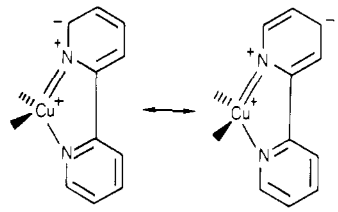
Scheme I



shifts in absorption band maxima are in accord with predictions based on the ligand acceptor properties.

With progressive methylation there is also a smooth hypsochromic shift in the emission maxima; however, the changes in the relative emission quantum yields are highly cooperative (Table I). Although progressive methylation leads to more efficient radiative decay within each group, a dramatic increase in efficiency occurs when the *second* methyl group is introduced into a "front-side" position. Ways in which the methyl groups can affect important decay processes are considered below.

Energy-Gap Effect. All else the same, the rate of nonradiative decay from an electronically excited state to the ground state is expected to decrease as the energy gap between the states increases. This principle has recently been invoked to explain trends in the emission of the MLCT states of a series of osmium(II) complexes.[14] The fact that the emission efficiency we observe increases with higher emission energy is in accord with this principle; however, this effect per se does not explain the sharp increases in emission efficiency that occur when both the 6- and 6′-positions carry methyl groups.

Perturbation of Acceptor Modes. On account of their lower frequency, C–C vibrations are less favorable than C–H vibrations as acceptor modes in electronic-to-vibrational energy conversion processes,[2,15] and this could in principle result in diminished nonradiative decay rates in the methylated derivaties. But there are at least three reasons for doubting the significance of this effect. (i) With the assumption that the electron in the π^* orbital of the excited state is delocalized over the entire ligand framework, the large differences between complexes with two "front-side" methyls as opposed to those with "front-side" methyl group are not anticipated. (ii) Corresponding substituent effects are not observed in the solid state.[16] (iii) Deuteration of the ring positions has little effect on the decay kinetics of the MLCT excited states of analogous ruthenium(II)[17] and osmium(II) systems.[14].

Solvent Interactions. Since the mixed-ligand complexes exhibit much lower emission yields in solution compared with those in the solid state,[16] coupling to solvent is apparently the key factor determining nonradiative decay rates. Accordingly, the most likely role of the methyl groups is in somehow influencing the interactions between solvent molecules and the excited state(s) of the complex. While the list of possibilities is perhaps not exhausted, two interaction mechanisms suggested by previous ground-state studies can be discussed.

Specific solvation effects might be expected at the 4- and 6-positions of the bipyridine moiety, where an accumulation of charge density is anticipated in the excited state; see, for example, the two resonance structures depicted in Scheme I. The introduction of methyl substituents at these positions could conceivably alter the solvation of the bipyridine ligand.[18] What seems unlikely is that such an effect could give rise to the strong distinction between "front-side" and "back-side" positions as demanded by the emission data.

On the other hand, an obviously distinctive characteristic of the "front-side" methyls is their proximity to the metal center, suggesting that the methyl groups in the 6- and 6′-positions might uniquely affect solvation of the metal center in the excited state. In studies of related $Cu(NN)_2^+$ systems, where Lewis bases have been found to quench the charge-transfer emission, we have pointed out that an expansion of the coordination number of copper might be expected in an MLCT excited state.[19,20] In the mixed-ligand complexes as well, association of a fifth ligand would open new channels for nonradiationless decay. Thus the effect of the "front-side" methyls could be to suppress the association of solvent by means of imposing a steric barrier.

Perturbation of Radiative Decay Rates. A reviewer has pointed out that the methyl groups may affect the radiative decay rates. However, insofar as the molar absorptivities reflect the relative probabilities of radiative decay,[21] no such effect is indicated.

Conclusions

Marked substituent effects are observed upon the photophysical properties of complexes of the type $Cu(PPh_3)_2(NN)^+$, especially with respect to substitution at the 6- and 6′-positions of the bpy moiety. They appear to be due to changes in the coupling of the excited states to the solvent. It is possible that the most significant role of the "front-side" methyls is in inhibiting quenching processes associated with expansion of the coordination number of the metal.[22]

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation through Grant No. CHE 81-05003.

Registry No. $[Cu(PPh_3)_2(bpy)]BF_4$, 80320-16-7; $[Cu(PPh_3)_2(mbp)]BF_4$, 84130-44-9; $[Cu(PPh_3)_2(6,6'\text{-}dmbp)]BF_4$, 84142-99-4; $[Cu(PPh_3)_2(4,4'\text{-}dmbp)]BF_4$, 84143-00-0; $[Cu(PPh_3)_2(trmbp)]BF_4$, 84130-46-1; $[Cu(PPh_3)_2(tmbp)]BF_4$, 84130-48-3.

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(22) That other effects are also important is shown by the fact that emission is readily detected from $Cu(tmbp)_2^+$ in CH_2Cl_2 solution but not from $Cu(6,6'\text{-}dmbp)_2^+$ under the same conditions: Del Paggio, A. A.; McMillin, D. R., unpublished results.

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Preparation and Use of $W(CO)_3(NCR)_3$ (R = Et, Pr) as Improved Starting Materials for Syntheses of Tricarbonyl(η^6-cycloheptatriene)tungsten and Other Substituted Carbonyl Complexes[1]

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Received April 13, 1982

The most prominent ligand feature of organonitriles in transition-metal complexes is the facility by which they can be replaced by other ligands.[2a] A very convenient and com-

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(1) This work was performed under the auspices of the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

mon synthetic route to zerovalent group 6 complexes of the type *fac*-$M(CO)_3L_3$ (M = Cr, Mo, W) is conversion of the metal hexacarbonyl to *fac*-$M(CO)_3(NCMe)_3$ in refluxing acetonitrile[2b] followed by addition of desired ligands. This technique is widely applicable to ligands ranging from monodentate species such as isocyanides[3] to polyolefins such as cycloheptatriene.[4,5] We have also found that mixed-ligand complexes, $M(CO)_3LL'$ (M = Mo, W; L = 2 PR_3, 2 py, bpy, dppe; L' = SO_2), can be prepared by sequential addition to $M(CO)_3(NCMe)_3$.[6] However, the utility of $W(CO)_3(NCMe)_3$ for preparation of tungsten complexes suffers greatly because of its slow rate of formation in refluxing MeCN[7] and its poor solubility in nearly all organic solvents.

We have found that these problems can be readily circumvented by using propionitrile or even higher boiling homologues in place of MeCN, and the resulting complexes $W(CO)_3(NCR)_3$ (R = Et, Pr) were discovered to be superior starting materials for syntheses of both polyolefin complexes such as $W(CO)_3(cht)$ (cht = η^6-cycloheptatriene) and phosphine-containing complexes.

Experimental Section

All preparations were carried out in a nitrogen atmosphere. Tungsten hexacarbonyl was purchased from Strem Chemicals, Newburyport, MA, nitriles from Aldrich Chemical Co., Milwaukee, WI, and olefins from Tridom Chemical, Hauppauge, NY. These materials were used without further purification. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer.

Preparation of *fac*-$W(CO)_3(NCR)_3$ (R = Et, Pr). A mixture of 35 g (0.1 mol) of $W(CO)_6$ and 300 mL of propionitrile was refluxed for 6 days (less time may be necessary at lower altitudes[7]). Reduction of the volume of the resulting red solution to 100–150 mL resulted in precipitation of fine yellow needles, which was completed by addition of 200 mL of diethyl ether. Storage of the reaction mixture in a freezer overnight (optional), filtration, washing with diethyl ether (3 × 40 mL), and brief drying in vacuo gave 35 g (81%) of yellow $W(CO)_3(NCEt)_3$. Anal. Calcd for $C_{12}H_{15}N_3O_3W$: C, 33.3; H, 3.5; N, 9.7. Found: C, 32.5; H, 3.3; N, 9.4.

The NCPr analogue was prepared in a similar manner, except that the reaction time was 3–4 days, the volume of the cooled reaction mixture was reduced to 50 mL, and 300 mL, of ether was added. A 30-g (63%) yield of light yellow microcrystals was obtained without overnight cooling; further product precipitated on cooling the filtrate. In some instances, discolored products were obtained, but they were found to be suitable for further reactions. Anal. Calcd for $C_{15}H_{21}N_3O_3W$: C, 38.0; H, 4.5; N, 8.9. Found C, 36.8; H, 4.3; N, 8.6.

The solid complexes can be weighed in air but slowly decompose on prolonged exposure. They are soluble in polar organic solvents, especially CH_2Cl_2.

Preparation of $W(CO)_3(cht)$ from $W(CO)_3(NCR)_3$. A suspension of 32 g (74 mmol) of $W(CO)_3(NCEt)_3$ in 100 mL of cycloheptatriene and 1200 mL of heptane was refluxed with vigorous magnetic stirring for 63 h. The solution phase became deep red, and the reaction mixture was cooled, filtered, and rotoevaporated to a volume of 200 mL. The mixture was then cooled in a freezer for several hours, and the resulting deep red precipitate was collected on a coarse frit and dried in air. At this point the product contained a yellow crystalline, air-sensitive impurity, in all probability unreacted $W(CO)_3(NCEt)_3$, which interfered with purification of the $W(CO)_3(cht)$ by sublimation (the nitrile complexes slowly disproportionate in vacuo to the metal hexacarbonyl, which cosublimes with the desired product). However, allowing the crude product to stand overnight in air eliminated the problem since the yellow impurity decomposed to nonvolatile materials while the air-stable $W(CO)_3(cht)$ remained unchanged. The latter was then sublimed at 90 °C to give 12.91 g (49%) of pure product (identified to be $W(CO)_3(cht)$ by comparison of infrared data with literature values[4]).

Table I. Infrared Carbonyl Stretching Frequencies (cm^{-1})

compd	soln[a]	solid[b]
$W(CO)_3(NCEt)_3$	1909, 1790	1895, 1767
$W(CO)_3(NCPr)_3$	1910, 1792	1893, 1766
$W(CO)_4(NCEt)_2$[c]	2021, 1898, 1840	
$W(CO)_4(NCPr)_2$[c]	2017, 1898, 1842	
$W(CO)_5(NCPr)$[c]	2077, 1975, 1938	
$W(CO)_3(PCy_3)_2(SO_2)$		1994, 1909, 1877[d]

[a] EtCN or PrCN. [b] Nujol mull. [c] Observed in solution only. [d] $\nu(SO) = 1237, 1070\ cm^{-1}$.

The analogous reaction of $W(CO)_3(NCPr)_3$ (17 g, 36 mmol) with cycloheptatriene (25 mL) in heptane (550 mL) proceeded more rapidly than that above (the solution became red even before reflux temperature was reached). An overnight reaction period resulted in a 36% yield of $W(CO)_3(cht)$. The slightly lower yield was at least partly due to the fact that even in refluxing hexane the partially soluble $W(CO)_3(NCPr)_3$ melted to form a viscous oil rather than remaining a solid suspension. Thus, problems with efficient stirring and decomposition along heated flask walls occurred. The use of proportionately larger amounts of solvent in a smaller scale reaction (300 mL of heptane, 20 mL of C_7H_8, 5.4 g of complex) remedied these difficulties, and a 50% yield was obtained.

Preparation of $W(CO)_2(chd)_2$ (chd = 1,3-Cyclohexadiene) from $W(CO)_3(NCEt)_3$. A suspension of $W(CO)_3(NCEt)_3$ (13 g, 30 mmol) in 1,3-cyclohexadiene (25 mL) and heptane (500 mL) was refluxed for 63 h, cooled, and filtered. The filtrate was cooled in a dry ice–isopropyl alcohol bath for several hours, and the resulting yellow precipitate was collected on a frit and sublimed at 100 °C. The yield of slightly air-sensitive $W(CO)_2(chd)_2$ (identified by comparison of infrared spectral data with literature values[4]) was 6.10 g (51%).

Preparation of *mer,trans*-$W(CO)_3(PCy_3)_2(SO_2)$. A slurry of $W(CO)_3(NCEt)_3$ (3.24 g) and PCy_3 (4.30 g) in 40 mL of acetone was stirred for ca. 10 min. A light yellow voluminous precipitate formed, and stirring was continued for 10 min. Saturation of the reaction mixture with SO_2 followed by heptane (5 mL) addition gave a red-brown precipitate of $W(CO)_3(PCy_3)_2(SO_2)$ (5.44 g, 81%), which was collected on a frit and washed with Et_2O. The use of $W(CO)_3(NCMe)_3$ as starting material resulted in lower yields (50%). Anal. Calcd for $C_{39}H_{66}O_5P_2SW$: C, 52.5; H, 7.5; P, 6.9; S, 3.6. Found: C, 54.5; H, 7.9; P, 7.1; S, 3.7.

Results and Discussion

The reaction of $W(CO)_6$ in refluxing[7] EtCN resulted in virtually complete substitution of three carbonyls within 6 days, and very little $W(CO)_4(NCEt)_2$ was detected in the reaction mixture by IR spectroscopy. The $W(CO)_3(NCEt)_3$ (**1**) product was isolated in 81% yield as fine yellow needles. The solid is stable in air for short periods and is much more soluble than $W(CO)_3(NCMe)_3$. Even more soluble (~1 g/mL in CH_2Cl_2) and somewhat more rapidly formed than **1** is $W(CO)_3(NCPr)_3$. After a 3-day reaction, the solution contained primarily the tricarbonyl along with a small amount of $W(CO)_4(NCPr)_2$. Formation of the isobutyronitrile analogue was found to be much slower, possibly due to steric effects. IR data (Table I) for these complexes and the intermediates, $W(CO)_{6-x}(NCR)_x$ (x = 1, 2), are quite similar to those for $W(CO)_{6-x}(NCMe)_x$.[8]

The synthetically useful but commercially unavailable organometallic complex, $W(CO)_3(cht)$, cannot be prepared directly from $W(CO)_6$ as for the Mo analogue.[4] Synthesis of this complex from $W(CO)_3(NCMe)_3$ and cycloheptatriene in

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(7) Up to 2 weeks was required for the preparation of $W(CO)_3(NCMe)_3$ since, at the elevation of Los Alamos (7100 ft), the atmospheric pressure is ~590 torr and the reflux temperatures of the nitriles are about 5–10 °C lower than at sea level (e.g., 89–90 °C for EtCN rather than 97 °C). Thus thermally activated reactions such as those described here can require as much as double the time needed at sea level.

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refluxing hexane was reported, but low yields[9] were obtained for large-scale reactions.[4] However, we have found the yields to be vastly improved by using **1** instead of the MeCN analogue. A large-scale reaction between **1** and cycloheptatriene in refluxing heptane for 64 h, followed by isolation essentially according to the published procedure, gave a 49% yield of $W(CO)_3(cht)$. An even more remarkable improvement was found for the analogous preparation[4] of $W(CO)_2(chd)_2$. Whereas we obtained only barely detectable amounts of this complex using $W(CO)_3(NCMe)_3$, a 51% yield resulted from **1**. The higher solubility of **1** undoubtedly is a key factor in these reactions, although EtCN may also be more readily displaced than MeCN. The reaction of $W(CO)_3(NCPr)_3$ with cycloheptatriene was more rapid than that of the NCEt analogue and also gave favorable yields, although its lower melting point was disadvantageous (see Experimental Section). As a final example of the propitious features of **1**, an 81% yield of *mer,trans*-$W(CO)_3(PCy_3)_2(SO_2)$[6] was obtained from **1** upon sequential addition of PCy_3 and SO_2 in acetone at room temperature, as opposed to 50% from $W(CO)_3(NCMe)_3$.

In conclusion, surprisingly few complexes containing alkyl cyanides other than MeCN have been reported. The results reported herein indicate that the use of the higher homologues of MeCN as ligands in transition-metal chemistry should be encouraged and may lead to complexes with properties significantly different from and more advantageous than those of MeCN complexes.

Registry No. **1**, 83732-33-6; *fac*-$W(CO)_3(NCPr)_3$, 83732-34-7; $W(CO)_6$, 14040-11-0; $W(CO)_3(cht)$, 12128-81-3; $W(CO)_2(chd)_2$, 12131-26-9; *mer,trans*-$W(CO)_3(PCy_3)_2(SO_2)$, 73682-35-6.

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(9) Although the reported yield for a 60-mmol scale reaction was 33%, we and others[10] obtained less than half this amount, even when heptane was used as solvent or when long reaction times were used.

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Full pH Study of the Incorporation of Zinc(II) into Uroporphyrin I

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Received July 9, 1982

The mechanisms of metal ion incorporation into porphyrin molecules have been studied by many workers.[1-3] While it seems apparent that different forms of the same metal exhibit differing reactivities,[4] such conclusions arise from work on various porphyrins where kinetics taken over a limited pH range have been used to assign relative rates. For example, literature data[5-8] might indicate that, for zinc, the incorporation order is $Zn(OH)^+ > Zn^{2+} > Zn(OH)_2(sol) > Zn(OH)_3^- > Zn(OH)_4^{2-}$. A careful stability constant study by Sekine,[9] however, showed the total absence of $Zn(OH)^+$ and the low concentration of $Zn(OH)_2(sol)$ at any pH in zinc(II) solutions. The reactivity sequence of zinc(II) forms is of some interest as the heavy metal lead acts as a poison in the body and blocks the insertion of Fe^{2+} into protoporphyrin IX, whereupon Zn^{II}(Proto-IX) is formed. By fluorometric analysis, the amount of Zn^{II}(Proto) in the blood is proportional to the amount of lead present.[10] Similarly, the explanation of the nature of the porphyrin N–H/N–D isotope effect on the rate of porphyrin metalation by zinc(II) in DMF was based on postulated $Zn(DMF)_5(OH)^+/Zn(DMF)_5(OD)^+$ reactants.[11]

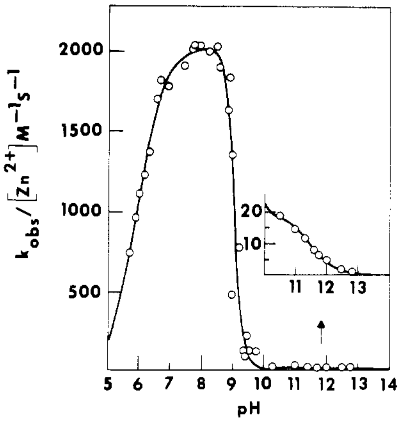

Figure 1. pH profile of the specific rates of zinc(II) perchlorate reactions with uroporphyrin I at 25 °C and $I = 0.1$ ($NaClO_4$/NaOH). Circles are the experimental points, and the solid line was calculated from eq 5.

We report the kinetics of Zn(II) incorporation into uroporphyrin I from pH 5.5 to 13 and the ionic strength dependence of the Zn^{2+}/porphyrin reactions using porphyrins of different peripheral charges. The results indicate that Zn^{2+} and $Zn(OH)_3^-$ are the major substrates for the free-base form of the porphyrin over the entire pH range.

Experimental Section

The kinetics of zinc perchlorate incorporation into uroporphyrin I were followed spectrophotometrically in the Soret region with use of total porphyrin concentrations of ca. 5 × 10^{-8} M at $I = 0.1$ ($NaOH/NaClO_4$) and 25 °C. The solutions were buffered with[12] 10^{-3} M Hepes, Pipes, Mes, and Tris from pH 5 to 9.5. Zn^{II}(uro) has bands at 574, 538, and 408 nm, with extinction coefficients of 1.4 × 10^4, 1.8 × 10^4, and 3.4 × 10^5 M^{-1} cm^{-1}, based on $\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1} (552 nm, 1 M HCl) for uroporphyrin I.[13] Under pseudo-first-order conditions, the reactions were first order in porphyrin over 3 half-lives and first order in zinc from 2 × 10^{-4} to 2 x 10^{-5} M at pH 12 and from 1 × 10^{-5} to 2 × 10^{-6} M at pH 7.6. At constant pH, the observed rate constant, k_{obsd}, was independent of buffer identity and concentration between 10^{-3} and 10^{-4} M, and duplicate kinetic runs agreed to within 8%.

Results

Figure 1 shows the pH profile of zinc incorporation into uroporphyrin I. As one goes from pH 5.5 to 8, the specific rates $k_{obsd}/[Zn]$ increase and reach a plateau. In this region, the reactions considered[14] were

$$H_3\text{-}P^+ = H_2\text{-}P + H^+ \quad K_e \qquad (1)$$

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