Photochemistry of $M(CO)_6$ (M = Cr, Mo, W) Solutions Containing Dipyridylalkane Ligands. First Examples of Stable Monodentate $M(CO)_5$(dipyridylalkane) Complexes

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Electronic absorption spectra recorded immediately following UV light irradiation of $M(CO)_6$ (M = Cr, Mo, W) solutions containing excess di-2-pyridylmethane (dpym) or 1,2-di-2-pyridylethane (dpye) indicate the formation of novel $M(CO)_5$(dipyridylalkane) species. In these $M(CO)_5$(dipyridylalkane) complexes the normally bidentate ligand is coordinated in a monodentate fashion. The photoproduced $Mo(CO)_5$(dpym) complex decomposes to form $Mo(CO)_4$(dpym) product via thermal ring closure. In contrast, the other $M(CO)_5$(dipyridylalkane) complexes are thermally stable; these have been isolated and characterized by elemental analyses and by their electronic absorption and infrared spectra. Factors influencing the CO extrusion mechanism of $M(CO)_5$(dipyridylalkane) are discussed.

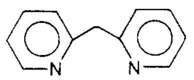
Introduction

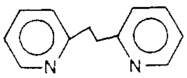
It is well-established that light irradiation of a group 6 metal hexacarbonyl solution containing an excess concentration of diimine ligand (e.g., 2,2′-bipyridine or 1,10-phenanthroline) results in a stable tetracarbonyl derivative.[1] This reaction is thought to proceed via a two-step process; initial photochemical formation of $M(CO)_5L$ and subsequent thermal extrusion of CO ligand to form $M(CO)_4L$ product (see eq 1 and 2). Recently, rapid scanning

$$M(CO)_6 \xrightarrow[\text{diimine}]{\text{UV}} M(CO)_5(\text{diimine}) + CO \quad (1)$$

$$M(CO)_5(\text{diimine}) \xrightarrow{\Delta} M(CO)_4(\text{diimine}) + CO \quad (2)$$

infrared and electronic absorption techniques have yielded spectroscopic data for the transient $M(CO)_5L$ complex, and the kinetics and mechanism of chelation (eq 2) have been studied for 2,2′-bipyridine and 1,4-diazabutadiene ligands.[2,3] However, to this date a monodentate $M(CO)_5L$ (L = diimine or dipyridylalkane) species has not been isolated. This paper reports on our investigation of $M(CO)_6$ (M = Cr, Mo, W) solution photochemistry containing the ligands di-2-pyridylmethane (dpym) and 1,2-di-2-pyridylethane (dpye); these ligands are closely related to 2,2′-bipyridine (bpy) and are shown below. Our study illustrates the unusual coordination behavior exhibited by dpym and dpye and has led to the first isolation of a stable $M(CO)_5$(dipyridylalkane) complex, in which the normally bidentate dipyridylalkane ligand is coordinated in a monodentate fashion.


dpym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Results and Discussion

A typical photolysis experiment consisted of 2-s UV irradiation of a 5×10^{-4} M $M(CO)_6$ (M = Cr, Mo, W) solution containing 10^{-2} M dipyridylalkane ligand (dpym or dpye) at 20 °C. Approximately 10^{-4} M $M(CO)_6$ is photodissociated during this light irradiation; this value has been estimated from the incident light intensity (measured by Ferrioxalate actinometry[4]) and the reported quantum yield of $M(CO)_6$.[5] Electronic absorption spectra recorded immediately after photolysis indicate visible spectral features that are characteristic of $M(CO)_5L$ type complexes (see Table I).[6] Moreover, these complexes (with the exception of $Mo(CO)_4$(dpym), vide infra) were determined to be thermally stable at room temperature, exhibiting no formation of a bidentate $M(CO)_4$(dipyridylalkane) product over a 72-h period. This stability is surprising in view of the thermal ring closure mechanism that normally takes place readily with bidentate ligands such as 2,2′-bipyridine, 1,10-phenanthroline, or 1,4-diazabutadiene derivatives.[3,7]

Table I. Electronic Absorption Data and Assignments for Low-Energy Features of $M(CO)_5L$ and $M(CO)_4L$ Complexes in Benzene at 20 °C

complex	band maxima, nm
$Cr(CO)_5$(dpym)	406 (d → d)
$Cr(CO)_5$(dpye)	388 (d → d)
$Cr(CO)_5$(2-Phpy)	404 (d → d)
$Mo(CO)_5$(dpym)	385 (d → d)
$Mo(CO)_5$(dpye)	384 (d → d)
$Mo(CO)_5$(2-Phpy)	378 (d → d)
$W(CO)_5$(dpym)	386 (d → d), 430 (d → d)[a]
$W(CO)_5$(dpye)	381 (d → d), 430 (d → d)[a]
$W(CO)_5$(2-Phpy)	376 (d → d), 430 (d → d)[a]
$Cr(CO)_4$(dpym)	406 (d → d), 738 (MLCT)
$Mo(CO)_4$(dpym)	380 (d → d), 682 (MLCT)
$W(CO)_4$(dpym)	380 (d → d), 696 (MLCT)

[a] Spin-forbidden transition observed as a shoulder.

The $Mo(CO)_5$(dpym) complex was observed to decompose thermally to form $Mo(CO)_4$(dpym), as noted by the growth of its metal to ligand charge-transfer (MLCT) feature at 682 nm. The analogous chromium and tungsten bidentate products could only be achieved by using further light irradiation (see eq 3); their MLCT bands being ob-

$$M(CO)_5(\text{dpym}) \xrightarrow{\text{UV}} M(CO)_4(\text{dpym}) + CO \quad (3)$$

served at 738 and 696 nm, respectively. Isolation of the

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(1) (a) Strohmeier, W.; von Hobe, D. *Chem. Ber.* **1961**, *94*, 2031. (b) Brunner, H.; Herrmann, W. A. *Chem. Ber.* **1972**, *105*, 770.

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

(3) (a) Schadt, M. J.; Gresalfi, N. J.; Lees, A. J. *Inorg. Chem.* **1985**, *24*, 2942. (b) Schadt, M. J.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 672.

(4) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(5) (a) Nasielski, J.; Colas, A. *J. Organomet. Chem.* **1975**, *101*, 215. (b) Nasielski, J.; Colas, A. *Inorg. Chem.* **1978**, *17*, 237.

(6) (a) Wensky, D. A.; Wensky, A. K. *Spectrochim. Acta, Part A* **1975**, *31A*, 23. (b) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105. (c) Daamen, H.; Oskam, A.; Stufkens, D. J.; Waaijers, H. W. *Inorg. Chim. Acta* **1979**, *34*, 253. (d) Boxhoorn, G.; Stufkens, D. J.; van de Coolwijk, P. J. F. M.; Hezemans, A. M. F. *Inorg. Chem.* **1981**, *20*, 2778.

(7) Bock, H.; tom Dieck, H. *Chem. Ber.* **1967**, *100*, 228.

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Table II. Melting Points[a] and Elemental Analyses for $W(CO)_5L$ Complexes

complex	mp, °C	elemental anal.
$W(CO)_5$(dpym)	88–90	found: C, 38.3; H, 1.79; N, 6.07 calcd: C, 38.9; H, 2.04; N, 5.67
$W(CO)_5$(dpye)	110–115	found: C, 39.3; H, 2.18; N, 5.14 calcd: C, 40.2; H, 2.38; N, 5.51
$W(CO)_5$(2-Phpy)	85–88	found: C, 39.1; H, 1.87; N, 2.78 calcd: C, 40.1; H, 1.90; N, 2.92

[a] Complexes undergo decomposition at this temperature.

Table III. Infrared and Raman C–O Stretching Frequencies for $W(CO)_5L$ Complexes[a]

	infrared bands, cm^{-1}				Raman bands, cm^{-1}			
complex	$A_1{}^1$	B_1	E	$A_1{}^2$	$A_1{}^1$	B_1	E	$A_1{}^2$
$W(CO)_5$(dpym)	2068	1978	1931	1898	2077	1985	*b*	1895
$W(CO)_5$(dpye)	2075	1978	1931	1902	2072	1978	*b*	1890
$W(CO)_5$(2-Phpy)	2070	1978	1930	1898	2080	1987	1928	1889

[a] Recorded in chloroform at 20 °C. [b] Not observed.

$W(CO)_4$(dpym) complex in this manner gave the following. Anal. Calcd for $W(CO)_4$(dpym): C, 38.9; H, 2.04; N, 5.67. Found: C, 38.2; H, 2.03; N, 5.95. Infrared C–O stretching frequencies were recorded from $W(CO)_4$(dpym) in chloroform at 2000, 1898, 1878, and 1840 cm^{-1}; these are consistent with the C_{2v} symmetry of the carbonyl ligands in this complex.[8]

Further irradiation of the $M(CO)_5$(dpye) (M = Cr, Mo, W) complexes did not yield the chelated complex. Instead, continuous photolysis over a 30-min period was accompanied by an early loss of isosbestic points and the formation of species that weakly absorb in the 400–450-nm region. These species are thought to arise from the coordination of solvent impurity species with the photoproduced $M(CO)_5$ complex.[3a] In these photolysis experiments the ligand was present in an approximately 100-fold excess concentration, and no evidence was found for the formation of binuclear complexes in the reaction mixture.

The $W(CO)_5$(dpym) and $W(CO)_5$(dpye) complexes, determined to be thermally stable in the photolysis experiments, have been isolated via the pentacarbonyl tetrahydrofuran (THF) adduct (see eq 4 and 5).[9] Melting

$$W(CO)_6 \xrightarrow[\text{THF}]{\text{UV}} W(CO)_5(\text{THF}) + CO \qquad (4)$$

$$W(CO)_5(\text{THF}) \xrightarrow[\text{diimine}]{\Delta} W(CO)_5(\text{diimine}) + \text{THF} \qquad (5)$$

points, elemental analyses, and spectroscopic results for these complexes are listed in Tables I and II. The data for the closely related $M(CO)_5$(2-Phpy) complexes are included for comparison.

Infrared and electronic absorption spectra obtained for $W(CO)_5$(dpye) are shown in Figure 1; these spectra are concordant with a pentacarbonyl species in which the ligand is coordinated in a monodentate fashion. The four infrared bands centered at 2075, 1978, 1931, and 1902 cm^{-1} correspond to the $A^1{}_1$, B_2, E, and $A_1{}^2$ modes, respectively.[8b,c] It is noted, however, that the enhanced intensity of the normally IR-forbidden B_2 mode implies that the CO ligands are significantly distorted from C_{4v} symmetry in this complex. The electronic absorption spectrum of $W(CO)_5$(dpye) is characteristic of those observed from other classes of $M(CO)_5L$ (M = Cr, Mo, W; L = *n*-electron donor)

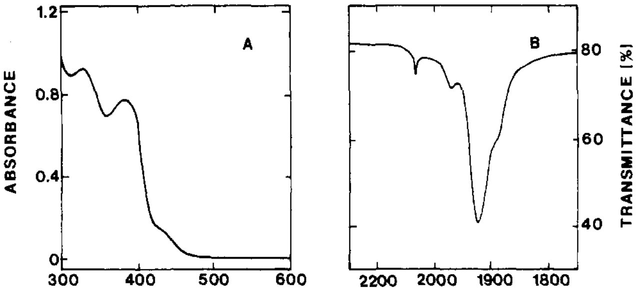

Figure 1. (A) Electronic absorption spectrum of $W(CO)_5$(dpye) in benzene at 20 °C. (B) Infrared spectrum in the CO stretching region of $W(CO)_5$(dpye) in chloroform at 20 °C.

complexes; the maximum at 381 nm is therefore assigned to the $^1A(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2a_1{}^1)$ transition.[6] The weak absorption at ~430 nm is only observed for the tungsten complexes and is attributed to a spin-forbidden $^1A(e^4b_2{}^2) \rightarrow {}^3E(e^3b_2{}^2a_1{}^1)$ band; this transition has been reported for a number of $W(CO)_5L$ complexes.[6] Furthermore, the low-energy UV–visible features of $W(CO)_5$(dpym) and $W(CO)_5$(dpye) are not appreciably moved in ethanol or isooctane solutions, in agreement with the d → d assignment.[10]

Isolation of these novel monodentate $M(CO)_5$(dipyridylalkane) species demonstrates that these types of complexes do not necessarily proceed via a spontaneous ring closure mechanism. The absence of chelation is attributed to poor σ-overlap between the σ-orbital of the uncoordinated nitrogen atom and the metal d orbital in these $M(CO)_5$(dipyridylalkane) apparently addition of bridging carbon atoms in bpy, to yield the dpym and dpye ligands, brings about a substantial reduction in M–N overlap. Experimental and theoretical studies on the bpy molecule have indicated that this ligand exists in an approximately *s-trans* conformation in the solution phase.[11] This π-conjugation will tend to hinder rotation about the C_2–C_2' bond that is required to achieve the cis geometry necessary for ligand chelation. Therefore, the lack of chelation in our $W(CO)_5L$ complexes cannot be attributed to the absence of π-electron conjugation in the dipyridylalkane system. Previous investigations of $M(CO)_5L$ complexes, where M = Cr, Mo, or W, and L = a bidentate phosphorus or arsenic donor ligand, have shown that the chelation reaction proceeds via a largely dissociative mechanism.[12] In contrast, however, the stable $M(CO)_5$(dpym) and $M(CO)_5$(dpye) complexes studied here have clearly illustrated that the incoming nitrogen atom has a major influence on the relative ease of CO extrusion.

Experimental Section

Materials. The parent metal hexacarbonyls (Cr, Mo, W) were purchased from Strem Chemicals, Inc., and used without further purification. Starting materials, 2-picoline, pyridine, and sodium amide, used in the preparation of dpym were obtained from Aldrich Chemical Co. as reagent grade materials. Spectroscopic grade benzene (J. T. Baker Chemical Co.) was further purified by absorptive filtration through Woelm alumina B (activity 1)

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(8) (a) Chatt, J.; Watson, H. R. *J. Chem. Soc.* **1961**, 4980. (b) Orgel, L. E. *Inorg. Chem.* **1962**, *1*, 25. (c) Kraihanzel, C. S.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 533.

(9) Strohmeier, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730.

(10) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825.

(11) (a) Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420. (b) Cumper, C. W. N.; Ginman, R. F. A.; Vogel, A. I. *J. Chem. Soc.* **1962**, *1188*. (c) Cureton, P. H.; LeFevre, C. G.; LeFevre, R. J. W. *J. Chem. Soc.* **1963**, 1736. (d) Spotswood, T. McL.; Tanzer, C. I. *Aust. J. Chem.* **1965**, *20*, 1227. (e) Castellano, S.; Gunther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.

(12) (a) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 347. (b) Connor, J. A.; Hudson, G. A. *J. Organomet. Chem.* **1974**, *73*, 351. (c) Connor, J. A.; Riley, P. I. *J. Organomet. Chem.* **1975**, *94*, 55.

obtained from ICN Biomedicals, Inc. Nitrogen used for deoxygenating was purified by passage through two 1 m × 2 cm drying tubes. The first tube contained alternating 20-cm lengths of dry $CaSO_4$ (W. A. Hammond Drierite Co.) and P_2O_5 (Fisher Scientific Co.), and the second contained a Cu catalyst (BASF R3-11, Chemical Dynamics Corp.). The Cu catalyst had been previously activated by heating to 120 °C while being flushed with a steady stream of H_2. In this activated form, the catalyst removes trace amounts of H_2O and O_2 from gases. *Caution*: The reduced catalyst is extremely pyrophoric.

The dpye ligand was obtained from Prof. W. R. Cherry (Louisiana State University). The ligand 2-phenylpyridine (2-Phpy) was purchased from Aldrich Chemical Co. and used without further purification.

Synthesis of Di-2-pyridylmethane. The synthesis used was similar to that reported previously.[13] 2-Picoline (5.0 g, 0.054 mol) was added dropwise to a 50% suspension of sodium amide (2.106 g, 0.054 mol) in benzene. The mixture was refluxed for 2 h and treated dropwise with pyridine (4.37 g, 0.054 mol). The resulting mixture was then refluxed for another 6 h and the product isolated by treating with distilled water (10 mL) at 60 °C and distilled at 176–180 °C to give 5.5 g (60% yield) of a yellow-brown oil. The dpym product was further purified by Kugelrohr distillation at 10^{-2} torr.

Synthesis of $M(CO)_5L$ Complexes. The $M(CO)_5L$ complexes, where M = Cr, Mo, or W and L = dpym or dpye, were prepared by prior generation of the corresponding tetrahydrofuran complex $M(CO)_5(THF)$.[9] A tetrahydrofuran solution (200 mL) of the parent hexacarbonyl (4 mmol) was deoxygenated by purging with purified nitrogen for 20 min and then irradiated with a 200-W medium-pressure Hg lamp for approximately 60 min. Throughout photolysis the solution was continuously purged with nitrogen to avoid oxidation of the complex. Following irradiation a stoichiometric amount of the desired ligand was added in the dark to the reaction vessel. In effect, the ligand was in excess because the conversion of $M(CO)_6$ to $M(CO)_5(THF)$ was not complete. The tetrahydrofuran was removed by rotary evaporation and the complex redissolved in isooctane and purified by chromatography on a 3-in. alumina column; both these steps were carried out in low-light conditions to minimize photoreaction. Successive washing with isooctane was effective at removing unreacted hexacarbonyl complex from the column as monitored by UV absorption spectra. Elution with benzene then removed the $M(CO)_5L$ complex. Further purification steps were usually required, either by repeated washings with isooctane or by sublimation of unreacted $M(CO)_6$ at 30 °C and 10^{-3} torr. The complexes were obtained in 45% yield and were stored under nitrogen in the dark at 5 °C.

Synthesis of $M(CO)_4L$ Complexes. These complexes were prepared by UV photolysis with a 200-W medium-pressure Hg lamp of an isooctane solution (300 mL) that contained the parent hexacarbonyl (0.2 mmol) and ligand (0.25 mmol). After irradiation for typically 30–40 min the solution was cooled in an ice bath to complete precipitation of $M(CO)_4L$. The product was obtained by vacuum filtration and purified by successive washings with isooctane and, if necessary, by column chromatography on 80–200 mesh alumina (Fisher Scientific Co.). The complexes were reasonably stable in the solid form and were kept in the dark at 5 °C; storing under nitrogen increased their long-term stability.

Physical Measurements. Photolyses were carried out with an Ealing 200-W medium-pressure Hg lamp. The $M(CO)_6$ solutions were deoxygenated prior to photolysis by purging the benzene solution with purified nitrogen for 15 min. Electronic absorption spectra were obtained in the dark within 2 s after excitation and at suitable time intervals thereafter on a microprocessor-controlled diode-array Hewlett-Packard 8450A UV–visible spectrophotometer. All absorption spectra were recorded in the dark. 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. Infrared spectra were recorded on a Perkin-Elmer Model 283B spectrometer. All complexes were recorded as chloroform solutions in a NaCl cell of 1-mm path length. Raman spectra were recorded on a Spex 1702/04 spectrometer following laser excitation at 500 nm. Samples were recorded as chloroform solutions.

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Registry No. dpym, 1132-37-2; $Cr(CO)_5(dpym)$, 103639-25-4; $Cr(CO)_5(dpye)$, 103639-26-5; $Cr(CO)_5(2\text{-}Phpy)$, 83005-98-5; $Mo(CO)_5(dpym)$, 103639-27-6; $Mo(CO)_5(dpye)$, 103639-28-7; $Mo(CO)_5(2\text{-}Phpy)$, 83005-96-3; $W(CO)_5(dpym)$, 103639-29-8; $W(CO)_5(dpye)$, 103639-30-1; $W(CO)_5(2\text{-}Phpy)$, 83005-91-8; $Cr(CO)_4(dpym)$, 90187-51-2; $Mo(CO)_4(dpym)$, 88814-40-8; $W(CO)_4(dpym)$, 88814-39-5; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; 2-picoline, 109-06-8; pyridine, 110-86-1.

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[13] Thiele, K.; Gross, A.; Posselt, K.; Schuler, W. *Chim. Ther.* **1967**, *2*, 366.