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Supplementary Material Available: Reviewers' comments and authors' reply during evaluation of this work, comprising an instructive dialogue on the relative merits of the present approach as compared to other theoretical studies of this type. At the suggestion of Reviewer No. 2 and with concurrence of all parties involved, these materials are offered as a supplement (19 pages) to this article; ordering information is given on any current masthead page. In considering this suggestion the Reviewers were asked and have agreed to reveal their identities: Reviewer No. 2, R. Hoffmann; Reviewer No. 1, W. A. Goodard, III.

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Ligand-Bridged Dimers of Pentacarbonyltungsten. Synthesis and Characterization[1]

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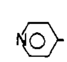
Monomeric and dimeric derivatives of the type $W(CO)_5L$ and $[W(CO)_5]_2L$ have been synthesized by a method involving the photochemical generation of the intermediate solvent adduct $W(CO)_5THF$. In each case L is a bifunctional nitrogen heterocycle such as 4,4′-bipyridine. The monomers and dimers were characterized by HPLC, ^1H NMR, ^{13}C NMR, elemental analysis, and electronic spectroscopy. One of the most interesting features of the electronic spectra of the dimers is that the metal-to-ligand charge-transfer absorption occurs at a significantly lower energy than the ligand field band at 405 nm for the dimers $[W(CO)_5]_2L$ containing the conjugated bridging ligands 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene.

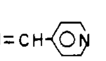
Introduction

The photosubstitutional reactivity of the zerovalent metal carbonyl complexes $M(CO)_5L$ is not only dependent on the wavelength but also dependent on the nature of the unique ligand L. Both Wrighton[3] and Zink[4] have examined the photosubstitution reactions of these compounds where M = W and L = a nitrogen heterocycle. Wrighton[3] first identified the metal-to-ligand charge-transfer (MLCT) state as being photochemically unreactive. Zink[4] later noted a correlation between (1) the relative positions of the metal-to-ligand charge-transfer absorption bands and the ligand field (LF) absorption bands in the tungsten compounds and (2) the quantum yields for both unique ligand and carbonyl ligand photosubstitution.

Accordingly, Zink[4b] has proposed a classification (based on the nature of the unique ligand L) of the photochemistries of the compounds $W(CO)_5L$. Compounds that fall into Zink's class 3(2) have metal-to-ligand charge-transfer absorption bands at lower energy than ligand field ($^1E \leftarrow {}^1A$) bands. Instead of efficient unique-ligand (L) substitution as is observed for Zink's class 1 compounds (such as the case where L = piperidine), class 3(2) compounds undergo both unique-ligand and CO photosubstitution reactions with extremely low ($\phi < 0.02$) quantum yields, when the irradiation wavelength corresponds to the lowest energy feature of the absorption spectra. There are, however, few examples of compounds that fall into Zink's class 3(2).

We report here on the synthesis and characterization of some new "class 3" homonuclear dimers of the general formula $[W(CO)_5]_2L$, where L = 4,4′-bipyridine (BPY), 1,2-bis(4-pyridyl)ethane (BPA), or 1,2-bis(4-pyridyl)ethylene (BPE). The dimers and the monomeric compound $W(CO)_5BPY$ have been characterized by elemental analysis, HPLC, electronic spectra, ^1H NMR, and ^{13}C NMR. In specific cases, the metal-to-ligand charge-transfer band of a dimer is lower in energy than the ligand field absorption bands. Our intent is to extend the number of compounds that fall into Zink's class 3 and then, in a related paper, to examine the photochemical reactivities of such compounds. Recently, similar dimers have been reported,[5] as well as monomeric derivatives[6] for which the MLCT band appears at significantly lower energy than LF bands in the electronic spectrum.


BPY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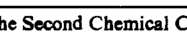
BPE

Experimental Section

Materials and Reagents. The starting hexacarbonyl, $W(CO)_6$, was obtained from Strem Chemicals and was used without further purification. The free ligands BPA and BPE were obtained from Aldrich and used without purification. The ligand BPY (Aldrich) was dissolved in THF, and the resulting solution was dried over 4-Å molecular sieves and under an atmosphere of dry nitrogen gas because the ligand was available only as the dihydrate. All THF solvent was distilled from $LiAlH_4$ and stored under dry nitrogen gas. THF was transferred under an atmosphere of dry nitrogen gas with syringe techniques. All solvents used in the syntheses were ACS reagent grade or better and were used without further purification. Solvents for HPLC and those for spectra were spectrophotometric grade.

Photolyses were carried out with a 450-W Hanovia medium-pressure mercury vapor lamp that was housed in an Ace Glass quartz immersion well. The photolyses were performed under an atmosphere of dry nitrogen gas. All of the products of the photolyses were handled in the dark or with a minimum amount of dim red light.

Synthetic Procedures. (a) $[W(CO)_5]_2L$. The homonuclear dimers were prepared by the general synthetic procedure in which a dry THF solution of the free ligands BPY, BPA, or BPE was thermally reacted with a THF solution of the solvent adduct, $W(CO)_5THF$.[7] The intermediate product $W(CO)_5THF$ was not isolated. A specific

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(2) (a) The College of Wooster. (b) The University of Toledo.

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example where L = BPY is typical of all of these syntheses.

$W(CO)_6$, 1.00 g (2.84 mmol), was dissolved in 300 mL of dry THF solvent and photolyzed under an atmosphere of dry nitrogen gas for 2 h at ambient temperature. The resulting yellow solution was transferred in the dark to a THF (100 mL) solution of BPY, 0.44 g (2.8 mmol), which had been previously dried over molecular sieves. The resulting reaction mixture was stirred for 10 h at room temperature, in the dark. The resulting dark yellow solution was rotoevaporated to dryness at 35 °C yielding a dark yellow paste. This crude product was proved to contain a mixture of unreacted BPY ligand and $M(CO)_6$, as well as the desired dimer and the monomeric derivative, $M(CO)_5$BPY. The crude product was either washed with warm hexane or Soxhlet extracted with pentane to remove as much of the unwanted products from the far less soluble dimer. $[W(CO)_5]_2$BPY was further purified by column chromatography on alumina (activity III). Elution with isooctane moved only the hexacarbonyl through the column while elution with acetone or THF moved monomer, free ligand, and dimer through the column rapidly. With diethyl ether the order of elution from alumina was $[W(CO)_5]_2$BPY > $W(CO)_5$BPY > BPY. This parallels the order in which these materials were found to elute in HPLC experiments on a C-18 RP column. In fact, the various components of the product mixture were identified by HPLC retention times, as will be discussed below. The product was also purified by multiple recrystallizations from THF/hexane. All three compounds were shown to be pure by exhaustive HPLC.

The yield for $[W(CO)_5]_2$L was 10–30%, depending on the ligand used. Anal.[8] Calcd for $(CO)_5W-N_2C_{10}H_8-W(CO)_5$: C, 29.88; H, 1.00; N, 3.48. Found: C, 30.02; H, 1.20; N, 3.57. Calcd for $(CO)_5W-N_2C_{12}H_{12}-W(CO)_5$: C, 31.76; H, 1.45; N, 3.37. Found: C, 32.08; H, 1.64; N, 3.36. Calcd for $(CO)_5W-N_2C_{12}H_{10}-W(CO)_5$: C, 31.83; H, 1.21; N, 3.38. Found: C, 31.64; H, 1.35; N, 3.42.

(b) $W(CO)_5$BPY. A pure sample of the monomeric compound $W(CO)_5$BPY was obtained during the Soxhlet extraction of the crude $[W(CO)_5]_2$BPY product above. The monomer was obtained as single crystals found growing on the walls of the lower solvent flask of the extractor once the solution in this lower flask had become concentrated with the monomeric $W(CO)_5$BPY. The compound was shown to be pure by exhaustive HPLC; yield 12%. Anal.[8] Calcd for $W(CO)_5-N_2C_{10}H_8$: C, 37.53; H, 1.68; N, 5.84. Found: C, 37.78; H, 1.67; N, 5.58.

High-Performance Liquid Chromatography. HPLC experiments were performed with a Varian 5000 instrument and an RP (C-18) Varian Micro Pac analytical column. The solvent program involved an elution (2.0 mL min^{-1}) with acetonitrile for 8 min, a switch to pure methanol over a 2-min period, and elution with pure methanol for 5 min, followed by a return to pure acetonitrile over a 2-min period. Detection was with a Vari-Chrom detector at 254 nm. Samples were prepared in the dark with acetonitrile.

Spectroscopic Methods. Electronic spectra were obtained on a Cary 14 spectrophotometer. Solutions were prepared and spectra were taken at 20.0 ± 0.5 °C. NMR spectra were obtained (Me_4Si reference) on a Varian T-60 (^{1}H NMR) or on a JEOL FX-90Q (^{1}H and ^{13}C NMR), either in $CDCl_3$ or in deuterated THF.

Results and Discussion

The HPLC retention times of the pure compounds available in this study are presented in Table I. The uncoordinated ligands BPY, BPA, and BPE, being dibasic, were most retained by the column. These materials did not elute at a conveniently short time in acetonitrile, apparently as a result of strong interactions with residual adsorption sites in the support, so the methanol elution was used, as described in the Experimental Section. The pure monomeric compound, $W(CO)_5$BPY, eluted at 5.5 min, and samples of similar monobasic compounds (e.g., pyridine) gave peaks with elution times of ca. 5 min. The dimeric products and other materials such as $W(CO)_6$ and $W(CO)_5$py were least retained by the column. This is understandable in terms of the absence of any exposed nitrogen atoms in these latter materials. We have routinely used HPLC work to analyze the components of crude product mixtures. The HPLC of the chromium analogues of the compounds reported here also followed this pattern in retention times.[10]

Table I. HPLC Retention Times[a]

compd	RT,[b] min	compd	RT,[b] min
	A. Reactants		
py	4.6	BPA	13.1
$W(CO)_6$	1.7	BPE	12.8
BPY	12.5		
	B. Monomeric Products		
$W(CO)_5$py[c]	1.7	$W(CO)_5$BPY	5.5
	C. Dimeric Products		
$[W(CO)_5]_2$BPY	1.6	$[W(CO)_5]_2$BPE	1.6
$[W(CO)_5]_2$BPA	1.6		

[a] Elution program as described in the Experimental Section. [b] Retention times are reported ±0.2 min, where the values represent averages of three to five runs. [c] Prepared by the method of Darensbourg.[9]

We have met with little success in attempts to synthesize the monomeric compounds $W(CO)_5$L. Not the relative amounts of reactants ($W(CO)_5$THF + L), the order of mixing the reactant solutions, or the concentration of either of the reactant solutions was useful in preventing contamination of the monomeric products with the dimers $[W(CO)_5]_2$L. We have also observed the formation of other side products, which we tentatively have identified as polymers on the basis of HPLC data, electronic spectra, and the insolubility of a certain percentage of the reaction products in nonpolar solvents such as pentane. The formation of such polymers can be explained by analogy to the known reactivities of the tungsten carbonyl. Product mixtures that did initially contain a large fraction of the desired $W(CO)_5$L (as determined by HPLC) reacted thermally in workup to give significant amounts of the dimeric materials $[W(CO)_5]_2$L. We were unable to use large proportions of free ligand L in the syntheses, as the chromatographic and recrystallization workup to remove the unreacted ligand on alumina was inefficient. Thus the isolation of a solid sample of $W(CO)_5$BPY may have been spurious. We are presently trying to develop a reliable synthesis of the compounds $W(CO)_5$L, as these are desired if heteronuclear dimers $(CO)_5M-L-M'(CO)_5$ are to be prepared. A method that circumvents this problem was recently published by Keiter et al.[5a]

It is noteworthy that Strohmeier has reported[11] the synthesis of monomeric derivatives of dibasic ligands, where the basic functions are nonequivalent. In the latter case, no dimeric derivatives were obtained. In contrast, we have used symmetrical dibasic ligands and have observed preferential formation of dimeric derivatives. In the case of BPY, this is understandable if the nucleophilicity of the second pyridine ring is increased[12] upon coordination of the first pyridine ring to form the monomeric derivative $M(CO)_5$L.[13]

The syntheses of the homonuclear dimeric materials $[W(CO)_5]_2$L were straightforward, as described in the Experimental Section. Repeated chromatography on alumina and recrystallizations from THF/pentane were needed to remove unreacted ligand L and hexacarbonyl. The products $[W(CO)_5]_2$L were more thermally stable, though, and thus did not present the purification difficulties discussed above. The dimeric compound $[W(CO)_5]_2$BPY was found to be only

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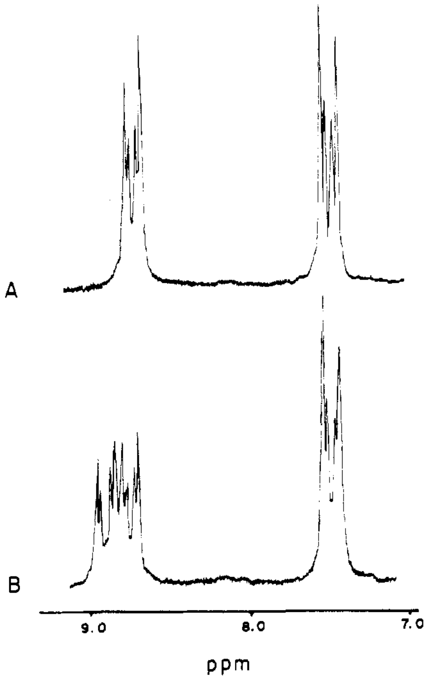

Figure 1. 60-MHz ^1H NMR spectra for (A) BPY and (B) W(CO)$_5$BPY. Chemical shifts are relative to Me_4Si.

Table II. ^1H NMR Spectroscopic Data[a]

compd	ortho[b]	meta[c]	other
BPY	8.73 (4)	7.51 (4)	
W(CO)$_5$BPY	8.95 (2), 8.80 (2)[d]	7.51 (4)	
[W(CO)$_5$]$_2$BPY	9.05 (4)	7.51 (4)	
BPA	8.42 (4)	7.02 (4)	2.85 (4)[e]
[W(CO)$_5$]$_2$BPA	8.95 (4)	7.41 (4)	3.04 (4)[e]
BPE	8.80 (4)	7.35 (4)	7.17 (2)[f]
[W(CO)$_5$]$_2$BPE	9.05 (4)	7.65 (4)	7.76 (2)[f]

[a] Chemical shifts in ppm, relative to Me_4Si. Spectra were obtained in either deuterated THF or $CDCl_3$. Numbers in parentheses represent numbers of protons assigned, as determined by integration. [b] Chemical shifts measured to the center of the downfield member of an aromatic doublet of multiplets and assigned to ring protons ortho to the ring nitrogens (except for W(CO)$_5$BPY as shown in Figure 1B and discussed in the text). [c] Chemical shifts measured to the center of the upfield member of an aromatic doublet of multiplets and assigned to the ring protons meta to the ring nitrogens. [d] See Figure 1B and discussion in the text. [e] Methylenic protons. [f] Olefinic protons.

Table III. ^{13}C NMR Spectroscopic Data[a]

compd	ortho[b]	meta[c]	para[d]	other	trans CO	cis CO
BPY	150.7	121.4	145.5			
W(CO)$_5$BPY	156.7, 151.1	123.3, 121.1	147.1, 143.3		202.4	198.8
[W(CO)$_5$]$_2$BPY	157.3	123.0	150.0[e]		*e*	*e*
BPA	149.7	123.6	149.2	35.4[f]		
[W(CO)$_5$]$_2$BPA	157.2	126.7	153.6	35.5[f]	202.8	199.4
BPE	150.4	121.8	143.2	130.4[g]		
[W(CO)$_5$]$_2$BPE	157.8	123.9	145.6	132.0[g]	202.8	199.4

[a] Chemical shifts in ppm, relative to Me_4Si. Spectra were obtained in either deuterated THF or $CDCl_3$. [b] Ring carbons ortho to the ring nitrogens. [c] Ring carbons meta to the ring nitrogens. [d] Quaternary ring carbons. [e] Low signal to noise makes this assignment speculative. [f] Methylenic carbons. [g] Olefinic carbons.

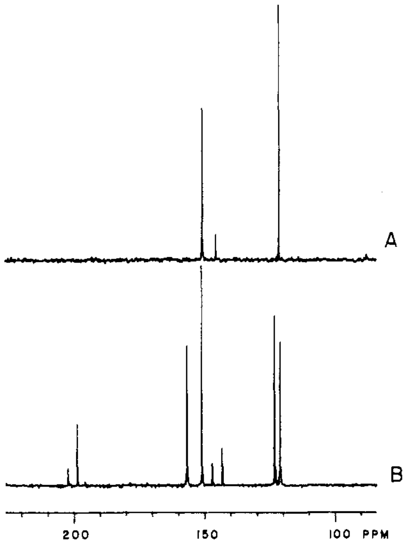

Figure 2. ^{13}C NMR spectra for (A) BPY and (B) W(CO)$_5$BPY. Chemical shifts are relative to Me_4Si.

moderately sensitive to photolysis at both 400 ± 10 and 500 ± 10 nm.[15]

The ^1H NMR spectrum of BPY is shown in Figure 1A. The spectrum consists of two multiplets, each typical of an AA'XX' spin system. Chemical shifts of these two resonances, measured to the centers of each multiplet relative to the peak of Me_4Si, are given in Table II. The aromatic portions of the spectra of BPE and BPA are similar in their splitting pattern, and these resonances are also listed in Table II.

The ^1H NMR spectrum of the monomeric derivative W(CO)$_5$BPY is shown in Figure 1B. Coordination of one nitrogen of BPY to tungsten pentacarbonyl disrupts the symmetrical equivalence of the two pyridine rings. Accordingly, the spectrum of the BPY ligand in W(CO)$_5$BPY (Figure 1B) has been altered. The multiplet centered at 7.51 ppm (4 H) is assigned to ring protons meta to both ring nitrogens. Although these two sets of protons are symmetrically nonequivalent, there is evidently considerable coincidental magnetic equivalence, as the multiplet is only slightly altered in splitting pattern and in chemical shift as compared to the comparable multiplet (7.51 ppm) for the free ligand BPY. In contrast, the multiplet (8.73 ppm, 4 H) assigned for the free ligand BPY to protons ortho to the ring nitrogen has been resolved into two identical multiplets of equal intensity, as shown in Figure 1B. Here the symmetrical and magnetic nonequivalence of the ortho protons in the two BPY rings of W(CO)$_5$BPY is pronounced. The multiplet centered at 8.80 ppm (2 H) is assigned to ring protons ortho to the free, uncoordinated nitrogen of W(CO)$_5$BPY, while the multiplet centered at 8.95 ppm (2 H) is assigned to ring protons ortho to the coordinated nitrogen of W(CO)$_5$BPY.

In the dimeric compound [W(CO)$_5$]$_2$BPY, the symmetrical equivalence of the two BPY rings is restored. Accordingly, the aromatic portion of the ^1H NMR spectrum of [W(CO)$_5$]$_2$BPY shows only the two multiplets reminiscent of the spectrum of BPY itself. The chemical shifts of these multiplets are listed in Table II. Comparable spectra were obtained for the compounds [W(CO)$_5$]$_2$BPE and [W(CO)$_5$]$_2$BPA.

These ^1H NMR spectra show the deshielding influence of the coordinated W(CO)$_5$ group. This is especially true in the extensively π-conjugated compound [W(CO)$_5$]$_2$BPE, where the olefinic protons are shifted to a point (7.76 ppm) downfield from the meta ring protons (7.65 ppm). The deshielding influence of a coordinated W(CO)$_5$ group is also seen in the ^{13}C NMR spectra discussed below.

^{13}C NMR spectroscopic data are listed in Table III. The spectra of the free ligand BPY and of the monomeric derivative W(CO)$_5$BPY are shown in Figure 2. As expected, each

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(15) Gaus, P. L.; Quinn, K. J., unpublished results.

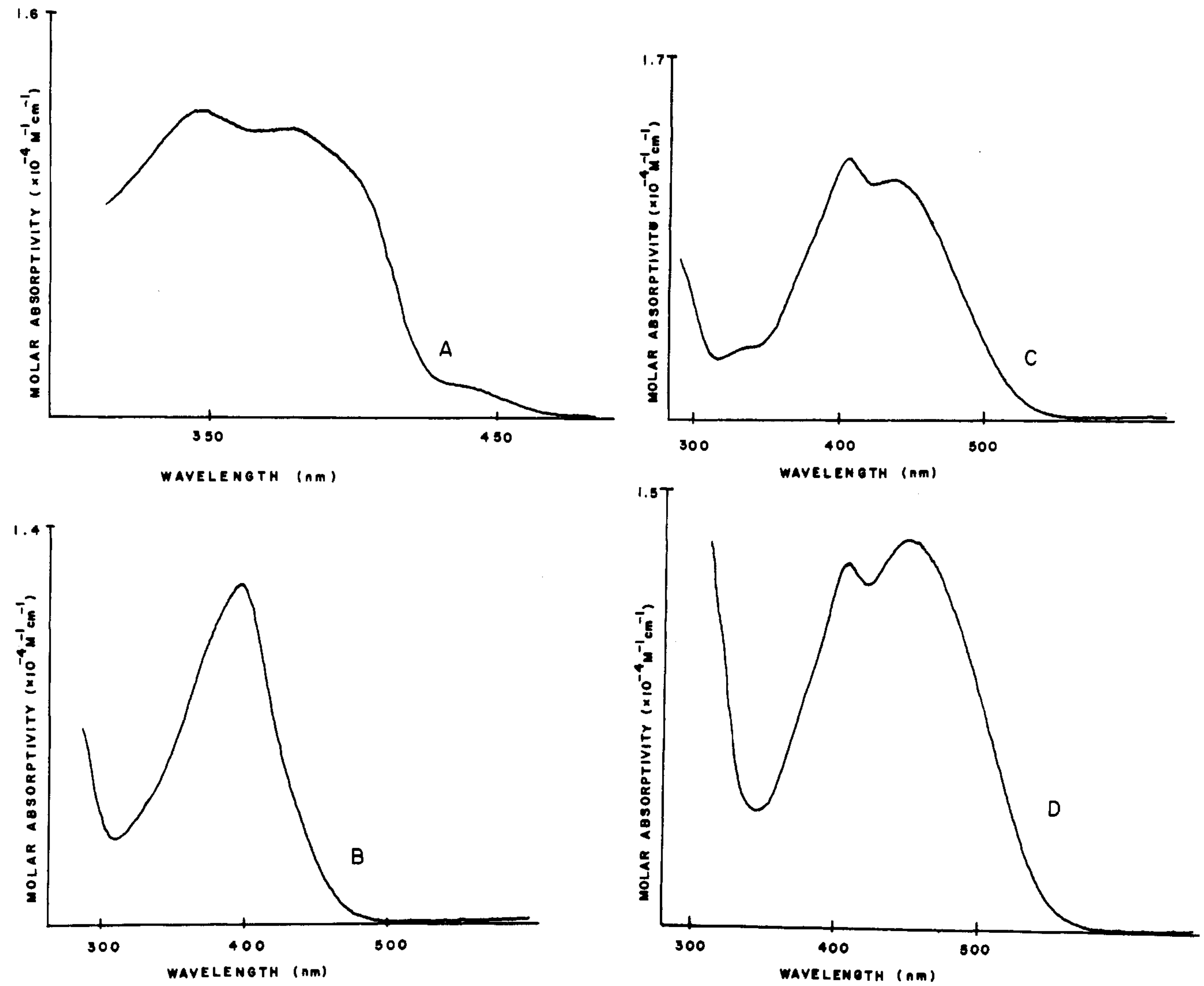

Figure 3. Electronic spectra for (A) $[W(CO)_5]_2BPA$, (B) $W(CO)_5BPY$, (C) $[W(CO)_5]_2BPY$, and (D) $[W(CO)_5]_2BPE$. Spectra were recorded in benzene at 20.0 ± 0.5 °C.

resonance in the spectrum of BPY appears as a pair of resonances in the spectrum of the monomeric derivative $W(CO)_5BPY$, where only one nitrogen of the BPY ligand is coordinated. The downfield member of each pair of resonances in the spectrum of $W(CO)_5BPY$ is assigned to carbon atoms in that pyridine ring that is coordinated to $W(CO)_5$, while the upfield member of each pair is assigned to carbons of the uncoordinated pyridine ring. Figure 2B also shows the resonances of the cis (198.9 ppm) and trans (202.4 ppm) carbonyl carbons of the $W(CO)_5$ moiety of $W(CO)_5BPY$. Comparable resonances were observed for the other $W(CO)_5$-containing compounds, and these are listed in Table III.

The electronic spectra of heterocyclic derivatives of the tungsten carbonyls have been studied previously.[3,4] These studies have made the assignment of the electronic spectra for our compounds straightforward. In Table IV are listed electronic spectroscopic data for the new compounds reported here. The spectra are shown in Figure 3. All of the spectra exhibit a maximum at ca. 405 nm (375 nm for $[W(CO)_5]_2BPA$) regardless of the identity of the heterocyclic ligand. These bands are also invariant as the solvent is changed to the more polar acetone. For these reasons, and by analogy to the assignments of Wrighton,[3] these peaks have been assigned to the ligand field ($^1E \leftarrow {}^1A$) variety. In all spectra but that of $[W(CO)_5]_2BPA$, the spin-forbidden $^3E \leftarrow {}^1A$ transition (440 nm) is obscured by more intense absorptions. All of the spectra of Figure 3 also exhibit a second absorption band, which is sensitive to the identity of the heterocyclic ligand system and which shifts to higher energy in more polar solvents such as acetone. These bands have been assigned in Table IV to metal-to-ligand charge-transfer ($\pi^* \leftarrow {}^1A$) transitions, in which electron density is promoted from an orbital of primarily tungsten (d-orbital) character to the π-antibonding orbital of the heterocyclic ligand.

Table IV. Electronic Spectroscopic Data[a]

compd	LF ($^1E \leftarrow {}^1A$)	MLCT ($\pi^* \leftarrow {}^1A$)
$[W(CO)_5]_2BPA$	375 (1.22)	347 (1.29)
$W(CO)_5BPY$	400 (1.03)	370 sh
$[W(CO)_5]_2BPY$	405 (1.18)	438 (1.08)
$[W(CO)_5]_2BPE$	405 (1.47)	450 (1.55)

[a] Wavelengths in nm of band maxima in benzene solutions at 20.0 ± 0.5 °C. Numbers in parentheses represent molar absorptivities (×10^{-4} M^{-1} cm^{-1}) determined in benzene at 20.0 ± 0.5 °C.

The compound $[W(CO)_5]_2BPA$ may be considered to be analogous to $W(CO)_5(4\text{-Mepy})$ reported by Wrighton.[3] The spectra of these two compounds are remarkably similar, as expected when one considers that the heterocyclic ligand system in $[W(CO)_5]_2BPA$ is unconjugated beyond the pyridine rings. In both compounds, the charge-transfer transition ($\pi^* \leftarrow {}^1A$) occurs at higher energy than the ligand field band, and the ligand field band is solvent insensitive. In the compound $W(CO)_5BPY$ (Figure 3B), the charge-transfer transition has

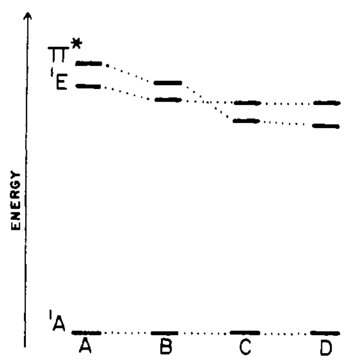

Figure 4. Relative energies (as inferred from the spectra of Figure 3) of the ligand field (^1E) and charge-transfer (π^*) excited states in the compounds (A) $[W(CO)_5]_2BPA$, (B) $W(CO)_5BPY$, (C) $[W(CO)_5]_2BPY$, and (D) $[W(CO)_5]_2BPE$.

moved to lower energy than that for $[W(CO)_5]_2BPA$, and in fact, it is observable only as a shoulder (more discernable in acetone) on the high-energy side of the LF band. In the compound $[W(CO)_5]_2BPY$ (Figure 3C), the CT band is lower in energy than the LF band and lower still for $[W(CO)_5]_2BPE$ (Figure 3D). The relative energies of these transitions (as inferred from the data of Table IV) are diagrammed in Figure 4. As can be seen in this figure, the more π conjugation present in the system $(CO)_5W\text{-}L\text{-}W(CO)_5$, the lower the energy of the π^* orbital of the heterocyclic ligand. This is as it should be. Accordingly, the compounds $[W(CO)_5]_2BPY$ and $[W(CO)_5]_2BPE$ should be placed into Zink's[4b] class 3(2).

We have synthesized and are characterizing other compounds of this class. We have good evidence that we will be able to separte the LF and CT transitions of these types of compounds by as much as 100 nm. It is then our hope to be able to study the photochemistries of such compounds as a function of the irradiation wavelength.

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Registry No. $W(CO)_5py$, 14586-49-3; $W(CO)_5BPY$, 81178-09-8; $[W(CO)_5]_2BPY$, 81178-10-1; $[W(CO)_5]_2BPA$, 81178-11-2; $[W(CO)_5]_2BPE$, 81178-12-3; BPY, 553-26-4; BPA, 4916-57-8; BPE, 1135-32-6; $W(CO)_6$, 14040-11-0.

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Synthesis of Chelating Bidentate Isocyano and Cyano Ligands and Their Metal Complexes

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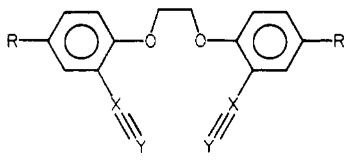
Three air-stable, odorless, solid, bidentate isocyano and cyano ligands of the following structure have been prepared:



DiCN, R = H, -X≡Y = -C≡N:
DiNC, R = H, -X≡Y = -N≡C:
t-BuDiNC, *t*-Bu, -X≡Y = -N≡C:

Molecular models indicate that they should chelate to metals with the donor groups at 90° with respect to each other. From reactions of the diisocyano ligand DiNC, the following complexes with chelating DiNC ligands have been isolated: $Cr(CO)_4(DiNC)$, $Mo(CO)_4(DiNC)$, $W(CO)_4(DiNC)$, $Mn(CO)_3(DiNC)Br$, $CpFe(CO)(DiNC)^+$, and $CpFe(CS)(DiNC)^+$. The characterization of these complexes demonstrates that DiNC can function as a chelating ligand despite its formation of a 13-member chelate ring. The *t*-BuDiNC ligand, which is much more soluble in organic solvents than DiNC, also gives complexes $Cr(CO)_4(t\text{-}BuDiNC)$, $Mo(CO)_4(t\text{-}BuDiNC)$, and $CpFe(CS)(t\text{-}BuDiNC)^+$, which are more soluble than their DiNC analogues. When only one ligand in a reacting complex such as $Cr(CO)_5[(CH_3)_2CO]$, $W(CO)_5[(CH_3)_2CO]$, or $W(CO)_4(piperidine)_2$ is substitution labile, DiNC reacts to give complexes in which the isocyano donors are coordinated to separate metal atoms; the resulting bridging DiNC complexes $[Cr(CO)_5]_2(\mu\text{-}DiNC)$, $[W(CO)_5]_2(\mu\text{-}DiNC)$, and $[cis\text{-}W(CO)_4(pip)]_2(\mu\text{-}DiNC)$ have been isolated. The dicyano ligand DiCN reacts to form the following complexes: $Mn(CO)_3(DiCN)Br$, $CpFe(CS)(DiCN)^+$, and $PtCl_2(DiCN)$. These are the first examples of complexes containing a bidentate cyano ligand that chelates to a metal through the nitrogen lone pairs. The formation of $PtCl_2(DiCN)$ from equimolar $PtCl_2(NCPh)_2$ and DiCN indicates that the chelating DiCN binds more favorably to the metal than do the monodentate benzonitrile ligands. The ligands and complexes described above have been characterized by their IR, ^1H and ^{13}C NMR, and mass spectra.

Introduction

Potentially chelating multidentate cyano and isocyano ligands have received relatively little attention, despite the fact that multidentate ligands often have unique properties with respect to those of their monodentate analogues. We know of no previous $AlCl_3/CH_3CN/N(CH_3)_4Cl$ of bidentate cyano ligands capable of chelating to a single metal center through the nitrogen lone pairs. The coordination of polymethylene-diisocyano ligands, $CN\text{-}(CH_2)_n\text{-}NC$ (n = 3–8), to Rh(I)[1-3] has been investigated. Ligands possessing six or fewer methylene units are sterically incapable of chelation and therefore bridge two metal centers to give the cationic dimers,

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