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SPECTROSCOPIC STUDIES OF [M(CO)₅M'(CO)₃(1,4-DIAZABUTA-1,3-DIENE)] (M,M' = Mn, Re) AND THEIR PHOTOLYSIS PRODUCTS

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ABSTRACT

Photolysis of $[M(CO)_5 M'(CO)_3 (dab)]$ (M, M' = Mn, Re; dab = 1.4-diazabuta-1,3-diene, RN=CH-CH=NR) in 2-Me-THF leads to both homolytic and heterolytic splitting of the metal-metal bond depending on the solution temperature. In a rigid medium such as a CH_4 -matrix no breaking of the metal-metal bond is observed but instead formation of $[M(CO)_3 M'(CO)_3 (dab)]$ in which compound the dab-ligand is $\sigma, \sigma, \tau, \pi$ bridging between M and M'.

INTRODUCTION

Much attention has been paid recently to the spectroscopy and photochemistry of dinuclear metal-metal bonded species such as $[Mn_2(CO)_{10}]$ (refs.1.2). All photochemical reactions of $[M_2(CO)_{10}]$ (M = Mn, Re) (ref.3) including their disproportionation in pyridine (ref.4) have been explained by a homolytic splitting of the metal-metal bond. We have investigated in detail the spectroscopy (resonance Raman, i.r., u.v. and u.v.-p.e.s.) and the photochemistry of $[M(CO)_5M'(CO)_3(deb)]$ (M, M' = Mn, Re),



Fig. 1. Structure of $[M(CO)_5 M'(CO)_3 (dab)]$

Fig. 2. Tentative Term Scheme

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the structure of which is shown in figure 1. These complexes possess an intense absorption band at about 550 nm. which has been assigned to a $\sigma_b + \pi^*(L)$ charge transfer (c.t.) transition (ref.5). Although an assignment to a $d_{\pi}(M') + \pi^*(L)$ c.t. transition is more likely in view of the close correspondence between the resonance Raman (r.R.) and absorption spectra of these complexes and their mononuclear d^6 analogues (refs. 6,7) photolysis might still occur from the ${}^{3}\sigma_{b}\pi^{*}$ state [thexi states (ref.8)]. A tentative term scheme is presented in figure 2. Photolysis from the ${}^{3}\sigma_{b}\pi^{*}$ state will cause cleavage of the metal-metal bond. This splitting can be homolytic as has been observed for $[M(CO)_{5}M'(CO)_{3}L]$ (M, M' = Mn, Re; L = 1,10-phenantroline, 2,2'-biquinoline) in CCl_4 (ref.5) or heterolytic because of the different electronegativities of the two metal fragments.

RESULTS

Photolysis of $[Mn(CO)_5Mn(CO)_3(dab-ipr)]$ (dab-ipr = $1-C_3H_7-N=CH-CH=N-1-C_3H_7$) in 2-Me-THF at 230 K with λ = 514.5 nm gives $[Mn_2(CO)_{10}]$ and $[Mn_2(CO)_6(dab-ipr)_2]$ (figure 3) after homolysis of the parent compound into $[-Mn(CO)_5]$ and $[-Mn(CO)_3(dab)]$





radicals, $[Mn_2(CO)_6(ab-ipr)_2]$ appears to be unstable and reacts with 2-Me-THF to $[Mn_2(CO)_6(2-Me-THF)_4]$ upon warming the solution to 293 K.

Upon photolysis at temperatures below 200 K new bands appear at the expense of those belonging to $[Mn_2(CO)_{10}]$ and $[Mn_2(CO)_6(dab-ipr)_2]$. These bands are assigned to $[Mn(CO)_5^-]$ and to the solvated cation $[Mn(CO)_3(dab-ipr)(2-Me-THF)^+]$. Apparently, at lower temperatures the diffusion of the radicals is hampered by the high viscosity of the solvent and they will recombine to the parent compound. Heterolysis of the metal-metal bond will then be favoured the more since the solvent molecules will coordinate to $[Mn(CO)_3(dab)^+]$ at these temperatures, thus inhibiting the recombination of the ions. When a solution of these ions is warmed to 140 K. 2-Me-THF is released and recombination of the ions to the parent compound is observed.

Photolysis in a CH,-matrix at 12 K



Fig. 4. I.r. spectral changes upon photolysis of $[Mn(CO)_5Re(CO)_3(dab-ipr)]$ with $\lambda = 514.5$ nm in a CH_4 -matrix at 12 K.

In a rigid medium such as a CH₄-matrix splitting of the metal-metal bond will be immediately followed by recombination to the parent compound. In that case a reaction can occur from the ${}^{3}d_{\pi}\pi^{*}$ state (fig. 2). For [Mn(CO)₅Re(CO)₃(dab-ipr)] this results

in loss of two carbonyl ligands from the $Mn(CO)_{c}$ mosety of the complex and a conformational change of the dab-ligand from σ . σ -chelate to σ . σ , π , π --bridging (figs. 4 and 5). The loss of CO is assumed to be caused by delocalization of the d_{π^*} state over these carbonyls, which is evident from the The carbonyl-stretching r.R. spectra. frequencies of the [Mn(CO)3Re(CO)3(dab--upr)] formed closely resemble those of $[Mn(CO)_{z}Mn(CO)_{z}(CH_{z}-N=C(CH_{z})-$ -C(CH₂)=N-CH₂)] which compound has been synthesized by Adams in quite another way (ref.9).

Further support for the $\sigma, \sigma, \tau, \pi$ -coordination of the dab-ligand is given by a shift of $v_{svm}(CN)$ from 1465 cm⁻¹ (parent compound) to 1389 cm⁻¹ (photoproduct). Such a lowering of the frequency will occur when the π^* level of the dab-ligand becomes more strongly involved in the bonding.



Fig. 5. Structures of parent compound and photoproduct in a CH ,-matrix.

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