

molar extinction coefficients are $\epsilon = 1240$ for $[\text{Os}(\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]^+$ and $\epsilon = 6460$ for $\text{Os}(\text{CHPh})(\text{CO})(\text{PPh}_3)_2\text{Cl}_2$ in mixtures of CH_2Cl_2 , ethanol, and aqueous HCl. The extinction coefficient of $\text{Os}(\text{CHPh})(\text{CO})(\text{PPh}_3)_2\text{Cl}_2$ was $\epsilon = 280$ at 535 nm in benzene. The neutral carbyne complex $\text{Os}(\text{CPh})(\text{CO})(\text{PPh}_3)_2\text{Cl}$ does not absorb at this wavelength.

Results

When solutions of $\text{Os}(\text{CPh})(\text{CO})(\text{PPh}_3)_2\text{Cl}$ (I) in benzene were saturated with gaseous HCl the complex I was converted to $\text{Os}(\text{CHPh})(\text{CO})(\text{PPh}_3)_2\text{Cl}_2$ (II) in a thermal reaction [11]. At low concentrations of HCl ($c < 10^{-4}$ M) this conversion was slow but could be accelerated by irradiation ($\lambda > 320$ nm). The photolysis was a smooth reaction as indicated by the spectral changes (Fig. 1). After longer irradiation times I was almost completely converted to II ($\lambda_{\text{max}} = 376$ nm, $\epsilon = 9800$). The spectrum f of Fig. 1 corresponds to a conversion of about 95%. In benzene solutions containing 5×10^{-5} M HCl the photolysis proceeds with a quantum yield of approximately $\varphi = 0.1$ ($\lambda_{\text{irr}} = 365$ nm). A precise determination was not possible due to the interference of the thermal reaction.

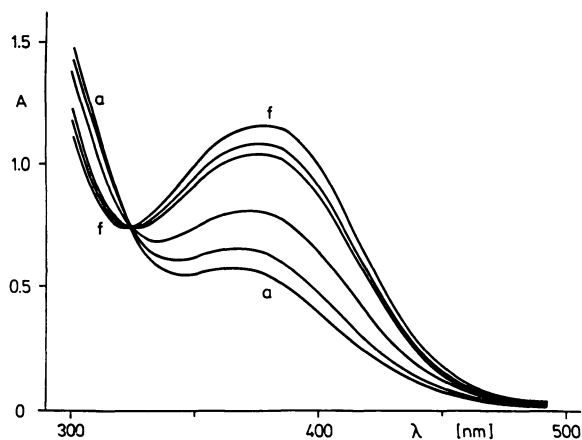


Fig. 1. Spectral changes during the irradiation of 4×10^{-4} M I in benzene solutions containing HCl ($\sim 10^{-4}$ M) at (a) 0 and (f) 30 min irradiation time, $\lambda_{\text{irr}} = 366$ nm, and 1 cm cell.

The cation $[\text{Os}(\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]^+$ (III) did not react thermally in mixtures of CH_2Cl_2 , ethanol, and hydrochloric acid ($c < 10^{-3}$ M HCl). However, upon irradiation ($\lambda > 305$ nm) III underwent a photolysis. The accompanying spectral changes are shown

in Fig. 2. At the beginning the photolysis was a smooth reaction as indicated by an isobestic point at 344 nm. The first photoproduct was identified as II by its absorption spectrum ($\lambda_{\text{max}} = 365$ nm, $\epsilon = 7000$ in solutions of CH_2Cl_2 , $\text{C}_2\text{H}_5\text{OH}$, and aqueous HCl). At the isobestic point II and III have the same extinction coefficient ($\lambda = 344$ nm, $\epsilon = 6800$). In this solvent II was apparently light sensitive and underwent a secondary photolysis. After continued irradiation the isobestic point at 344 nm disappeared. It is assumed that II was photodecomposed since a decrease of extinction was observed over a large wavelength region ($\lambda > 300$ nm). The primary photochemical reaction, the conversion of III to II, proceeds with a quantum yield of $\varphi = 0.2$ ($\lambda_{\text{irr}} = 313$ nm, 10^{-3} M HCl) upon irradiation of the absorption band in the near UV.

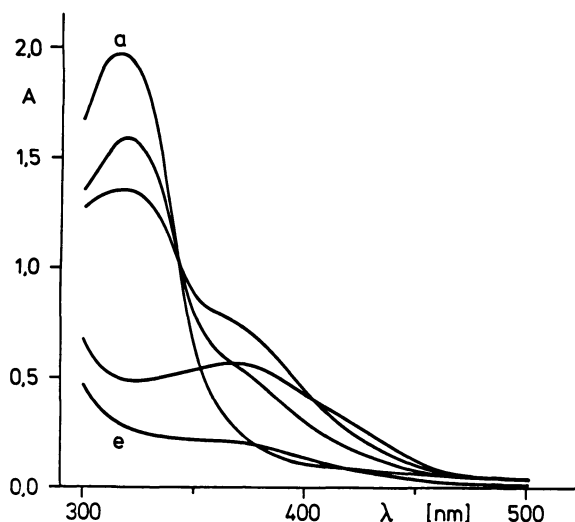


Fig. 2. Spectral changes during the irradiation of 1.3×10^{-4} M III in mixture of CH_2Cl_2 , $\text{C}_2\text{H}_5\text{OH}$, and aqueous HCl (6×10^{-4} M HCl) at (a) 0 and (e) 60 min irradiation time, $\lambda_{\text{irr}} > 305$ nm, and 1 cm cell.

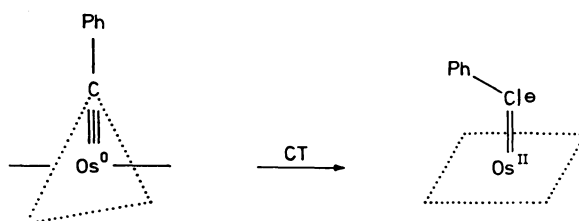
Discussion

The electronic absorption spectra of the carbyne complexes I (Fig. 1) and III (Fig. 2) exhibit fairly intense long-wavelength absorption maxima at 318 ($\epsilon = 13500$) and 366 nm ($\epsilon = 4700$) which we assign to charge transfer metal to ligand (CTML) transitions from osmium to the carbyne ligand. This assignment is based on several considerations. A trigonal-bipyramidal structure of I was confirmed

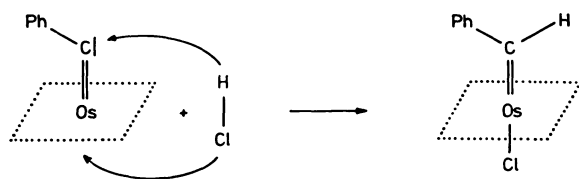
by X-ray analysis [11]. The cation III has probably the same structure which is characteristic of many low-valent metal complexes with a d^8 electron configuration. This requires formally as Os(0) metal center and a carbyne cation $IC-Ph^+$ as a ligand. Carbyne cations seem to be among the best π -acid ligands due to their energetically rather low-lying empty π^* orbitals which can accept a large portion of charge by the interaction with occupied $d\pi$ -orbitals of the metal [5–7]. The empty π^* -orbitals which are formed by the antibonding interaction may be localized to large extent at the carbyne ligand. A calculation on $[Fe(CPh)(CO)_2(PH_3)_2]^+$ which may be used as a model for III has shown [7], that the LUMO is indeed localized on the carbyne ligand to a large degree (63%). In analogy to many other carbyne complexes the HOMO of III is assumed to be essentially a metal d -orbital. Consequently, it is quite reasonable to assign the low-energy absorption band of the cation III to the CTML (Os to carbyne) transition. The long-wavelength absorption of the neutral complex I may be of the same origin. The photochemical results are also consistent with these assignments.

With regard to the photochemistry we suggest that the carbyne ligand has much in common with the nitrosyl ligand. Both cations, CR^+ [5–7] and NO^+ [12] are very good π -acceptor ligands due to their low-energy empty π^* -orbitals. On the basis of this similarity we adopt an approach introduced by W. Evans and J. I. Zink for the interpretation of the photochemistry of nitrosyl complexes [13]. If we neglect the non-equivalence of the other four ligands of I and III we can apply the qualitative MO model developed by Enemark and Feltham for trigonal-bipyramidal complexes with a linear NO ligand (or carbyne ligand in our case) in an equatorial position [12]. In this C_{2v} symmetry the HOMO ($4a_1$) is derived from the d_{z^2} -orbital while the π^* -orbitals of NO (or the carbyne) contribute to the antibonding LUMO ($3b_1$) to a large degree. The $4a_1$ to $3b_1$ CTML (Os to carbyne) transition terminates in an excited state which may undergo considerable structural rearrangement. According to Enemark and Feltham a shift of electron density from the metal to the ligand will change the geometry from trigonal-bipyramidal to square-pyramidal with a bent NO (or carbyne) ligand in an axial position. This rearrangement decreases the

energy of the antibonding π^* -orbitals of NO or the carbyne ligand and thus stabilizes the CT excited state. In a limiting description the CT transition induces a two-electron transfer from Os(0) to the carbyne ligand. As a result a square-pyramidal Os(II) complex is obtained with a bent carbyne in an axial position. The bent carbyne ligand carries now a lone pair at the coordinating carbon atom.



In another description the relaxed CT state could be envisaged as a coordinatively unsaturated octahedral Os(II) complex containing a deprotonated phenyl carbene ligand. In this situation the complex can be easily attacked by electrophiles such as a proton to generate a carbene ligand. At the same time a sixth ligand such as chloride should be attached to the metal to complete the octahedral coordination. Hydrochloric acid provides both functions. It adds apparently to the CT excited state of I or III to form the photoproducts II or $[Os(CHPh)(CO)_2(PPh_3)_2Cl]^+$ (IV).



The cation IV is apparently not stable but undergoes a substitution of CO by chloride to yield II in a subsequent thermal reaction.

Even the addition of HCl to I in the thermal reaction may be explained by the Enemark-Feltham model [12]. If Cl^- interacts with the carbyne complex in the ground state it could distort the trigonal-bipyramidal structure in direction to an octahedral geometry. This in turn should induce a transfer of two electrons from Os(0) to the carbyne which then bends. A stabilization occurs by the addition of a proton to the lone pair of the

bent carbyne ligand leading to an octahedral carbyne complex. In the cation III the $4a_1$ -orbital is apparently much more stable [12]. Consequently, III will be more resistant towards the thermal addition of HCl. In this context it is of interest that the five-coordinate complex $[\text{CoNO}(\text{das})_2]^{2+}$ with $\text{das} = o$ -phenylene-bis(dimethylarsine) easily adds a halide ion as sixth ligand to yield a stable

octahedral complex $[\text{CoNO}(\text{das})_2\text{X}]^+$. This structural change is accompanied by a bending of the nitrosyl ligand [12, 13].

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