₃Cl at −78 °C. The resulting mixture was stirred at room temperature for 4 h. The reaction mixture was then filtered through Celite. Solvent was removed from the filtrate at 25 °C (25 mm). Crystallization of the residue from a mixture of dichloromethane and hexane gave 3.1 g (85% yield) of deep red-orange [(CH₃)₂CNNC₆H₅]Mo(CO)₂C₅H₅. The analytical sample, mp 133–135 °C dec, ν(CO) 1953 and 1868 cm⁻¹, was purified by a second crystallization from a mixture of dichloromethane and hexane. Anal. Calcd for C₁₆H₁₆MoN₂O₂: C, 52.7; H, 4.4; N, 7.7. Found: C, 52.6; H, 4.5; N, 7.6.

An attempt to prepare [(CH₃)₂CNNC₆H₅]Mo(CO)₂C₅H₅ by reaction of 10 mmol each of acetone phenylhydrazone and C₅H₅Mo(CO)₃Cl in 200 mL of pyridine at 70 °C for 5 h was unsuccessful owing to the preferential formation of a purple complex, mp 97–98 °C, identified as the pyridine derivative C₅H₅Mo(CO)₂(NC₅H₅)Cl from its infrared spectrum in the 4000–5000 cm⁻¹ region and its proton NMR spectrum.

**Preparation of [(CH₃)₂CNNC₆H₅]W(CO)₂C₅H₅ (III, M = W).** A solution of 1.48 g (10 mmol) of acetone phenylhydrazone in 100 mL of diethyl ether was treated with 4 mL of a 2.5 M hexane solution of *n*-butyllithium (10 mmol). After stirring for 20 min at room temperature the resulting light orange solution was treated with 2.3 g (6 mmol) of C₅H₅W(CO)₃Cl and then irradiated at room temperature with a 125 W mercury ultraviolet lamp in a Pyrex well for 1 h. The resulting reaction mixture was filtered through Celite and the Celite was washed with 150 mL of diethyl ether. Evaporation of the filtrate at 25 °C (25 mm) followed by two crystallizations from mixtures of dichloromethane and hexane gave 1.3 g (48% yield) of red-orange [(CH₃)₂CNNC₆H₅]W(CO)₂C₅H₅, mp 154–155 °C dec, infrared ν(CO) 1944 and 1856 cm⁻¹. Anal. Calcd for C₁₆H₁₆N₂O₂W: C, 42.5; H, 3.5; N, 6.2; mol wt, 452. Found: C, 42.4; H, 3.5; N, 6.1; mol wt, 400.

**Preparation of (C₆H₅)₂N₃Mo(CO)₂C₅H₅ (II, M = Mo) by the Pyridine Method.** A mixture of 1.0 g (5.1 mmol) of 1,3-diphenyl-