Steric and Electronic Effects on the Quantum Yield of Photosubstitution of CO in W(CO)$_4$(α-diimine) Complexes

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Abstract

Photolysis of the complexes W(CO)$_4$(α-diimine) in the presence of a nucleophilic ligand causes photosubstitution of CO. The quantum yields are low and depend on the basicity, cone angle and concentration of the phosphine ligands used, indicating an associative mechanism.

Apart from steric effects electronic effects determine the quantum yield of this reaction. These electronic effects are connected with the MLCT character of the lowest excited state of these complexes which strongly decreases from W(CO)$_4$ (1,10-phenanthroline) to W(CO)$_4$(1,4-diaza-1,3-butadiene) according to the Resonance Raman Spectra.

Introduction

Currently there is considerable interest in the photophysics and photochemistry of metal complexes having a lowest metal-to-ligand charge transfer (MLCT) state [1–17]. Many of these complexes are photostable in solution, having a long-lived ^{3}MLCT state from which luminescence [18–22] and electron or energy transfer reactions [23–27] can take place.

This photostability, which contrasts with the dissociative character of most complexes in a lowest ^{3}LF state, is caused by the fact that on going from the ground- to the MLCT-state, the weakening of the metal to ligand π-backbonding is largely compensated by the increase of ionic interaction. This is *e.g.* evident from the Resonance Raman (RR) spectra of the complexes Ru(bipy)$_3$$^{2+}$ [28] and ReCl(CO)$_3$ (α-diimine) [29], which hardly show a RR effect for the symmetrical metal–nitrogen stretching mode upon excitation into the MLCT band.

If such a complex still shows a photochemical reaction with rather high quantum yield ($\phi \geqslant 0.1$),

this reaction is always assumed to proceed from a close-lying photoactive state or from a thermally-activated ground state. The former mechanism has *e.g.* been proposed for complexes of the type [Ru-(NH$_3$)$_5$(py-X)]$^{2+}$ [30, 31], Re(π-C$_5$H$_5$)(CO)$_2$(py-X) [32], [Fe(CN)$_5$(py-X)]$^{2+}$ [33] and M(CO)$_5$L (M = Cr, Mo, W; L = py-X, pyridazine) [14, 34].

In these complexes the photosubstitution reactions occur from a close-lying ^{3}LF state while in the case of complexes (CO)$_5$MnM'(CO)$_3$(α-diimine) (M' = Mn, Re) the homolysis of the metal–metal bond is assumed to proceed from a $^3\sigma_b\pi^*$ state close in energy to the ^{3}d$_\pi\pi^*$ MLCT state [35].

The second mechanism was proposed for complexes of the type Fe(CO)$_3$(L–L) (L–L = 1,4-diaza-1,3-butadiene, 1,4-tetrazadiene) [15–17] and for Ph$_3$SnMn(CO)$_3$(α-diimine) [43]. For these complexes the MLCT-state energy is converted, due to strong vibronic coupling, into vibrational motions of the complex leading to breaking of a metal ligand bond.

In the case of Cr(CO)$_5$(pyridazine) [14] and Fe-(CO)$_3$(1,4-diaza-1,3-butadiene) [15] reactions from the ^{3}MLCT state have been observed in rare gas matrices at 10 K, although the quantum yields were very low. In solution, reactions from the ^{3}MLCT state have been observed for complexes of the type M(CO)$_4$(α-diimine) (M = Cr, Mo) [13] with $\phi <$ 0.1. In these complexes the ^{3}MLCT state appeared to be delocalized over the carbonyls in the *cis*-position with respect to the α-diimine ligand, causing a weakening of the metal to CO π-backbonding in the excited state.

Much lower quantum yields are observed for the photosubstitution of CO in the corresponding W(CO)$_4$(α-diimine) complexes. It will be shown that in this case the reaction proceeds via an associative mechanism and that the photosubstitution quantum yield depends on steric and electronic effects of both the substituting and α-diimine ligand. The α-diimine ligands used are 1,10-phenanthroline (phen), 4,7-Ph$_2$-phen, 5,6-Me$_2$-phen, 2,9-Me$_2$-phen, 5-NO$_2$-phen, 2,2'-bipyridine (bipy), 4,4'-Me$_2$-bipy, 1,4-bis-isoprop-

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yl-1,4-diaza-1,3-butadiene (i-Pr-DAB), 1,4-bis-mesitylene-DAB (Mes-DAB), 1,4-bis-cyclopropyl-DAB(c-Pr-DAB), 1,4-bis-neopentyl-DAB (Neop-DAB) and 1,4-bis-cyclohexyl-DAB (c-Hex-DAB).

The infrared, RR and electronic absorption spectra of several of these complexes have been studied in detail [10, 11] and recently the emission spectra of some of them have been reported [22].

Experimental

Materials and Preparations

The metal hexacarbonyls (Strem Chemicals), phen, 4,7-Ph$_2$-phen, 5,6-Me$_2$-phen, 5-NO$_2$-phen, bipy and 4,4'-Me$_2$-bipy (Merck) were purchased and used without further purification. The preparations of the R-DAB ligands and of the W(CO)$_4$(α-diimine) complexes have been described before [36, 37]. The complexes and the substituting phosphines were carefully purified before use.

Spectra

Electronic absorption spectra were recorded on Cary 14 and Perkin-Elmer Lambda 5 spectrophotometers and RR spectra on a Jobin Yvon HG2S Ramanor using a SP model 171 Ar$^+$ laser and a CR 490 tunable dye-laser with Rhodamine 6G and Coumarin 6 as dyes. The RR spectra were measured for 2–8 × 10^{-4} M C$_6$H$_6$-solutions of the complexes in a spinning cell.

Photochemistry

Photosubstitution quantum yields were measured at the maximum of the MLCT band by irradiating dry and carefully degassed, stirred benzene solutions (±10^{-4} M) in 40 × 10 × 10 mm quartz cells, with a 100–200 mW laser beam. The photon flux was calculated from the laser power which was measured by a Coherent model 201 powermeter. Before calculation of the quantum yields corrections were applied for absorption of the photoproduct and reflections of the light within the cell. The same photosubstitution quantum yields were obtained by following the product formation as by studying the disappearance of the parent compound. The reactions only proceeded upon exposure to light.

Results and Discussion

Upon irradiation into the MLCT band, several of the W(CO)$_4$(α-diimine) complexes react with phosphines to W(CO)$_3$(α-diimine)(PR$_3$) derivatives which were identified by infrared.

First of all, photosubstitution quantum yields were determined for the reaction of W(CO)$_4$(5,6-Me$_2$-phen) with different phosphines in order to study the

dependence of ϕ on the cone-angle and basicity of the phosphine. In each case the ratio PR$_3$/complex was kept at 750. The wavelength of irradiation was 488 nm, which is close to the maximum of the MLCT band. The photosubstitution of CO by PR$_3$ is accompanied by a shift of the MLCT band to lower energy (Fig. 1) and the spectra show isosbestic points indicative of complete conversion of the parent compound into one photoproduct. Upon irradiation in the absence of a substituting ligand all complexes appeared to be completely photostable.
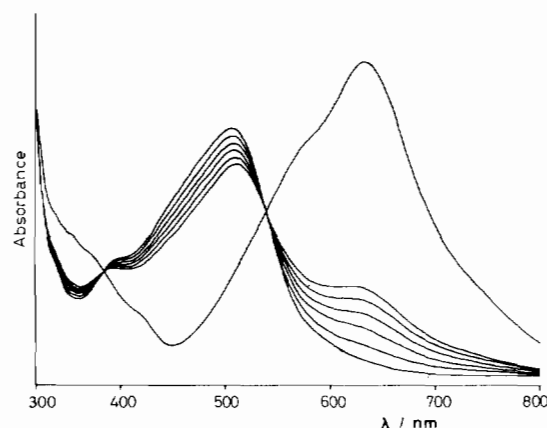

Fig. 1. UV-Vis. spectral changes during the reaction of W(CO)$_4$(5,6-Me$_2$-phen) with P(n-Bu)$_3$.

In Table I the photosubstitution quantum yields are collected for the reaction of W(CO)$_4$(5,6-Me$_2$-phen) with different phosphines. These results clearly show that ϕ decreases with increasing cone-angle for ligands with comparable basicities and decreases for ligands with lower basicity (P(OMe)$_3$ and PPh$_3$).

Next, quantum yields were determined for the photochemical reaction of W(CO)$_4$(5,6-Me$_2$-phen) with P(n-Bu)$_3$ at different concentration ratios P(n-Bu)$_3$/complex and with a constant concentration

TABLE I. Dependence of the Quantum Yield on the Phosphine Cone-Angle for the Photochemical Reaction of W(CO)$_4$(5,6-Me$_2$-phen) with PR$_3$ (λ_{irr} = 488 nm).

R	Cone-angle [42]	Quantum Yield[a]
ethyl	132°	8.0 × 10^{-3}
n-butyl	132°	2.5 × 10^{-3}
iso-butyl	142°	7.0 × 10^{-5}
iso-propyl	162°	4.0 × 10^{-5}
cyclohexyl	170°	6.0 × 10^{-5}
phenyl	145°	5.7 × 10^{-5}
methoxy	107°	3.0 × 10^{-5}

[a]Estimated error: 15%.

TABLE II. Dependence of the Quantum Yield on the Concentration Ratio Phosphine/Complex for the Photochemical Reaction of W(CO)$_4$(5,6-Me$_2$-phen) with P(n-Bu)$_3$ at a Constant Concentration of the Complex of 10^{-4} M (λ_{irr} = 488 nm).

Concentration ratio	Quantum yield
10	8.0×10^{-5}
100	7.4×10^{-4}
750	2.5×10^{-3}
3750	1.2×10^{-2}

of the complex. The results, presented in Table II, clearly show that ϕ strongly increases with a higher relative concentration of the ligand. The quantum yields appeared to be independent of the energy of the radiation source since irradiation at different positions within the MLCT band (458, 488 and 577 nm) gave the same quantum yield.

Thus, the quantum yield strongly depends on the basicity, the cone-angle and the concentration of the phosphine ligand. The complexes do not show any dissociative loss of CO upon irradiation in the absence of a substituting ligand. We therefore have a second order reaction with the association of the phosphine ligand to the oxidized metal in the MLCT state being the rate determining step. Such an associative mechanism has also been found by Gray *et al.* [38] for the photochemical reaction of W(CNR)$_6$ complexes with pyridine. For this reaction steric effects of R appeared to influence the nucleophilic attack by pyridine and therefore also the photosubstitution quantum yield.

Similar steric effects may be induced by substituents close to the coordinating nitrogen atoms of the α-diimine ligands, and we therefore varied the steric properties of these substituents. Table III

TABLE III. Quantum Yields for the Photochemical Reaction of W(CO)$_4$L with P(n-Bu)$_3$ at a Constant Concentration Ratio Phopshine/Complex of 750.

L	Quantum Yield
phen	2.7×10^{-3}
4,7-Ph$_2$-phen	1.6×10^{-3}
5,6-Me$_2$-phen	2.5×10^{-3}
2,9-Me$_2$-phen	1.0×10^{-4}
5-NO$_2$-phen	4.0×10^{-4}
bipy	1.1×10^{-3}
4,4'-Me$_2$-bipy	5.0×10^{-4}
i-Pr-DAB	0
Mes-DAB	0
Neop-DAB	$\ll 10^{-5}$
c-Hex-DAB	$\ll 10^{-5}$
c-Pr-DAB	4.6×10^{-5}

shows the quantum yields for the reaction of different α-diimine complexes with P(n-Bu)$_3$ at a constant high concentration of P(n-Bu)$_3$. It is evident from these results that substitution of two methylgroups close to the nitrogen atoms of phen (2,9-Me$_2$-phen) indeed lowers the quantum yield appreciably.

Steric effects also influence the quantum yields of the R-DAB complexes. When the small cyclopropyl groups at the nitrogen atoms are replaced by bulkier ones the quantum yield decreases (Table III).

Apart from these steric effects, electronic effects influence the quantum yields. Thus, ϕ appears to decrease appreciable when a strongly-withdrawing group such as NO$_2$ is introduced in the phenanthroline ligand.

In order to study the electronic effects of substituting one α-diimine ligand by another, steric effects should be excluded. For this purpose photosubstitution quantum yields are compared for the reactions of W(CO)$_4$(phen) and W(CO)$_4$(c-Pr-DAB) with substituting ligands of varying basicity. The small cyclopropyl substituent will not impede the formation of a seven coordinated intermediate. Just as in the case of the 5,6-Me$_2$-phen complex (Table I) the quantum yield for W(CO)$_4$(phen) increases with the basicity of the substituting ligand, whereas no such dependence is observed for W(CO)$_4$-(c-Pr-DAB) (Table IV).

TABLE IV. Quantum Yields for the Photochemical Reaction of W(CO)$_4$(phen) and W(CO)$_4$(c-Pr-DAB) with Different Substituting Ligands (Concentration Ratio Complexes/Ligand is 1:750).

Ligand	ϕ (reaction with W(CO)$_4$(phen))	ϕ (reaction with W(CO)$_4$(c-Pr-DAB))
CH$_3$CN	2.0×10^{-5}	7.9×10^{-5}
Cyclohexylisocyanide	6.5×10^{-5}	7.3×10^{-5}
propylamine	1.3×10^{-4}	8.8×10^{-5}
pyridine	5.0×10^{-5}	8.5×10^{-5}
P(OMe)$_3$	3.0×10^{-5}	9.0×10^{-5}
P(n-Bu)$_3$	2.7×10^{-3}	4.3×10^{-5}

Furthermore, although the quantum yields for both complexes are similar for weak bases, they differ appreciably when the strong base P(n-Bu)$_3$ is used. The most important electronic effect is the MLCT character of the lowest excited state. When the electronic transition has a strong MLCT character the metal will be oxidized in the excited state and will therefore be sensitive to nucleophilic attack. When metal- and α-diimine orbitals are strongly mixed in ground and excited state, the charge separaraion in the excited state however will be reduced

and the quantum yield will not depend on the basi-city of the entering ligand. It will be shown that this MLCT character of the excited state strongly decreases going from W(CO)$_4$(phen) to W(CO)$_4$-(c-Pr-DAB).

A valuable technique for determining the charge transfer character of an allowed electronic transition is RR spectroscopy [29]. A strong Resonance Raman effect observed for a certain vibration upon excitation into an electronic transition implies that the normal coordinate of that vibration is severely affected by the electronic transition. Usually such a normal coordinate is confined to only a few bonds of the complex, which means that RR spectra give direct information about the bond changes during an electronic transition. RR spectra have been recorded for all complexes under study and two extreme cases are shown in Fig. 2.
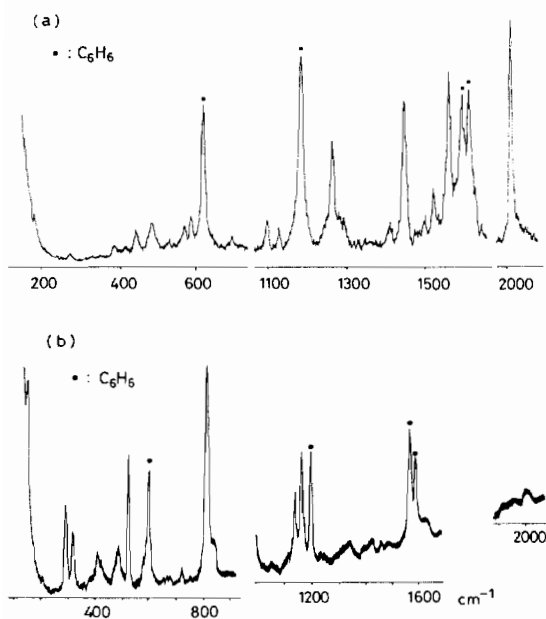

Fig. 2. Resonance Raman spectrum of W(CO)$_4$(4,7-Ph$_2$-phen) (a) and W(CO)$_4$(Mes-DAB) (b) in C$_6$H$_6$. Excitation wavelength: 514.5 nm.

These spectra are indeed very different. The 4,7-Ph$_2$-phen complex shows strong RR effects for the stretching modes of the ligand at 1450 and 1570 cm^{-1}, whereas the symmetrical metal—ligand stretching modes (200—500 cm^{-1}) are very weak. In contrast, ν_s(CN) of the coordinated Mes-DAB ligand cannot be observed whereas strong RR effects are observed for the metal—ligand stretching modes and for ligand deformation modes at 830 cm^{-1}.

The RR spectrum of the 4,7-Ph$_2$-phen complex is in accordance with an electronic transition posses-sing much MLCT-character. During such a transi-tion the ligand is reduced and as a result the ligand

bonds will change, which is reflected in the strong RR effects for the ligand stretching modes. In the phen complexes the mixing between the metal d$_\pi$ and the π^* orbital (belonging to symmetry b$_2$ in C$_{2v}$) is rather weak which means that the h.o.m.o. still has mainly metal d$_\pi$ and the l.u.m.o. mainly phen π^* character. The electronic transition between these levels, which is z-polarized [40], therefore has a strong MLCT character.

Since the Mes-DAB complex (and the c-Pr-DAB complex) does not show a RR effect for the symmetri-cal CN-stretching mode, no charge will be transferred here from the metal to the ligand. In these R-DAB complexes the π-backbonding is indeed much stronger than in the phen and bipy ones since the π^* level of the R-DAB ligand is lower in energy [41] and the electron density at the coordinating nitrogen atoms in the π^* level is much higher. As a result the h.o.m.o. of the R-DAB complexes is strongly metal (d$_\pi$)-ligand(π^*) bonding and the l.u.m.o. metal (d$_\pi$)-ligand(π^*) anti bonding.

During the electronic transition between these levels no charge is transferred to the ligand but instead the metal nitrogen bonds are severely affect-ed. This is reflected in the absence of a RR effect for ν_s(CN) and a strong RR effect for ν_s(M—N) at 290 cm^{-1}. This difference in character between the z-polarized electronic transitions of the phen, bipy and R-DAB complexes is of great importance for the photochemistry of these complexes. The central metal atom will be oxidized in the case of the phen and bipy complexes in the excited state and nucleophilic attack by a phosphine ligand can occur. In the case of the R-DAB complexes there is no charge separation in the excited state and so nucleo-philic attack will be prevented. The lowering of the quantum yield upon substituting a strongly electron-withdrawing group such as NO$_2$ in phen is due to the increase of the metal to ligand π-backbonding in this complex.

In conclusion it can be said that apart from steric effects the MLCT character of the electronic transi-tion, which can be derived from the RR spectra, largely determines the photoreactivity of these com-plexes.

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