trated solution chromatographed on Al_2O_3 (neutral, activity grade III). With benzene, an orange-yellow fraction was eluted from which a yellow microcrystalline solid was obtained; yield 113 mg (81%). IR (KBr) ν(OsH) 2050 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C, 200 MHz) δ 4.70 (s, 3 H, $C_6H_3Me_3$), 2.37 (d of sept, J_{HH} = 7.2, J_{PH} = 10.0 Hz, 3 H, PCHCH_3), 2.08 (s, 9 H, $C_6H_3Me_3$), 1.20 (dd, J_{HH} = 7.2, J_{PH} = 12.9 Hz, 9 H, PCHCH_3), 1.09 (dd, J_{HH} = 7.2, J_{PH} = 12.9 Hz, 9 H, PCHCH_3), –8.92 (d, J_{PH} = 44 Hz, OsH). ^{31}P NMR (C_6D_6, 25 °C, 36.2 MHz) δ 22.6 (s). Anal. Calcd for $C_{18}H_{34}ClOsP$: C, 42.63; H, 6.76; M_r, 507.1. Found: C, 42.40; H, 6.98; M_r, 508 (MS). (b) The reaction was analogous to that described for (a) but with EtOD as the solvent. Yield of complex **9** 80%.

Photooxidation of the Molybdenum and Tungsten Carbynes (η^5-C$_5$H$_5$)L$_2$M≡CR [L = P(OMe)$_3$, CO and R = Ph, Me, c-C$_3$H$_5$]

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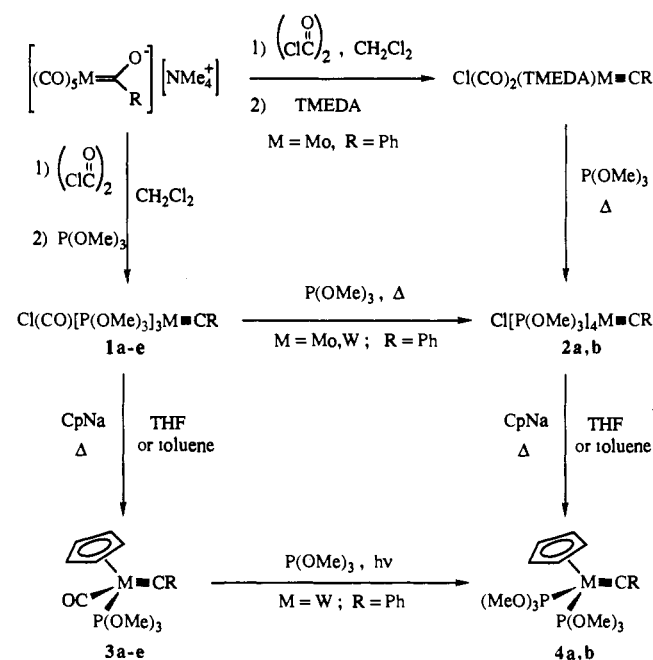
Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received August 14, 1990. Revised Manuscript Received December 13, 1990

Abstract: Photolysis of the carbyne complexes CpL$_1$L$_2$M≡CR, **3a–d** and **4a,b** (M = Mo, W; L$_1$ = P(OMe)$_3$; L$_2$ = CO, P(OMe)$_3$; R = Ph, Me, c-C$_3$H$_5$), in chlorinated solvents in the presence of PMe$_3$ results in the formation of the cationic complexes [Cp(Cl)(PMe$_3$)$_2$M≡CR]$^+$Cl$^-$ (**5a–d**). All of the carbyne complexes were spectroscopically characterized. The formation of **5a–d** is postulated to involve electron transfer from the MLCT excited states of the carbynes to the chlorinated solvent. The resulting 17e$^-$ species then undergo ligand exchange followed by halogen atom abstraction to afford the observed cationic complexes. UV–visible spectroscopy of **3a–d** and **4a,b** has established that electron transfer occurs upon MLCT excitation rather than from CTTS transitions, while EHMO calculations on the model system Cp[P(OH)$_3$]$_2$Mo≡CPh are in agreement with the MLCT band being d – π^* in nature. For the cases L$_1$ = P(OMe)$_3$, L$_2$ = CO, R = Ph or tolyl, the MLCT state was also responsible for emission in fluid solution at room temperature. The carbyne Cp(CO)[P(OMe)$_3$]W≡C(o-Tol) (**3e**) was characterized by X-ray crystallography: monoclinic, C2/c, a = 32.754 (10) Å, b = 7.294 (3) Å, c = 15.521 (7) Å, β = 98.982 (5)°, V = 3662.5 (5) Å^3, Z = 8, R(F) = 5.0%, R(wF) = 5.6% for 1692 reflections, F$_o$ ≥ 3σ(F$_o$).

Introduction

Although the photochemistry of organometallic compounds generally leads to ligand loss as the primary photoprocess,[1] photolysis of metal–carbyne complexes has recently been shown to lead to several interesting reaction types. The carbyne Cp(CO)$_2$W≡CTol undergoes intramolecular coupling of the carbyne ligand to a carbonyl.[2] The resulting coordinatively unsaturated η^2-ketenyl complex can be trapped with PPh$_3$. Similar photochemical coupling reactions have been postulated to occur in Br(PMe$_3$)$_2$(CO)$_2$W≡CPh[3] and Tp'(CO)$_2$Mo≡CPh.[4] There are reports of photochemical addition of HCl to the metal–carbon triple bonds of both the neutral and cationic osmium phenyl carbynes, Os(CPh)(CO)Cl(PPh$_3$)$_2$ and [Os(CPh)(CO)$_2$(PPh$_3$)$_2$]$^+$.[5] The unusual photochemical rearrangement of (Cp)[P(OMe)$_3$]$_2$Mo≡CCH(^{t}Bu)CO^{t}Bu results in a π-allyl complex, suggesting insertion of the carbyne carbon into a C–H bond.[6] Photolysis of the related neopentyl carbyne, (Cp)[P(OMe)$_3$]$_2$Mo≡CCH$_2$^{t}Bu, in the presence of diphenylacetylene was reported to produce an η^3-cyclopropenyl complex.[7] All of

Scheme I

(1) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York; 1976.

(2) (a) Sheridan, J. B.; Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 289–294. (b) Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1514–5.

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these modes of reactivity have been attributed to the presence of low-lying metal-to-ligand charge-transfer (MLCT) excited states, from which reaction occurs.

We recently reported an additional class of reaction for excited state metal carbynes in which photooxidation produces highly

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reactive $17e^-$ intermediates.[8,9] Photolysis of the complex $(Cp)[P(OMe)_3]_2Mo\equiv CPh$ in $CHCl_3$ or CH_2Cl_2 containing PMe_3 leads to formation of the cationic complex $[(Cp)Cl-(PMe_3)_2Mo\equiv CPh]^+Cl^-$ (eq 1). The reaction mechanism was proposed to involve electron transfer from the MLCT excited state to the chlorinated solvent, followed by rapid ligand exchange in the resulting $17e^-$ carbyne species. Abstraction of ·Cl from the solvent gave the final product. The reaction sequence also generates 2 equiv of ·$CHCl_2$ radicals, which are scavenged by the excess PMe_3. We now report that this reaction is a general one for carbyne complexes of the type $CpL_2M\equiv CR$ where M = Mo, W; L = CO, $P(OMe)_3$; R = Ph, Me, c-C_3H_5.

$$\text{(1)}$$

4a   **5a**
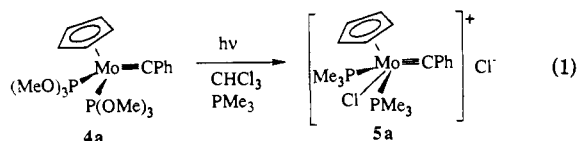
Synthesis of Carbynes. The carbyne complexes $CpL_2M\equiv CR$ were synthesized as shown in Scheme I. The trisphosphite complexes, $Cl(CO)[P(OMe)_3]_3M\equiv CPh$ (Mo = **1a**, W = **1b**), were made by the method of Mayr[10,11a] as was the tungsten tetrakisphosphite complex, $Cl[P(OMe)_3]_4W\equiv CPh$ (**2b**). In the case of the molybdenum complex $Cl[P(OMe)_3]_4Mo\equiv CPh$ (**2a**), very poor yields were obtained by this method. Instead, **2a** was prepared by stirring a suspension of $Cl(CO)_2(TMEDA)Mo\equiv CPh^{11b}$ in neat $P(OMe)_3$ for 24 h.

Reaction of carbynes **1a**, **2a**, **1b**, and **2b** with cyclopentadienyl sodium led to displacement of the chloride anion and two $P(OMe)_3$ ligands to give the desired compounds **3a**, **4a**, **3b**, and **4b**, respectively. A cleaner route to **4b** involved photolysis of benzene or toluene solutions of **3b** with excess trimethyl phosphite. Prolonged irradiation of **3b** with 20 equiv of $P(OMe)_3$ at room temperature resulted in quantitative conversion to **4b**.

Since the phenyl group in the previously described carbynes is derived from addition of phenyllithium to the metal hexacarbonyl, the same synthetic route could be used for the methyl and cyclopropyl carbynes by using the appropriate lithium reagent in the first step.

Results and Discussion

The carbyne complex $Cp[P(OMe)_3]_2Mo\equiv CPh$ (**4a**) does not undergo thermal reaction with $CHCl_3$ or CH_2Cl_2, and no reaction takes place when **4a** is irradiated in a nonchlorinated solvent, such as benzene or tetrahydrofuran. However, upon irradiation of **4a** in CH_2Cl_2 or $CHCl_3$ the pink solution rapidly turned green. ^1H NMR did not reveal any identifiable products. However, photolysis of **4a** in either CH_2Cl_2 or $CHCl_3$ in the presence of excess PMe_3 resulted in a bright yellow solution. ^1H NMR showed that the starting material was entirely consumed and 1 equiv of an organometallic product had formed, together with 2 equiv each of free $P(OMe)_3$ and an unidentified compound whose ^1H NMR revealed the presence of a PMe_3 fragment. After workup, the organometallic product was obtained as a yellow powder in approximately 60% yield. ^1H NMR, ^{13}C NMR, and FAB mass spectrometry led to the identification of this compound as the cationic complex, $[Cp(Cl)(PMe_3)_2Mo\equiv CPh]^+[Cl]^-$ (**5a**).[8]

Under the same conditions as previously described for the photolysis of **4a**, the photoreactions of carbynes **3a**, **3b**, and **4b** were followed by ^1H NMR. The substitution of a carbonyl for one of the phosphite ligands in the starting complexes did not seem to affect the photooxidation reaction as **5a** was cleanly produced by irradiation of a $CDCl_3/PMe_3$ solution of **3a**. Photolysis of red solutions of **3b** or **4b** in $CDCl_3/PMe_3$ gave golden solutions containing the analogous cationic tungsten carbyne $[Cp(Cl)-$

Scheme II
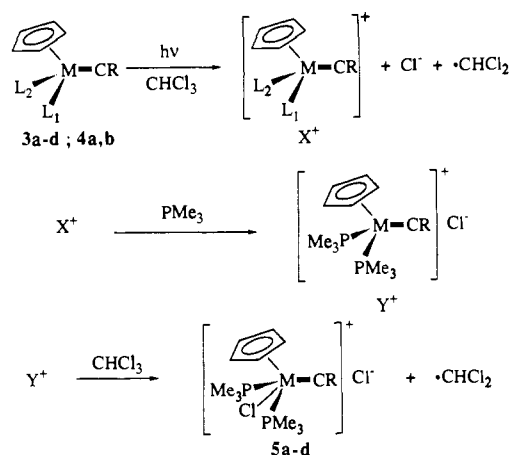
Compound	M	L₁	L₂	R
3a	Mo	$P(OMe)_3$	CO	Ph
3b	W	$P(OMe)_3$	CO	Ph
3c	W	$P(OMe)_3$	CO	c-C_3H_5
3d	W	$P(OMe)_3$	CO	Me
4a	Mo	$P(OMe)_3$	$P(OMe)_3$	Ph
4b	W	$P(OMe)_3$	$P(OMe)_3$	Ph

$(PMe_3)_2W\equiv CPh]^+[Cl]^-$ (**5b**). In each case, 2 equiv of free $P(OMe)_3$ and a second PMe_3-containing product were formed, the latter as a white insoluble solid. Isolation of **5b** using the technique for **5a** proved difficult. A purer 50% yield was obtained by chromatography on neutral alumina by using $CH_2Cl_2/MeOH$ (40:1) as eluent, followed by recrystallization from CH_2Cl_2 and hexane at -78 °C.

The generality of this photooxidation reaction was illustrated by further studies on the cyclopropyl compound **3c** and $Cp(CO)[P(OMe)_3]W\equiv CCH_3$, **3d**. Photolysis of $CDCl_3$ solutions of **3c** and **3d** in the presence of PMe_3 afforded the cationic complexes $[Cp(Cl)(PMe_3)_2W\equiv CR]^+[Cl]^-$ (**5c**, R = c-C_3H_5; **5d**, R = CH_3) in about 60% yield as determined by ^1H NMR. Isolation of **5c** as dark yellow crystals was successful, although it decomposed significantly during purification. Repeated chromatography with 10:1 $CH_2Cl_2/MeOH$ resulted in a much reduced isolated yield.

Control experiments involving irradiation of the molybdenum and tungsten phenyl carbynes in the absence of phosphine did not lead to identifiable products even upon subsequent addition of PMe_3 to the reaction mixture. However, a new photoreaction involving conversion of the carbyne ligand to cyclopentenone took place upon photooxidation of the cyclopropyl complex in the absence of phosphine.[9] Cyclic voltammetry of **4a** in the absence of any ligands showed an irreversible oxidation at 0.35 V vs Ag/Ag^+. Consistent with the rapid decomposition of the cation radical, there was no evidence of a return wave at scan rates up to 1 V/s. Since PMe_3 oxidizes at a much less positive potential, oxidation of **4a** in the presence of phosphine could not be accomplished electrochemically.

These observations are consistent with the mechanism shown in Scheme II. The first step involves electron transfer[12] from the carbyne excited state to a molecule of chloroform, which then fragments to a chloride anion and the ·$CHCl_2$ radical.[13] This radical has been detected previously in the photochemical electron transfer from Cp_2Fe to $CHCl_3$.[14] Under our reaction conditions, this radical is apparently scavenged by excess phosphine to give

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Photooxidation of Mo and W Carbynes

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the unidentified PMe_3-containing product.

The 17-electron metal radical species, $[CpL_1L_2M\equiv CR]^+$, then undergo rapid ligand exchange of phosphines for phosphites (carbonyls), probably via associative substitution.[15,16] No intermediates were detectable when the photolysis was monitored by ^{1}H NMR. Examples of the increased substitutional lability of 17-electron cationic complexes relative to their neutral 18-electron analogues are well-documented.[15,16] For instance, irradiation of $Ni(phen)(S_2C_2Ph_2)$ in $CHCl_3$ gives a cationic species which undergoes rapid ligand exchange to give the symmetric complexes $Ni(S_2C_2Ph_2)_2$ and $[Ni(phen)_2]^{2+}$.[17] Given the strong π-acidity of carbonyl and phosphite ligands, it is not unreasonable that dissociation of $P(OMe)_3$ and/or CO from the associative substitution intermediate $[CpL_1L_2(PMe_3)M\equiv CR]^+$ should be facile and exchange for phosphines should be favorable. However, photolysis of a $CHCl_3$ solution of **4a** with triphenylphosphine did not lead to isolable products, possibly due to the increased steric bulk of the phosphine.

The products are consistent with abstraction of a chlorine atom from a second molecule of solvent by $[Cp(PMe_3)_2M\equiv CR]^+$ to give the final product, $[Cp(Cl)(PMe_3)_2M\equiv CR]^+$ $[Cl]^-$, and another $^\bullet CHCl_2$ radical. The latter is again scavenged by PMe_3, giving the second equivalent of an unidentified phosphine-containing product. Such halogen abstractions are well-known for metal radicals such as $Mn(CO)_5$ and $CpFe(CO)_2$.[18,19] Pathways involving addition of Cl^- to the $17e^-$ intermediates Y^+ (Scheme II) followed by electron transfer can be ruled out by experiments performed in the presence of bromide ion that show no incorporation of bromide in the product. This result implies that the chlorine atom comes from the solvent and not from the free ions. After formation of the photooxidized carbyne, the mechanistic steps thus consist of ligand exchange and halogen atom abstraction, typical reactions for 17-electron species.[16]

This order of events (exchange before abstraction) is consistent with the fact that we see no $[Cp(Cl)\{P(OMe)_3\}_2M\equiv CR]^+[Cl]^-$ complexes in solution either as products in the absence of PMe_3 or as intermediates in the presence of PMe_3. If atom abstraction were to occur first, the 18-electron cationic complexes, $[Cp(Cl)\{P(OMe)_3\}_2M\equiv CR]^+[Cl]^-$, would result. We believe this to be unlikely as the analogous neopentyl carbyne, $[Cp(Br)\{P(OMe)_3\}_2Mo\equiv CCH_2^tBu]^+[BF_4]^-$, has been prepared by Green.[20] If the $[Cp(Cl)\{P(OMe)_3\}_2M\equiv CR]^+$ $[Cl]^-$ complexes were formed in our reactions, they should be stable enough under the reaction conditions to be observed.

Green has recently reported[21] the reactions of $Cp[P(OMe)_3]_2Mo\equiv CCH_2^tBu$ (**6**) with potential one-electron oxidants. Treatment of neopentyl carbyne **6** with $[4\text{-}FC_6H_4N_2][BF_4]$ affords the vinylidene complex, $Cp(N_2C_6H_4F\text{-}4)[P(OMe)_3]Mo=C=CH^tBu$, while reaction with CF_3I gives both a vinylidene complex, $Cp(I)[P(OMe)_3]_2Mo=C=CH^tBu$ (**7**), and the unusual chelate carbene, $Cp(I)[P(OMe)_3]Mo[=C(CH_2^tBu)P(O)(OMe)_2]$ (**8**).

7   8
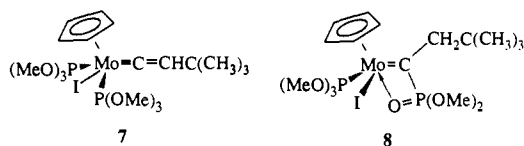
The common first step in these reactions is postulated to be electron transfer to form the $17e^-$ species, $[Cp\{P(OMe)_3\}_2Mo\equiv CCH_2^tBu]^+$. Subsequent ligand exchange and/or proton abstraction gives the

compd	μ_{max}, (nm)	ϵ	μ_{max}, (nm)	ϵ
3a	328	4000	477	60
4a	326	13000	500	210
3b	329	8000	483	50
4b	319	5000	488	120
3c	230 (sh 290, 350)		438	80
3d	242 (sh 290, 350)		436	70
3e	331		476	
10	326		470	

[a] Experiments were performed in THF solution at room temperature.

vinylidene products. The pathway for formation of chelate complex **8** from **6** is thought to involve $^\bullet CH_3$ abstraction from a coordinated phosphite of the $17e^-$ species. Subsequent charge collapse and migration of the σ-bonded phosphonate group to the carbyne carbon affords the carbene product.

In contrast, we have not detected the formation of vinylidene or chelate complexes in the photooxidation reactions. For the phenyl carbynes **3a**, **4a**, **3b**, and **4b**, the deprotonation pathway is impossible. Although the alkyl carbynes **3c** and **3d** have the option of undergoing deprotonation at the β-carbon, the original carbyne substituents are intact in the products **5c** and **5d**. The observation that vinylidene and chelate complexes are not formed under our reaction conditions suggests that ligand exchange with PMe_3 is faster than either conversion of the carbyne ligands to vinylidenes or reactions of coordinated $P(OMe)_3$.

In yielding a cationic carbyne species with a chloride ligand, this photoreaction results in a net two-electron oxidation. Similar photooxidations have previously been described. Electron transfer from the MLCT states of the hexakis(arylisocyano) complexes, $M(CNPh)_6$ (M = Mo, W), to $CHCl_3$ resulted in the seven-coordinate products, $[M(CNPh)_6Cl]^+[Cl]^-$.[22] The two-electron oxidation was proposed to proceed via an inner-sphere mechanism after initial formation of the lowest spin-orbit excited "triplet" state. No ML_6 absorptions in $CHCl_3$ attributable to charge-transfer-to-solvent (CTTS) transitions were observed in the visible region of spectra of the $M(CNPh)_6$ complexes.

Photochemical reduction of halocarbons by metal complexes has, however, been observed upon excitation of CTTS transitions in other complexes. Photooxidation of $[CpFe(CO)]_4$ occurs upon excitation of a band that is dependent on the nature of the halocarbon solvent.[23a] In addition, conversion of $Fe(S_2CNEt_2)_3$ to $Fe(S_2CNEt_2)_2Cl$ by photolysis in chlorinated hydrocarbons[23b] was determined to have a CTTS component as was photoxidation of a series of 1,2-dithiolene complexes of Ni, Pd, and Pt[23c] in CCl_4 and $CHCl_3$.

UV-Visible Spectra. In order to determine whether electron transfer is occurring from MLCT or CTTS excited states, the UV-vis spectra of **3a-d** and **4a,b** were investigated in a variety of solvents. THF solutions of phenyl carbynes **3a**, **4a**, **3b**, and **4b** all gave similar spectra with two main features: a strong band at approximately 320 nm and a weaker broad absorption at about 490 nm (Table I). Complexes **3c** and **3d**, which have alkyl substituents, showed blue shifts of these transitions. The longer wavelength transitions in the phenyl complexes thus reflect considerable conjugation of the $M\equiv C$ π-system with the phenyl ring. For both alkyl carbynes, shoulders appear in the shorter wavelength band suggesting that in the phenyl complexes there are similar overlapping transitions to higher lying excited states.

By analogy to the known compounds $X(CO)_2L_2W\equiv CR$[24] (R = Ph, t-Bu; X = Cl, Br; L_2 = tmeda, py_2, dppe), we have assigned the lowest energy absorption as MLCT ($d\rightarrow\pi^*$). Extended Hückel calculations (vide infra) suggest that the longest wavelength band in **3a-d** and **4a,b** should be $d\rightarrow\pi^*$ in nature. The more intense

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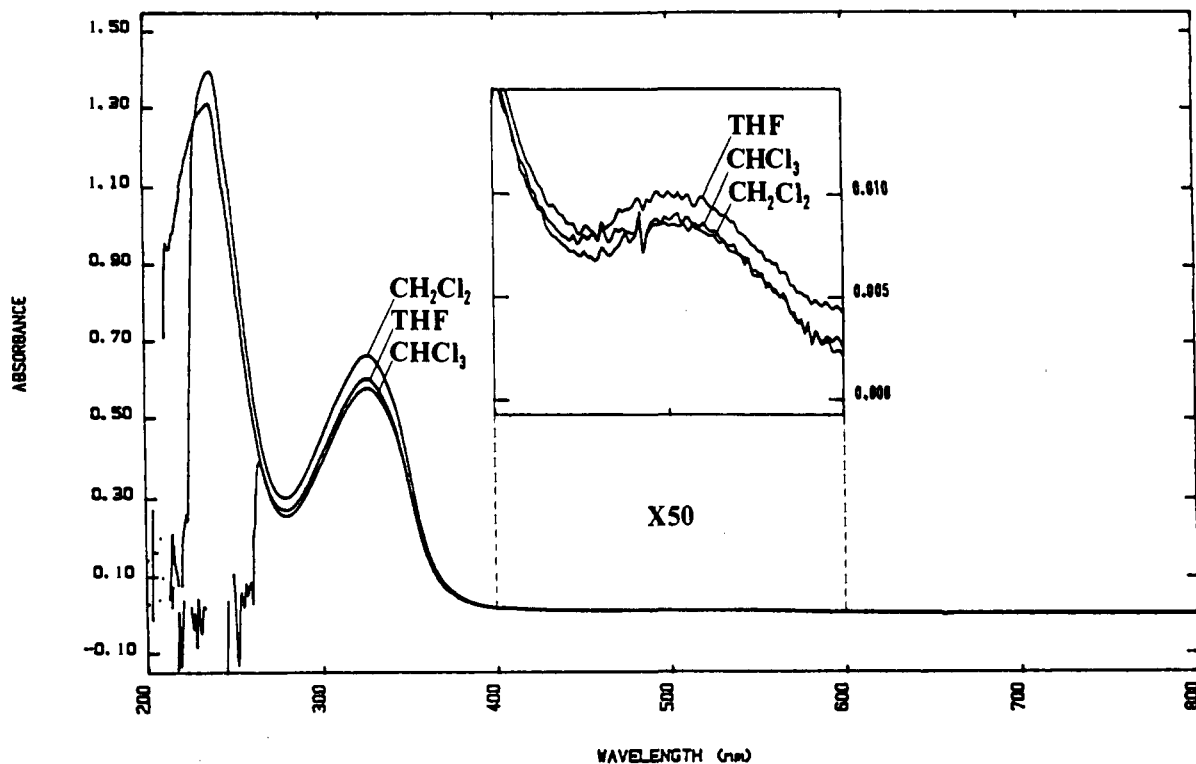
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Figure 1. Absorption spectra of **4a** in solution at room temperature. The solutions are 5×10^{-5} M in $CHCl_3$, CH_2Cl_2, or THF.

Table II. Emission Data[a]

compd	λ (nm)	τ (ns)
3a	696	<7
4a	no.[b]	
3b	705	141 ± 5
4b	no.	
3c	no.	
3e	698	170 ± 5

[a] Luminescence experiments were performed in THF solution at room temperature. [b] Not observed.

absorption at 320 nm is assigned to $\pi-\pi^*$ transitions of the metal–carbon triple bond. The blue shifts after replacement of the phenyl group in **3b** by a cyclopropyl or methyl group are consistent with the removal of conjugation from the LUMO π^* (M≡C). Substitution of a trimethylphosphite ligand by a carbonyl does not noticeably affect the position of either band, indicative of the similar σ-donor and π-acceptor abilities of phosphites[25] and carbonyls. However, the extinction coefficients of the MLCT bands of **3a** and **3b** are somewhat higher than their bisphosphite counterparts, **4a** and **4b**.

Photooxidation of **4a** using a 520-nm long pass filter revealed complete conversion to **5a**, demonstrating that the state from which electron transfer occurs is populated upon excitation of the low-energy band. The solvent dependence of this band was then examined. UV–visible spectra of **4a** in THF, CH_2Cl_2, and $CHCl_3$ at room temperature are shown in Figure 1. Allowing for experimental error, the position and extinction coefficients of both absorption bands were nearly invariant (Figure 1), ruling out the involvement of CTTS states in the photooxidation of **4a**. Similar studies on the remaining carbynes also showed no solvent dependence.

The evidence suggests that the photoactive state arises from promotion of a metal-based d-electron into a metal–carbyne carbon π^* orbital, in agreement with previous assignments[24] and calculations on a model for **4a** (vide infra). In chlorinated solvents, the MLCT $(d-\pi^*)$ excited state is "quenched" via outer-sphere single electron transfer, while in poor electron acceptor solvents such as THF, it simply decays to the ground state.
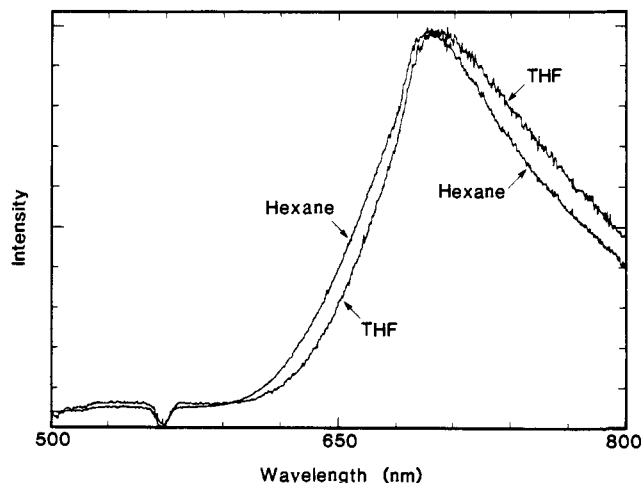

Figure 2. Emission spectra of **3b** in solution at room temperature. The solutions are 1×10^{-4} M in hexane or THF.

Luminescence Studies. Complexes **3a**, **3b**, and the related o-tolyl carbyne $Cp(CO)[P(OMe)_3]W≡C(o\text{-tolyl})$, **3e**, have been found to luminesce at room temperature in fluid solution upon excitation with visible light (Table II). Excitation of **3b** at 483 nm in polar solvents such as tetrahydrofuran, acetonitrile, and toluene gave fairly strong emission centered at 705 nm (Figure 2), while in the nonpolar solvents, hexane and petroleum ether, there was a blue shift of approximately 15 nm. Essentially the same observations were made with tolylcarbyne **3e**. Despite a reduced intensity, comparable results were obtained after 477-nm excitation of **3a**, with the emission centered at 696 nm in toluene. Each of the emissions was very broad (Figure 2), with a Stokes shift of about 220 nm. This could be due to stretching of the metal–carbon triple bond or, more likely, bending of the carbyne ligand in the excited state. Bocarsly has reported a similar Stokes shift of 180 nm for $X(CO)_2L_2W≡CPh$ (X = Cl, Br; L_2 = tmeda, py_2, dppe) and associates the luminescence with the low-lying MLCT state.[24,26]

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(26) Bocarsly, A. B.; Cameron, R. E.; Mayr, A.; McDermott, G. A. In *Photochemistry and Photophysics of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berlin, 1987; p 213.

Excitation spectra of **3a**, **3b**, and **3e** have shown that the MLCT (d–π^*) state which results in electron transfer is also responsible for emission. In addition, the excitation spectra revealed that some of the higher lying excited states are in part converted to the (d–π^*) state by an inefficient nonradiative pathway.

Rather surprisingly, solutions of complexes **4a** and **4b** do not show any emission on excitation of the MLCT band at room temperature. Changing the concentration of carbyne and the polarity of solvent had no effect. The only structural difference between **4a/4b** and the luminescent complexes is that the second trimethyl phosphite has been substituted by a carbonyl. There seems no obvious reason why **4a** and **4b** should not be emissive at room temperature, although their larger extinction coefficients suggest a more facile conversion between the ground and excited states which could lead to the inability of radiative pathways to compete with internal conversion to the ground state. To test the hypothesis that involvement of the carbonyl ligand in the excited states of **3a**, **3b**, and **3e** was critical for luminescence, the dicarbonyl complex Cp(CO)$_2$W≡CPh (**10**) was prepared. However, excitation of the MLCT band of **10** in either hexane or THF gave no appreciable emission above 500 nm.

Not surprisingly, replacement of the phenyl ring with an alkyl group has a strong influence on solution emission. When solutions of the cyclopropyl carbyne **3c** were excited at 444 nm, no emission was found at room temperature, even at high concentrations. This seems to confirm that conjugation of the metal–carbon triple bond with the aromatic π system extends the lifetime of the MLCT (d–π^*) excited state.

Luminescence lifetimes of the three emissive complexes were also determined. The time dependence of emission of **3b** was monitored in tetrahydrofuran at 650 nm and followed an exponential decay. A linearized least-squares analysis of the data gave a lifetime of 141 ± 5 ns at room temperature. An identical value was obtained for a toluene solution of **3b**, at a reduced concentration. A similar study on the emission of the *o*-tolylcarbyne **3e** in tetrahydrofuran gave a slightly longer lifetime of 170 ± 5 ns. Molybdenum complex **3a** had a much lower emission intensity as well as a shorter lifetime of approximately 5 ns.

The relatively long lifetimes found for the emissive MLCT excited states of tungsten complexes **3b** and **3e** suggest the transition to the ground state is spin forbidden,[27] consistent with substantial triplet character.[28] However, the extremely short lifetime of **3a** suggests its emissive state possesses either competitive nonradiative pathways to the ground state or additional thermally accessible excited states with rapid decay pathways.

Luminescence of the emissive complexes X(CO)$_2$L$_2$W≡CPh was found to be quenched by a variety of organic compounds at rates dependent on the triplet energy of the quencher.[26] Complexes **3b** and **3e** were thus excited in the presence of known quenchers whose triplet states are sufficiently low-lying to undergo energy transfer from the MLCT (d–π^*) state of **3b** at 59 kcal/mol. Both **3b** and **3e** were easily quenched by azulene, which has low-lying triplet and singlet excited states ($E_t \simeq$ 30 kcal/mol, $E_s \simeq$ 40 kcal/mol). Anthracene ($E_t \simeq$ 47 kcal/mol, $E_s \simeq$ 76 kcal/mol) also quenched the emission of both complexes. Since the energy of anthracene S_1 is too high for energy transfer from the MLCT state of **3b** to occur, quenching of the MLCT state must be occurring to the triplet state of the organic molecule. These results are consistent with substantial triplet character in the excited states of the carbyne complexes. Similar energy-transfer processes have been previously observed for other third-row transition-metal complexes in the presence of organic triplet quenchers.[29]
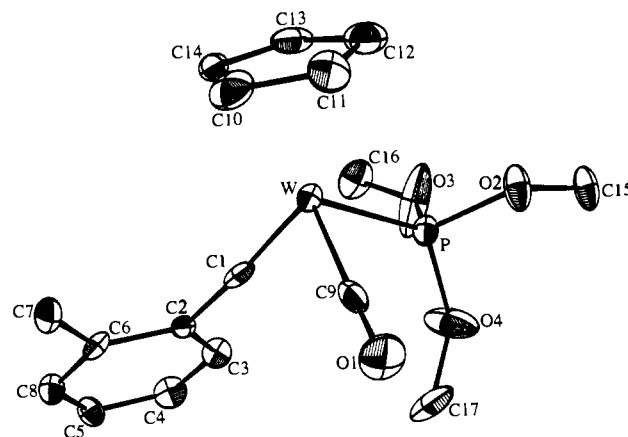
Figure 3. Molecular structure of Cp(CO)[P(OMe)$_3$]W≡C(*o*-Tol) (**3e**). Thermal ellipsoids are drawn at the 25% probability level. Selected bond distances (Å) and angles (deg) are as follows: W–C(1), 1.82 (2); W–P, 2.353 (4); W–C(9), 1.96 (2); C(1)–C(2), 1.46 (2); P–W–C(1), 90.0 (4); P–W–C(9), 91.7 (4); C(1)–W–C(9), 94.1 (6); W–C(1)–C(2), 176 (1).

X-ray Crystallography of 3e. In order to determine whether the luminescent monophosphite complexes **3a** and **3b** exhibit unusual structural features that might account for the difference between them and their nonluminescent bisphosphite analogues **4a** and **4b**, we determined the structure of Cp(CO)(P{OMe}$_3$)-W≡C(*o*-Tol) (**3e**) by X-ray crystallography. As shown in the ORTEP drawing of **3e** (Figure 3), the complex has a three-legged piano-stool geometry typical of CpML$_3$ compounds. The W–C(1) distance is 1.82 (2) Å, and the W–C(1)–C(2) angle is 176 (1)°. These features are identical with those in the related complex Cp(CO)$_2$W≡C(*p*-Tol)[31] (**12**) [W–C(carbyne) = 1.82 (2) Å, W–C(carbyne)–C(Tol) = 176 (2)°]. Replacement of one of the two CO groups of **12** with a phosphite ligand appears to have no effect on the geometry of the W≡C(*o*-Tol) moiety.

The dihedral angle between the plane of the tolyl substituent and the C(1)–W–P plane is 9 (2)°. The tolyl π-system is thus nearly in alignment with the W–CO bond. However, this feature cannot be critical for luminescence since the dicarbonyl complex **10** is not emissive. Overall, the structure of **3e** is very similar to both that of Cp(CO)$_2$W≡C(*p*-Tol)[31] (**12**) and that of Cp[P-(OMe)$_3$]$_2$MoCCH$_2$^{t}Bu (**11**) reported by Green.[32] Since neither **10** (the phenyl analogue of **12**) nor **4a** and **4b**, whose structures are not expected to be significantly different from that of **11**, are emissive under our conditions, the crystal structure of **3e** provides no clue to the luminescence properties of **3a** and **3b**.

Extended Hückel Calculations. In order to gain insight into the electronic structure of these carbyne complexes, extended Hückel calculations[33] were performed on Cp[P(OH)$_3$]$_2$Mo≡CPh (**9**) as a model for **4a** in which the phosphite methyl groups have been replaced by hydrogens. The geometry of the Cp[P-(OH)$_3$]$_2$Mo≡C fragment was adapted from the X-ray structure of Cp[P(OMe)$_3$]$_2$Mo≡CCH$_2$^{t}Bu.[32] Three limiting orientations for the phenyl ring were examined: one with the ring lying in the *yz* plane, one with the ring in the *xz* plane, and one with the plane of the phenyl ring rotated 45° about the *z* axis so that the ring plane is aligned with a Mo–P bond (see Figure 4 for axes). As the rotamer with the phenyl ring rotated 45° was calculated to be of the lowest energy, further discussion will be limited to that conformation. It should be noted that this conformation is analogous to the one found in the X-ray structure of **3e** (vide supra), where the plane of the tolyl ring is aligned with the W–P bond so that the tolyl π-system is parallel to the W–CO axis.

Figure 4 shows a partial molecular orbital diagram for the formation of **9** from the fragments Cp[P(OH)$_3$]$_2$Mo$^-$ and CPh$^+$,

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(28) Although it has been argued that pure triplet spin states can be assigned for the excited states of third-row metal complexes,[29a] such species are generally described as having mixed spin states with considerable triplet character.[30] This issue is also discussed in ref 27.

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(31) Fischer, E. O.; Lindner, T. L.; Huttner, G.; Friedrich, P.; Kreissl, F. R.; Besenhard, T. O. *Chem. Ber.* **1977**, *110*, 3397–3404.

(32) Allen, S. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591–604.
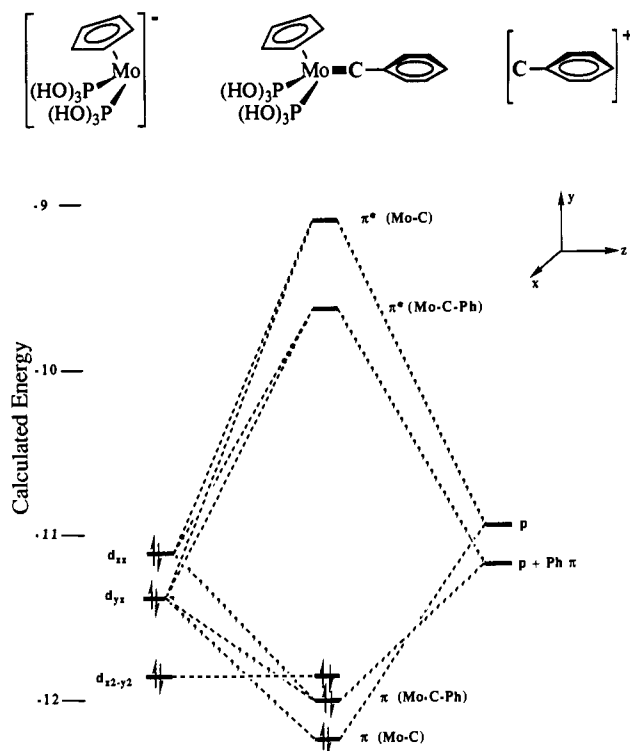
Figure 4. Orbital mixing diagram for the formation of **9** from the fragments Cp[P(OH)₃]₂Mo⁻ and CPh⁺. Energy levels are from the extended Hückel calculations described in text.

Table III. Selected Orbital Energies and Compositions for **9**[a]

		% composition		
orbital	energy (eV)	Mo d	≡C p	Ph π
π*	−8.98	16	35	
π* (LUMO)	−9.53	19	24	27
d$_{x^2-y^2}$ (HOMO)	−11.87	43		
π	−11.99	28	20	26
π	−12.24	34	30	

[a] Computational details are in the text.

both calculated in the same manner as **9**.[33] The HOMO of the complex is comprised largely of Mo d$_{x^2-y^2}$, and below it are the two metal–carbon π bonds. The LUMO and NLUMO are the π* orbitals, with the one that is conjugated into the phenyl π-system lying lower in energy.

This picture of the electronic structure of the carbyne complex **9** is consistent with the assignment of the lowest energy feature of the UV–vis spectra of complexes **3a–d** and **4a,b** as a d–π* transition. Table III gives the AO composition of the MO's calculated for **9**. Although the lowest energy excitations show a significant amount of charge transfer to the carbyne ligand, it is interesting to note all of these orbitals are highly delocalized, and there is still a reasonable contribution of Mo d AO's to the virtual orbitals. The low-energy transitions would thus still have some residual d–d character. This is consistent with the lack of solvent dependence and low extinction coefficients seen in the excitation to the lowest excited states.

Conclusions

Photolysis of the carbyne complexes, CpL₁L₂M≡CR, in chlorinated solvents in the presence of trimethylphosphine produces the cationic complexes, [Cp(Cl)(PMe₃)₂M≡CR]⁺[Cl]⁻. Variation of the metal, carbyne substituent, and ancillary ligands has shown this new class of carbyne reaction to be a general one for the complexes **3a–d** and **4a,b**. Studies of the wavelength dependence of the photooxidation have demonstrated that the excited state

(33) Extended Hückel calculations were carried out by using the program FORTICON8, obtained from QCPE as program QCMP011. Weighted H_{ij}s were used, and the parameters for Mo were taken from ref 34.

arises from a d–π* (MLCT) transition. UV studies were consistent with the presence of MLCT excitation and ruled out the possibility of CTTS transitions. For the cases R = aryl, L₁ = CO, and L₂ = P(OMe)₃, the MLCT (d–π*) state was responsible for emission in fluid solution at room temperature. Electron transfer from this low-lying (d–π*) state gives a 17-electron carbyne species, which rapidly undergoes ligand exchange and subsequent halogen abstraction, chemistry typical of metal radicals. Photooxidation of these complexes thus adds electron transfer to the photoprocesses that have been observed for carbynes. Use of photochemical electron transfer to generate highly labile 17e⁻ metal–carbyne species provides a means of increasing the reactivity of these complexes.

Experimental Section

General Methods. Standard inert atmosphere techniques were used throughout. Diethyl ether, THF, and toluene were distilled from Na/Ph₂CO. Hexane, petroleum ether, chloroform, methylene chloride, and carbon tetrachloride were distilled from CaH₂. Acetonitrile was distilled from P₂O₅. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene-d_6, and THF-d_8 were vacuum transferred from Na/Ph₂CO. CDCl₃, CCl₄, CD₂Cl₂, and CD₃CN were stored over 3A molecular sieves. All other starting materials were purchased in reagent grade and used without further purification.

¹H and ¹³C NMR spectra were recorded on a Varian XL-400 NMR spectrometer and ³¹P NMR spectra on a Nicolet NT-300 NMR. IR spectra were recorded on an IBM IR/90 FTIR spectrometer. A Hewlett-Packard 8450A diode array spectrophotometer was used to obtain UV–vis spectra. Emission spectra were obtained with a Spex Fluorolog 2 series spectrofluorimeter, equipped with a DM1-SLC unit. Gas chromatography was performed on a HP5890A chromatograph containing a 5 m × 0.25 mm column of SE-54 on fused silica. Elemental analyses were performed by UC Berkeley Microanalytical Laboratories or by Robertson Laboratories, Madison, NJ. Mass spectra were obtained at the University of California, Berkeley.

Unless otherwise stated, all photolyses were performed at room temperature in 5-mm NMR tubes by irradiation with a Hanovia medium pressure mercury vapor lamp in a Pyrex immersion well. The instrumentation for lifetime measurements has been described previously.[35]

The acyl–metal complexes [(CO)₅M(COR)][NMe₄] (R = C₆H₅, M = Mo, W; R = CH₃, M = W; R = c-C₃H₅, M = W) were prepared by the methods of Fischer.[10] Cl(CO)₂(TMEDA)Mo≡CPh was prepared by the method of Mayr[11b] as were (Cl)(CO)[P(OMe)₃]₃M≡CPh (**1a** and **1b**) and (Cl)[P(OMe)₃]₄W≡CPh (**2b**).[11a] Cp(CO)₂W≡CPh was synthesized by Fischer's method.[36]

Cl[P(OMe)₃]₃Mo≡CPh (2a). Cl(CO)₂(TMEDA)Mo≡CPh (430 mg, 1.09 mmol) was suspended in neat P(OMe)₃ and stirred at room temperature for 24 h. The orange solution was then heated to 70 °C for 4 days. The solution was chromatographed on neutral alumina (8 cm × 1.5 cm) at −30 °C with 1:1 CH₂Cl₂/hexane as eluent. The solvent mixture was removed in vacuo, and the orange-yellow powder recrystallized from ether to give orange crystals (220 mg, 28%). Spectral data were identical with those previously reported.[11]

Cp(CO)[P(OMe)₃]Mo≡CPh (3a). Cl(CO)[P(OMe)₃]₃Mo≡CPh (241 mg, 0.39 mmol) was dissolved in 10 mL of THF. A 2-fold excess of 2.0 M CpNa in THF (380 μL, 0.78 mmol) was added, and the solution was refluxed for 6 h during which the reaction mixture turned from orange-yellow to dark red. Excess CpNa was removed by filtering through 2 cm of alumina, and THF was removed in vacuo. The red solid was purified by chromatography on neutral alumina (8 cm × 1.5 cm) with 5:1 Et₂O/hexane at −30 °C. The solvent was removed in vacuo to give **3a** as a red oil in 46% yield: ¹H NMR (CD₃CN) δ 7.30 (dd, 2 H, Ph), 7.21 (m, 3 H, Ph), 5.51 (s, 5 H, Cp), 3.54 (d, 9 H, P[OMe]₃), J = 12.2 Hz); ¹³C NMR (C₆D₆) δ 297.8 (Mo≡C), 242.6 (d, J = 68 Hz, CO), 148.3, 129.2, 128.5 (Ph), 91.7 (Cp), 51.4 (P[OMe]₃); ³¹P NMR (C₆D₆) δ 201.6 (s); IR (CD₃CN) νCO 1904 cm⁻¹; UV (THF) 328 (ε = 4000), 477 (ε = 60) nm. Anal. Calcd for C₁₆H₁₉O₄PMo: C, 47.78, H, 4.76. Found: C, 48.06; H, 4.92.

Cp[P(OMe)₃]₂Mo≡CPh (4a). Cl[P(OMe)₃]₄Mo≡CPh (490 mg, 0.684 mmol) was dissolved in 30 mL of THF. A 2-fold excess of 2.0 M

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Photooxidation of Mo and W Carbynes

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CpNa in THF (680 μL, 1.37 mmol) was added, and as the solution was refluxed for 5 h, it turned from orange to dark red. The reaction mixture was filtered through alumina to remove excess CpNa and then chromatographed on neutral alumina with cold THF as eluent. Removal of the solvent gave **4a** as a dark red solid (365 mg, 90%): ^{1}H NMR (C_6D_6) δ 7.51 (d, 2 H, H_o), 7.05 (t, 2 H, H_m), 6.97 (t, 1 H, H_p), 5.34 (s, 5 H, Cp), 3.49 (virtual triplet, 18 H, P(OMe)$_3$, J = 11.6 Hz); ^{13}C NMR (C_6D_6) δ 286.3 (t, J = 26.5 Hz, Mo≡C), 149.9, 128.5, 128.1, 125.7 (Ph), 89.8 (Cp), 51.1 (P[OMe]$_3$); ^{31}P NMR (C_6D_6) 213.4 (s); UV (THF) 326 (ε = 13 000, 500 (ε = 210) nm; HRMS (FAB), *m/e* calcd for M$^+$ (C_{16}-$H_{28}O_6P_2Mo$) 494.0418, found 494.0429.

[Cp(Cl)(PMe₃)₂Mo≡CPh]Cl] (5a). Cp[P(OMe)₃]₂Mo≡CPh (15 mg, 0.03 mmol) was dissolved in 2 mL of CHCl₃; and PMe₃ (20 μL, 0.26 mmol) was added. The mixture was placed in an NMR tube and irradiated for 30 min, turning from orange/pink to bright yellow. The solvent and excess ligands were removed in vacuo. The product was then dissolved in CH₂Cl₂ and precipitated with hexane. This procedure was repeated a total of three times to give **5a** as a yellow powder in approximately 60% yield: ^{1}H NMR (CDCl₃) δ 7.43 (m, 3 H, Ph), 7.25 (d, 2 H, Ph), 6.18 (t, 5 H, Cp, J = 2.0 Hz), 1.78 (virtual triplet, 18 H, PMe₃, J = 10.4 Hz); ^{13}C NMR (CDCl₃) δ 354.6 (t, J = 35 Hz, Mo≡C), 144.2, 132.4, 129.5, 128.9 (Ph), 101.5 (Cp), 17.8 (t, J = 17.5 Hz, PMe₃); ^{31}P NMR (CDCl₃) δ 14.8; MS (FAB); M$^+$ 439. Isotope abundance for the molecular ion matched simulation for $C_{18}H_{28}P_2ClMo$. Anal. Calcd for $C_{18}H_{28}P_2Cl_2Mo$: C, 45.70; H, 5.96; Cl, 14.99. Found: C, 45.47; H, 6.09; Cl, 15.15.

Cp(CO)[P(OMe)₃]W≡CPh (3b). Cl(CO)[P(OMe)₃]₃W≡CPh (668 mg, 0.94 mmol) was dissolved in 10 mL of toluene, and a 2.0 M solution of CpNa in THF (500 μL, 1.03 mmol) was added. The mixture was refluxed at 70 °C for 6 h and then stirred for 6 h at room temperature. The toluene was removed in vacuo, cold Et₂O added, and the solution was filtered through alumina to remove excess CpNa. The red product was purified by chromatography on neutral alumina (8 cm × 1.5 cm) with cold Et₂O. The solvent was then removed, leaving a dark red oil which afforded dark red crystals (0.20 g, 53%) after recrystallization from hexane: ^{1}H NMR (C_6D_6) δ 7.50 (d, 2 H, Ph), 7.02 (m, 3 H, Ph), 5.25 (s, 5 H, Cp), 3.40 (d, 9 H, P(OMe)₃, J = 11.9 Hz); ^{13}C NMR (C_6D_6) δ 286.8 (d, J = 18 Hz, W≡C), 235.7 (CO), 153.3, 128.5, 128.1, 126.7 (Ph), 90.1 (Cp), 52.2 (P[OMe]₃); ^{31}P NMR (C_6D_6) δ 172.8 (J_{PW} = 671 Hz); IR (CD₃CN) $ν_{CO}$ 1893 cm⁻¹; UV (THF) 329 (ε = 8000), 483 (ε = 50) nm. Anal. Calcd for $C_{16}H_{19}O_4PW$: C, 39.21; H, 3.91. Found: C, 38.88; H, 3.93.

Cp[P(OMe)₃]₂W≡CPh (4b). Cl[P(OMe)₃]₄W≡CPh (180 mg, 0.22 mmol) was dissolved in 12 mL of toluene. A 2.0 M solution of CpNa in THF (250 μL, 0.5 mmol) was added and heated at 80 °C for 6 h, followed by stirring for a further 6 h at room temperature. After removal of the toluene in vacuo, the residue was dissolved in THF and filtered through Celite. Removal of solvent left a bright red oil. Recrystallization from 1:4 Et₂O/hexane gave dark red crystals in 85% yield: ^{1}H NMR (C_6D_6) δ 7.50 (m, 2 H, Ph), 7.08 (m, 3 H, Ph), 5.28 (s, 5 H, Cp), 3.49 (virtual triplet, 18 H, P(OMe)₃, J = 11.6 Hz); ^{13}C NMR (C_6D_6) δ 275.0 (t, J = 18 Hz, W≡C), 155.3, 128.5, 128.1, 124.7 (Ph), 87.8 (Cp), 51.8 (P[OMe]₃); ^{31}P NMR (C_6D_6) δ 181.2 (J_{PW} = 671 Hz); UV (THF) 319 (ε = 5000), 488 (ε = 120) nm. Anal. Calcd for $C_{18}H_{28}O_6P_2W$: C, 36.87; H, 4.78. Found: C, 36.84; H, 4.61.

[Cp(Cl)(PMe₃)₂W≡CPh][Cl] (5b). Cp(CO)[P(OMe)₃]W≡CPh (50 mg, 0.10 mmol) was dissolved in 5 mL of CHCl₃. PMe₃ (2.5 mL, 24.18 mmol) was added, and the mixture was irradiated for 25 min, during which time the color changed from red to gold. The solvent and excess ligands were immediately removed in vacuo. The product was then purified by chromatography on neutral alumina with CH₂Cl₂/MeOH (40:1) as eluent. Recrystallization from CH₂Cl₂/hexane afforded large orange crystals (28 mg, 50%): ^{1}H NMR (CD₃CN) δ 7.45 (m, 3 H, Ph), 7.23 (d, 2 H, Ph), 6.07 (t, 5 H, Cp, J = 2.2 Hz), 1.73 (virtual triplet, 18 H, PMe₃, J = 10.5 Hz); ^{13}C NMR (CDCl₃) δ 343 (W≡C), 131.1, 130.0 129.0 (Ph), 99.8 (Cp), 17.5 (t, J = 17.0 Hz, PMe₃); ^{31}P NMR (CDCl₃) δ −0.73 (J_{PW} = 220.4 Hz). Anal. Calcd for $C_{18}H_{28}Cl_2P_2W$: C, 38.53; H, 5.03; Cl, 12.64. Found: C, 37.95; H, 5.03; Cl, 12.51.

Cl(CO)[P(OMe)₃]₃W≡C(c-C₃H₅) (1c). [(CO)₅W{CO(c-C₃H₅)}]-[NMe₄] (2.214 g, 4.74 mmol) was dissolved in 50 mL of CH₂Cl₂ and cooled to −98 °C in a liquid N₂/MeOH bath. Oxalyl chloride (414 μL, 4.74 mmol) was added slowly to the yellow suspension. The dark brown reaction mixture was allowed to warm up slowly. Effervescence began at −20 °C, whereupon the solution turned dirty yellow. On reaching −12 °C, the reaction mixture was returned to the low-temperature bath, and excess P(OMe)₃ was added (5.58 mL, 47.4 mmol). The bright yellow solution was warmed to room temperature and then refluxed at 55 °C for 24 h. After removal of CH₂Cl₂ in vacuo, the brown residue was dissolved in cold THF and filtered to remove NMe₄Cl. Following removal of the THF, the product was extracted with Et₂O and purified by

chromatography on neutral alumina (8 cm × 1.5 cm) at −30 °C with 3:1 Et₂O/hexane as eluent. Removal of the solvent mixture gave **1c** in 47% yield: ^{1}H NMR (CDCl₃) δ 3.72 (m, 27 H, P[OMe]₃), 1.10 (tt, 1 H, $H_α$), 0.85 (m, 2 H, $H_β$), 0.50 (m, 2 H, $H_β$); IR (CD₃CN) $ν_{CO}$ 1936 cm⁻¹.

Cp(CO)[P(OMe)₃]W≡C(c-C₃H₅) (3c). Cl(CO)[P(OMe)₃]₃W≡C-(c-C₃H₅) (2.00 g, 2.97 mmol) was dissolved in 20 mL of toluene. A 2.0 M solution of CpNa in THF (3.0 mL, 6.0 mmol) was added, and the reaction mixture was refluxed at 65 °C for 8 h. The toluene was removed in vacuo, cold Et₂O added, and the solution was filtered to remove excess CpNa. Following removal of Et₂O, the product was chromatographed on a neutral alumina column (12 cm × 1.5 cm) at −30 °C with 1:4 Et₂O/hexane as eluent. After removal of the solvent mixture, recrystallization from 1:4 Et₂O/hexane gave yellow crystals of **3c** in 74% yield: ^{1}H NMR (C_6D_6) δ 5.18 (s, 5 H, Cp), 3.43 (d, 9 H, P(OMe)₃, J = 12.2 Hz), 0.94 (m, 3 H, $H_α$ + $H_β$), 0.45 (m, 2 H, $H_{β'}$); ^{13}C (C_6D_6) δ 301.2 (d, J = 18 Hz, W≡C), 234.0 (CO), 89.4 (Cp), 52.0 (P[OMe]₃), 33.3 ($C_α$), 10.5, 9.9 ($C_β$ + $C_{β'}$); ^{31}P NMR (C_6D_6) δ 175.0 (J_{PW} = 674 Hz); IR (CD₃CN) $ν_{CO}$ 1881 cm⁻¹; UV (THF) 230, 290 (sh), 350 (sh), 444 nm. Anal. Calcd for $C_{13}H_{19}O_4PW$: C, 34.38; H, 4.22. Found: C, 34.41; H, 4.30.

[Cp(Cl)(PMe₃)₂W≡C(c-C₃H₅)][Cl] (5c). Cp(CO)[P(OMe)₃]W≡Cc-C₃H₅ (2.50 g, 5.52 mmol) was dissolved in 25 mL of CHCl₃. PMe₃ (9.0 mL, 87.05 mmol) was added, and the mixture was uniformly irradiated at room temperature for 15 h, during which time the color changed from yellow to orange. The solvent was immediately removed in vacuo, and the residue was dissolved in a small amount of CHCl₃ and filtered. The solvent was removed, and the resultant solid was purified by repeated column chromatography on neutral alumina at −40 °C, with 10:1 CH₂Cl₂/MeOH as eluent. Recrystallization from CH₂Cl₂/hexane at −40 °C gave small yellow crystals of **5c** in less than 10% yield: ^{1}H NMR (CDCl₃) δ 5.99 (t, 5 H, Cp, J = 2.1 Hz), 2.74 (m, 1 H, H_a), 1.86 (virtual triplet, 18 H, PMe₃, J = 10.1 Hz), 1.16 (m, 2 H, H_b), 0.98 (m, 2 H, $H_{b'}$); ^{13}C NMR (CDCl₃) δ 356.7 (t, J = 47 Hz, W≡C), 95.7 (Cp), 31.7 (C_a), 17.1 (t, J = 38 Hz, PMe₃), 13.7, 13.1 ($C_β$ + $C_{β'}$); ^{31}P NMR (CDCl₃) δ −0.1 (J_{PW} = 225 Hz). Lability of the compound precluded obtaining an elemental analysis.

Cl(CO)[P(OMe)₃]₃W≡CMe (1d). Prepared from [(CO)₅W-(COCH₃)][NMe₄] as a yellow oil in 77% yield using the same procedure as for **1c**: ^{1}H NMR (C_6D_6) δ 3.69 (virtual triplet, 18 H, P(OMe)₃, J = 10.8 Hz), 3.64 (d, 9 H, P(OMe)₃, J = 10.7 Hz), 1.76 (q, 3 H, Me, J = 5.6 Hz); IR (CDCl₃) $ν_{CO}$ 1942 cm⁻¹.

Cp(CO)[P(OMe)₃]W≡CMe (3d). Prepared from **1d** as yellow crystals in 18% yield by the procedure for **3c**: ^{1}H NMR (C_6D_6) δ 5.18 (s, 5 H, Cp), 3.39 (d, 9 H, P(OMe)₃, J = 12.1 Hz), 1.67 (d, 3 H, Me, J = 4.3 Hz); ^{13}C NMR (CDCl₃) δ 294.3 (d, J = 17 Hz, W≡C), 233.7 (d, J = 11 Hz, CO), 89.3 (Cp), 52.0 (P[OMe]₃), 39.2 (−CH₃); ^{31}P NMR (CDCl₃) δ 173.6 (J_{PW} = 684 Hz); IR (CH₂Cl₂) $ν_{CO}$ 1885 cm⁻¹; UV (THF) 242, 290 (sh), 350 (sh), 450 nm. Anal. Calcd for $C_{11}H_{17}O_4PW$: C, 30.86; H, 4.00. Found: C, 31.04; H, 3.83.

Cp(CO)[P(OMe)₃]W≡C(o-tolyl) (3e). Made via the same methods as for **3b**. Recrystallization from 1:1 Et₂O/hexane and washing with cold hexane gave purple crystals, suitable for X-ray structure determination. ^{1}H NMR (CDCl₃) δ 7.24 (d, 1 H, o-Tol), 7.14 (t, 1 H, o-Tol), 6.99 (d, 1 H, o-Tol), 6.97 (t, 1 H, o-Tol), 5.50 (s, 5 H, Cp), 3.56 (d, 9 H, P(OMe)₃, J = 12.1 Hz), 2.39 (s, 3 H, CH₃); IR (CH₃CN) $ν_{CO}$ 1892 cm⁻¹. Anal. Calcd for $C_{17}H_{21}O_4PW$: C, 40.41; H, 4.19. Found: C, 40.50; H, 4.02.

Crystal Structure of 3e. X-ray data collection was performed on a crystal mounted on a glass fiber and protected from air by epoxy cement. The diffractometer was a Siemens P2₁ equipped with Mo radiation. Data reduction was done on a VAX computer by using the SDP programs.[37] Observed data were corrected for decay and Lorentz and polarization factors but not for absorption because of the relatively small size of the crystal and its decomposition late in data collection. The structure was solved by using the Patterson heavy atom method and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically, and hydrogens were refined in idealized positions with the C–H distance fixed at 0.95 Å. U_{iso}s for the hydrogen atoms were fixed at 1.2U_{iso} of the attached carbon atom.

Crystal data for 3e: Empirical formula, $C_{17}H_{21}O_4PW$; color, habit, purple blocks; crystal size, 0.30 × 0.20 × 0.15 mm³; crystal system, monoclinic; space group, *C2/c*; *a* = 32.754 (10) Å, *b* = 7.294 (3) Å, *c* = 15.521 (7) Å; β = 98.982 (5)°; *V* = 3662.5 (5) Å³, *Z* = 8, fw = 505.26, D_{calc} = 1.829 g/cm³; abs coeff 65.44 cm⁻¹; diffractometer, Siemens P2₁; radiation, graphite monochromated Mo Kα (0.71073 Å) 2θ range = 3–50°; scan type = θ–2θ; scan speed = variable 4–29; standard reflections = 3 standard/97 reflections; reflections collected = 7622 (includes unobserved); independent reflections = 2894; observed reflections (F_o > 3σ(F_o)) = 1692; data/parameter = 8.1/1; final $R(F)$, $R(wF)$ = 5.0%, 5.6%; weighting scheme, $1/w$ = $σ^2(I)/4F^2$ + 0.000225F^2; final

Photophysical Studies in Solution of the Tetranuclear Copper(I) Clusters Cu₄I₄L₄ (L = Pyridine or Substituted Pyridine)[1-3]

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Abstract: Reported are the emission and excitation spectra and emission lifetimes of a series of tetranuclear copper(I) clusters of the type $Cu_4I_4L_4$ (L = pyridine, substituted pyridine, or a saturated amine) in solution and in the solid state. These materials are bright, relatively long-lived emitters in room-temperature solution which display two emission bands, an intense lower energy (LE) band (λ_{max} = 690 nm, $\tau_{(LE)}$ = 11.1 μs for $Cu_4I_4(py)_4$, I, in 293 K toluene), and a much less intense higher energy (HE) band (λ_{max} = 480 nm, $\tau_{(LE)}$ = 0.45 μs for I, in 293 K toluene). Comparisons of substituent and solvent effects as well as the observation that this band is not seen for L = saturated amine have led to the conclusion that the HE emissiion is from an excited state either metal-to-ligand charge transfer (MLCT) or iodide-to-ligand charge transfer (XLCT) in character. The LE band is assigned as emission from a cluster-centered (CC) excited state, possibly an iodide-to-metal charge transfer. The two emissions show different excitation spectra as well as different lifetime and relative intensity profiles as the temperature is lowered. At lower T (e.g., 77 K), the emission spectra of the well-characterized solids display properties similar to the solutions of the same compounds in frozen solutions. The rates of selective quenching of the HE excited state by Lewis bases as well as by energy transfer (at room temperature) are reported as are the quenching rates of both states by O_2. The independent behavior of the lifetimes and excitation spectra of the HE and LE emissions for various $Cu_4I_4L_4$ all indicate that the excited states responsible are essentially uncoupled.

Introduction

There has been considerable recent interest in the photophysical properties of mononuclear and polynuclear complexes of transition metals in oxidation states having the d^{10} electronic configuration.[3-13] Among these, the tetranuclear clusters of copper(I) display remarkably rich photoluminescence properties.[3,9-13] One particularly notable example is the pyridine cluster $Cu_4I_4(py)_4$ (I), which has been shown by X-ray crystallographic analysis[14] to have a tetrahedral structure, such as A. The Cu–Cu distances in this structure are quite short (2.69 Å in I),[14] although, to a first approximation, there is no formal covalent metal–metal bonding between these ground-state d^{10} metal centers. This structure and others of analogous $Cu_4I_4L_4$ clusters can be viewed as tetrahedra of copper centers with the tetrahedral faces capped by iodides comprising a larger tetrahedron (I–I distances of 4.50 Å in I[14] and ligands L coordinated at the apices of the Cu_4 tetrahedron). For simplicity, clusters having this configuration will be referred to as being the "cubane" isomers to distinguish them from those having a "staristep" configuration as illustrated by B.

With the exception of several recent reports[3,12,13] including preliminary communications of the present work, photophysical properties of the tetranuclear copper(I) clusters have been largely concerned with studies in the solid state. Among earlier studies, Hardt and co-workers[9] showed that emission maxima of pyridine adducts of cuprous halides when excited in the UV are markedly temperature-dependent for solids of stoichiometry CuIL. This phenomenon was termed *luminescence thermochromism*. These studies were largely phenomenological, reporting syntheses, lu-

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(3) Preliminary communications describing this work in part: (a) Kyle, K. R.; DiBenedetto, J. A.; Ford, P. C. *J. Chem. Soc., Chem. Commun.* **1989**, 714–715. (b) Kyle, K. R.; Ford, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 5005–5006.

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