12322 *J. Am. Chem. Soc.* **1995,** *117,* 12322−12327

Metal-to-Ligand Charge Transfer Photochemistry: Potential Energy Curves for the Photodissociation of $HMn(CO)_3(dab)$

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Received June 5, 1995[⊛]

Abstract: The photodissociation of $HMn(CO)_3(dab)$ has been studied through contracted configuration interaction (CCI) calculations on top of CASSCF wave functions for the metal−hydrogen bond homolysis and the photodissociation of an axial carbonyl ligand. The corresponding potential energy curves (PEC) connect the ground and excited states of the reactant to the ground and excited states of the primary products. The calculations were carried out under C_s symmetry constraint with a basis set that is at least of double-ζ quality. The multireference CCI calculations that correlate the 3d electrons and the two electrons of the Mn−H bond were based on CASSCF wave functions with eight electrons in ten active orbitals ($3d_{yz}$, $3d_{x^2-y^2}$, $3d_{xz}$, σ_{Mn-H}, σ^*_{Mn-H}, $3d_{xy}$, $4d_{yz}$, $4d_{x^2-y^2}$, $4d_{xz}$, π^*) optimized for the required state. From the shape of the PEC it appears that the interaction between the two lowest a^3A' ($d_{xz} \rightarrow \pi^*$) and b^3A' ($d_{x^2-y^2} \rightarrow \pi^*$) metal-to-ligand charge transfer (MLCT) excited states and the c^3A' ($\sigma \rightarrow \pi^*$) ligand-to-ligand charge transfer (LLCT) dissociative state plays a key role in the homolysis mechanism. It is proposed that excitation of $HMn(CO)_3(dab)$ at low energy (500 nm) will bring the molecule in the lowest ^{1}MLCT states (calculated at 18 030 and 21 710 cm^{-1}). From these singlet states, after ^{1}MLCT → ^{3}MLCT fast intersystem crossing, the system may either get trapped in the potential well of the long lifetime triplet excited states and provide emission or be able to overcome the energy barriers yielding a small fraction of the primary products H + $Mn(CO)_3(dab)$ in their ground states. Direct dissociation of the CO loss primary products with a rather low quantum yield is not excluded from the shape of the lowest MLCT PEC along the $Mn-CO_{ax}$ elongation. Excitation of $HMn(CO)_3(dab)$ at high energy (around 300 nm) will bring the system in one of the singlet states corresponding to d → d or $\sigma \rightarrow \pi^*$ excitations (calculated between 28 980 and 37 980 cm^{-1}). After fast intersystem crossing to the c^3A' ($\sigma \rightarrow \pi^*$) excited state calculated at 31 509 cm^{-1}, the system may either dissociate after two successive internal conversions (at 2.02 and 2.11 Å) along the a^3A' PEC to the primary products H + $Mn(CO)_3(dab)$ in their ground states or get trapped in the potential well of the a,b^3A' MLCT PEC and provide emission.

1. Introduction

The photochemistry of organometallic compounds with low-lying metal-to-ligand charge transfer (MLCT) states was mainly used to understand and to reproduce photoenergy and -electron transfer processes occurring in natural phenomena.[1−9] The design of new molecular devices able to govern these processes and to perform specific functions is the most spectacular application developed in this field in the past ten years.[10]

Until recently, the MLCT states were mostly assumed to be unreactive, and their long lifetime made them suitable for spectroscopic analysis.[2−4,11,12] However, according to a number of experiments reported for a family of dab mono- or dinuclear transition metal carbonyls,[13−22] it seems that these molecules may either behave like transition-metal complexes without low-lying MLCT states, undergoing ligand dissociation or radical formation upon irradiation, or manifest the photophysics of MLCT complexes. The duality between these two different behaviors may be used to promote different applications like energy and electron transfer processes or formation of reactive intermediates used in substitution reactions and catalytic processes. A fundamental question concerns the function of the MLCT states in the observed photochemistry of this class of molecules, which depends strongly on the metal center, the ligand π acceptor, and the other ligands. The role of the MLCT states in the photochemical behavior is difficult to rationalize

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[⊛] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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and is not well understood. The relative position in the electronic spectra of the photodissociative states corresponding to d → d, $\sigma \rightarrow \sigma^*$, and $\sigma \rightarrow \pi^*$ with respect to the MLCT states is probably the key of the photochemical behavior of this family of molecules.

If the photochemistry of transition-metal carbonyls is well documented experimentally[23-29] and theoretically,[30-33] the density and the diversity of states which characterize the electronic spectrum of complexes with low-lying MLCT states, the position of which depends on the experimental conditions, is responsible for the incomplete understanding of their photochemical and photophysical behavior. Most of the time, the future of the molecule after irradiation is followed either by emission mesasurement or by wavelength dependence of the quantum yield of the primary reactions.[11] Current understanding of excited states properties of transition-metal coordination compounds is generally based on molecular orbital diagrams, coupled with an analysis in terms of bonding and antibonding character. This analysis, although conceptually appealing and certainly useful, has a number of drawbacks and may turn partly erroneous in some cases.[33] One way for getting insights in the nature of the photoexcited states involved in the photochemistry of these molecules is to calculate the excitation energies to the lowest electronic states and the corresponding potential energy curves for the observed primary reactions.[30-32] This approach constitutes the first step of a more complete study based on the calculation of the potential energy surfaces, followed by an investigation of the photodissociation dynamics.[34-37]

In order to analyze the complexity of the electronic spectrum of transition-metal complexes with low-lying MLCT states, we have investigated the nature of the lowest excited states in two model systems, HMn(CO)$_3$(dab) and CH$_3$Mn(CO)$_3$(α-diimine).[38] A comparison between the results of this preliminary study and a previous one reported for HMn(CO)$_5$[32] shows that the presence of MLCT states affects only slightly the lowest part of the electronic spectrum of transition-metal hydrides. The theoretical results based on ab initio correlated calculation agree with the main features of the absorption spectra usually produced for this family of molecules (i) an intense band at around 500 nm corresponding to MLCT states and (ii) a shoulder around 350 nm which could be assigned to excited states corresponding to d → d and $\sigma \rightarrow \pi^*$ excitations. The replacement of hydrogen by an alkyl group does not modify quantitatively the excitation energies calculated for the lowest singlet excited states corresponding to d → d, d → π^*, and $\sigma \rightarrow \pi^*$ excitations. The next step of the theoretical study is the computation of the PEC that connect the ground and excited states of the model system HMn(CO)$_3$(dab) to the corresponding electronic states of the products of the two primary reactions, namely the metal–hydrogen bond homolysis (reaction 1) and the departure of a carbonyl ligand (reaction 2).

$$\mathrm{HMn(CO)_3(dab)} \xrightarrow{h\nu} \mathrm{H} + \mathrm{Mn(CO)_3(dab)} \qquad (1)$$

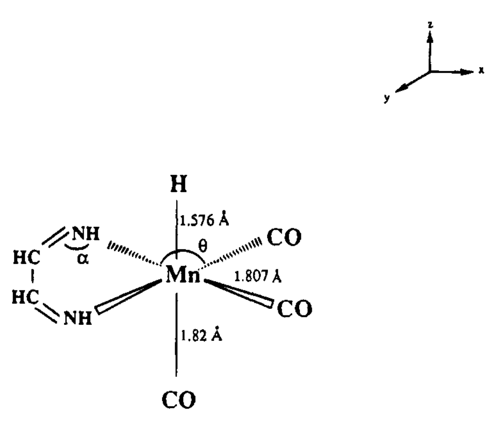
$$[\mathrm{HMn(CO)_3(dab)} \xrightarrow{h\nu} \mathrm{CO} + \mathrm{HMn(CO)_2(dab)}] \qquad (2)$$

In a recent work[39] we have shown, on the basis of the PEC computed for the metal–hydrogen bond cleavage (reaction 1), that the presence of a reactive ^{3}LLCT ($\sigma \rightarrow \pi^*$) excited state interacting with the low-lying MLCT states and leading to the primary products H + Mn(CO)$_3$(dab) in their ground state is responsible for the formation of the radical species in this family of molecules.

The aim of the present study is the calculation of the potential energy curves that connect the electronic ground state and some of the low-lying excited states of HMn(CO)$_3$(dab) to the corresponding states of the metal–hydrogen bond homolysis and of the CO$_{\mathrm{ax}}$ loss primary products, through contracted configuration interaction (CCI) calculations based on complete active space self-consistent field (CASSCF) reference wave functions. The calculation of the potential energy curves is restricted to the lowest triplet excited states corresponding to d → π^*, $\sigma \rightarrow \pi^*$, and $\sigma \rightarrow \sigma^*$ excitations for two reasons (i) the nature of the electronic structure of the primary products and (ii) the existence of experimental emission spectra from the low-lying triplet states.

2. Computational Details

The calculations were carried out for HMn(CO)$_3$(dab) (dab=1,4-diaza-1,3-butadiene = dab) with the conformation reported in Figure 1 in the C_s symmetry. Idealized geometries



were deduced from the structures of Mn(CO)$_3$(dab)Cl[40] and of HMn(CO)$_5$[41] with bond lengths and angles of Mn–H = 1.576 Å, Mn–C$_{\mathrm{CO}}$ = 1.82 Å for the carbonyl ligand trans to the hydrogen or 1.807 Å for the other carbonyls: $\theta = 96°$, $\alpha = 117.5°$. It has been assumed that the C_s symmetry is retained along the reaction path corresponding to the homolysis of the metal–hydrogen bond (Scheme 1). For the sake of simplicity, the loss of an axial ligand which produces HMn(CO)$_2$(α-

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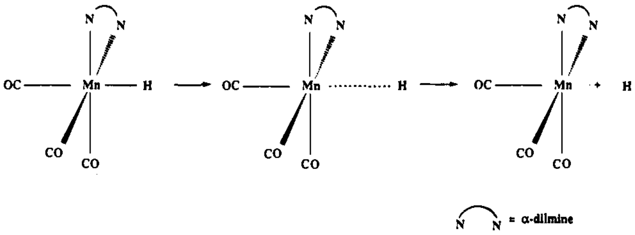
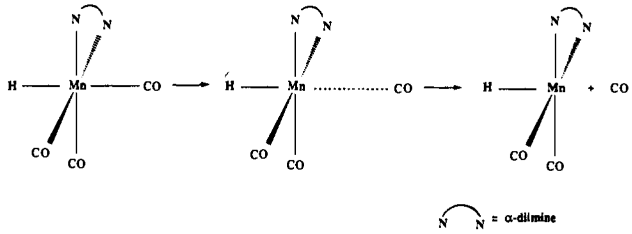
Scheme 1



Scheme 2



diimine) unrelaxed has been considered for the photodissociation of a carbonyl ligand. For this reason, we have assumed that the C_s symmetry is retained along this reaction path (Scheme 2).

The rigorous way to calculate the PES consists of optimizing the geometrical structure for each electronic state. However, this method is not adapted to the studies reported here for four reasons: (i) this procedure is very expensive, (ii) the convergence of the CASSCF has to be driven with care when we deal with problems characterized by many excited states in a same symmetry[42] and a gradient procedure would be hazardous, (iii) restriction of the geometry optimization to the electronic ground state would not be significant, and (iv) we are concerned by extremely fast events occurring in a time domain of 20 to 200 fs[34-35,37] on dissociative PEC. However, geometry relaxation effects, especially for the lowest quasi-bound MLCT excited states, will have to be included in a further analysis of the photodissociation dynamics.[43,44]

The following Gaussian basis sets were used: for the manganese atom a (15,11,6) set contracted to [9,6,3],[45] for the first row atoms a (10,6) set contracted to [4,2],[48] for hydrogen either a (6,1) set contracted to [3,1][49] (for the atom directly linked to the metal center) or a (4) set contracted to [2][49] for the other hydrogen atoms.

Table 1. Calculated CASSCF/CCI Excitation Energies (in cm^{-1}) to the Lowest $^{1,3}A'$ and $^{1,3}A''$ Excited States of $HMn(CO)_3(dab)$

	one-electron excitation in the main configuration	
$a^1A' \rightarrow a^3A'$	$3d_{xz} \rightarrow \pi^*$	16 050
$a^1A' \rightarrow a^3A''$	$3d_{yz} \rightarrow \pi^*$	17 180
$a^1A' \rightarrow a^1A''$	$3d_{yz} \rightarrow \pi^*$	18 030
$a^1A' \rightarrow b^3A'$	$3d_{x^2-y^2} \rightarrow \pi^*$	19 900
$a^1A' \rightarrow b^1A'$	$3d_{x^2-y^2} \rightarrow \pi^*$	21 710
$a^1A' \rightarrow c^1A'$	$3d_{xz} \rightarrow \pi^*$	26 630
$a^1A' \rightarrow b^1A''$	$3d_{x^2-y^2} \rightarrow 3d_{xy}$	28 980
$a^1A' \rightarrow c^3A'$	$\sigma \rightarrow \pi^*$	31 509
$a^1A' \rightarrow c^1A''$	$3d_{xz} \rightarrow 3d_{xy}$	34 030
$a^1A' \rightarrow d^1A'$	$\sigma \rightarrow \pi^*$	37 980
$a^1A' \rightarrow d^3A'$	$\sigma \rightarrow \sigma^*$	45 170

Complete active space SCF (CASSCF) calculations[50] are carried out to obtain wave functions which are used as references in the multireference contracted configuration interaction (CCI) calculations.[51] For each electronic state a CASSCF calculation followed by a multireference CI calculation has been performed. Since our interest will center mostly on the lowest excited states corresponding to d → d, d → π^*, $\sigma \rightarrow \sigma^*$, and $\sigma \rightarrow \pi^*$ excitations, eight electrons are correlated (the 3d electrons and the two electrons involved in the Mn−H bond) in ten active orbitals corresponding to the 3d orbitals and the 4d orbitals which correlate them, the σ and σ^* orbitals (σ and σ^* denote the molecular orbitals that are bonding and antibonding with respect to the Mn−H bond, respectively) and the lowest π^* orbital localized on the dab group. For each electronic state a multireference CCI calculation is performed, including all the configurations which appear with a coefficient larger than 0.08 in the CASSCF calculations (the number of references may vary from 4 to 12 states in these CI calculations depending on the state of interest). Single and double excitations to all virtual orbitals, except the counterparts of the carbonyls and diimine 1s and of the metal 1s, 2s, and 2p orbitals, are included. The number of configurations ranged from 250 000 to 960 000, but this number is reduced to at most a few thousand by contraction. The integral calculations were carried out either with the system of programs ARGOS[53] or with the system of programs ASTERIX.[52]

3. Results

$HMn(CO)_3(dab)$ Lowest Excited States. The calculated excitation energies to the lowest $^{1,3}A'$ and some of $^{1,3}A''$ excited states of $HMn(CO)_3(dab)$ are reported in Table 1. The lowest $^1A'$ and $^1A''$ states, accessible through spin allowed transitions, are calculated between 18 030 and 26 630 cm^{-1} and correspond to d → π^* excitations, in excellent agreement with the main feature of the UV−vis absorption spectra obtained for this family of molecules, namely a large and very intense band around 500 nm assigned to MLCT states.[6,13-17] The singlet and triplet states corresponding to the $3d_{yz} \rightarrow \pi^*$ and $3d_{x^2-y^2} \rightarrow \pi^*$ excitations are nearly degenerate, while the energy gap between the singlet and triplet components of the MLCT states corresponding to the $3d_{xz} \rightarrow \pi^*$ excitation is rather large (more than 1 eV). This feature is explained by an analysis of the CASSCF wave functions characterized by a strong interaction between the a^1A'

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(42) Especially at the avoided crossing points sudden change of electronic configurations or mixing between several states may occur and wrong solutions may be obtained by automatic convergence of CASSCF wave functions in the course of gradient optimization cycles.

(43) From preliminary results based on gradient CASSCF calculations of the structure of the a^1A' and a^3A' (MLCT) electronic states, it appears that the metal−carbonyl bond lengths are elongated by 15% and the metal−hydrogen bond length is shortened by 5% in the ^{3}MLCT excited state.[44]

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(45) This basis set is made from the (14.9.5) basis of Wachters[46] by adding an additional s function (exponent 0.3218), two diffuse p functions, and one diffuse d function. All the exponents were chosen according to the even-tempered criterion of Raffenetti.[47]

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Table 2. CCI Energies Values (in au and Relative to −1675.) Along the Potential Energy Curves for the Reaction $HMn(CO)_3(dab) \rightarrow H + Mn(CO)_3(dab)$ as a Function of the Distance Mn−H

	1.4 Å	1.576 Å	1.8 Å	2.0 Å	2.1 Å	2.2 Å	2.3 Å	2.5 Å	2.9 Å	3.5 Å	50.0 Å
d^3A'		0.080 03	0.103 39			0.128 60		0.122 00			
c^3A'		0.142 28	0.157 96		0.168 17	0.150 88	0.139 53	0.145 43			
b^3A'	0.188 44	0.195 18	0.187 66	0.174 00			0.156 71		0.169 52	0.173 09	0.170 67
a^3A'	0.203 43	0.212 73	0.200 65		0.178 16	0.182 30		0.184 40	0.186 65	0.189 48	0.190 31
a^1A'	0.274 85	0.285 85	0.279 85		0.255 73	0.251 17		0.230 10	0.205 52	0.194 45	0.190 28

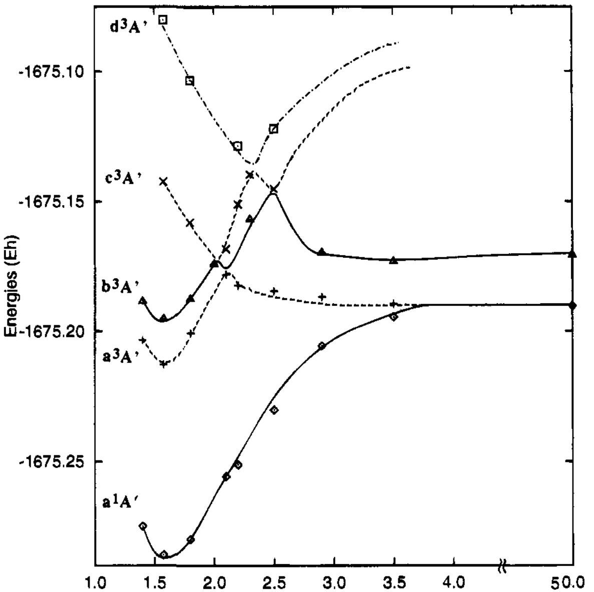

Figure 1. CASSCF/CCI potential energy curves for the homolysis of the metal−hydrogen bond in $HMn(CO)_3(dab)$ as a function of the metal−hydrogen bond distance (the points correspond to the ab initio values).

electronic ground state and the c^1A' excited state which rejects the later state in the upper part of the spectrum. These results cannot be directly compared with those reported in a previous preliminary paper,[38] namely a b^1A' state calculated at 17 330 cm^{-1} and a c^1A' state calculated at 22 280 cm^{-1}. The excitation energies differences of 0.5 eV between the values obtained in the present study and in ref 38 are due to the use of different computational strategies. Indeed, the method based on averaged CASSCF wave functions[38] overestimates the energy of the electronic ground state and is responsible for an underestimation of the excitation energies to the b^1A' and c^1A'MLCT states.

The excitation energies to the singlet states corresponding to d → d excitations range between 28 980 and 34 030 cm^{-1}, while the excitation energies to the ligand-to-ligand charge transfer ^{1,3}LLCT excited states are calculated at 37 980 cm^{-1} for the singlet component and 31 509 cm^{-1} for the triplet which is photoactive for the homolysis of the Mn−H bond. The high value obtained for the excitation energy to the d^3A' ($\sigma \rightarrow \sigma^*$) excited state (45 170 cm^{-1}) indicates that the direct participation of this state in the homolysis of the Mn−H bond is unlikely.

Potential Energy Curves for the Hydrogen Dissociation. The CCI energies for the a^1A' electronic ground state and the four lowest $^3A'$ excited states of $HMn(CO)_3(dab)$, calculated along the Mn−H bond homolysis reaction path under C_s symmetry constraint, are reported in Table 2. The corresponding potential energy curves are shown in Figure 1.

From the values reported in Table 2, reaction 1 is calculated to be endothermic by 60.0 kcal mol^{-1}. This value is in good agreement with the values usually reported for the Mn−H bond energy in transition-metal hydrides which range from 51 to 68 kcal mol^{-1}.[54−60] The character of the a^1A' PEC is modified around 3.5 Å due to its interaction with the dissociative PEC corresponding to the d^1A' ($\sigma \rightarrow \pi^*$) excited state (not represented here). At the equilibrium geometry, the a^1A' state corresponds to the closed shell configuration of the electronic ground state of $HMn(CO)_3(dab)$. At dissociation, the main contribution represents 84% of the state a^1A' configuration and corresponds to the $\sigma \rightarrow \pi^*$ excitation.

The lowest a^3A' and b^3A' potential energy curves, corresponding to MLCT states in the vicinity of the equilibrium geometry, are quasi bound, in agreement with the absorption and emission spectra reported for this family of molecules.[6,13−17]

The a^3A' PEC corresponds, in its dissociative part, to the $\sigma \rightarrow \pi^*$ excitation and leads to the primary products H + $Mn(CO)_3(dab)$ in their $^{1,3}A'$ ground state. The b^3A' PEC does avoid two crossings, the first one with the a^3A' PEC giving an energy barrier around 2.11 Å of the order of 20.0 kcal mol^{-1}, the second one with the upper c^3A' PEC around 2.02 Å. This second avoided crossing generates an energy barrier of the order of 14.0 kcal mol^{-1} on the b^3A' PEC. The b^3A' and c^3A' PEC cross the upper d^3A' PEC around 2.60 and 2.32 Å, respectively, giving two energy barriers. Beyond 2.60 Å, the main character of the b^3A' PEC becomes $\sigma \rightarrow \sigma^*$ and the curve dissociates toward the diradical H + $Mn(CO)_3(dab)$ in the degenerate b^1A' and b^3A' states, corresponding to the closed shell electronic ground state configuration and to the $\sigma \rightarrow \sigma^*$ excitation, respectively.

Before a Mn−H distance of 1.8 Å and beyond 2.9 Å, the triplet excited states are rather pure with CI coefficients on the main configuration greater than 0.9. In the vicinity of the avoided crossings, the main contributions may represent less than 60% of the state configuration due to a strong mixing between the a^3A', b^3A', and c^3A' states around 2.1 Å and between the b^3A', c^3A', and d^3A' around 2.6 Å.

Potential Energy Curves for the Dissociation of an Axial Carbonyl Ligand. The CCI energies for the a^1A' electronic ground state and the lowest triplet MLCT and LLCT excited states of $HMn(CO)_3(dab)$, calculated along the $Mn-CO_{ax}$ elongation under C_s symmetry constraint, are reported in Table 3. The corresponding potential energy curves are shown in Figure 2.

From the values reported in Table 3, reaction 2 is calculated to be endothermic by 25.3 kcal mol^{-1}. This value is in the range of the experimental data available for the metal−carbonyl

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Table 3. CCI Energies Values (in au and Relative to −1675.) Along the Potential Energy Curves for the Reaction $HMn(CO)_3(dab) \rightarrow CO + HMn(CO)_2(dab)$ as a Function of the Distance $Mn-CO_{ax}$

	1.6 Å	1.82 Å	2.0 Å	2.2 Å	2.5 Å	3.5 Å	50.0 Å
c^3A'	0.087 83	0.142 28	0.146 94	0.142 71	0.137 10	0.133 68	0.128 94
b^3A'	0.141 45	0.195 18	0.210 70	0.215 00	0.214 62	0.212 39	0.209 14
a^3A'	0.143 65	0.212 73	0.227 18	0.233 70	0.234 15	0.227 69	0.223 74
a^3A''	0.132 54	0.207 55	0.230 29	0.240 39	0.244 11	0.247 46	0.244 76
a^1A'	0.242 63	0.285 85	0.288 34	0.280 34	0.267 32	0.251 15	0.245 52

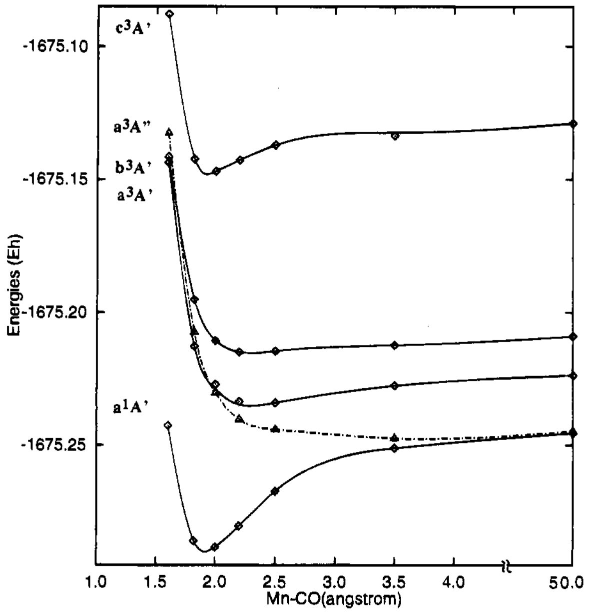

Figure 2. CASSCF/CCI potential energy curves for the loss of a carbonyl ligand in $HMn(CO)_3(dab)$ as a function of the metal−CO_{ax} bond distance (the points correspond to the ab initio values).

bond dissociation energy (24.0−42.0 kcal mol^{-1}) in transition-metal carbonyls.[61−63] These results agree rather well with the theoretical values published on other systems.[64−67] One significant feature of Table 3 and Figure 2 is the presence of a minimum in the vicinity of 1.92 Å on the a^1A' ground state PEC, to be compared with the experimental bond length of 1.82 Å in related complexes.[41] This rather long $Mn-CO_{ax}$ bond distance is certainly due to a defect of geometry optimization and related to the trans effect of the H atom enhanced by the short Mn−H distance of 1.576 Å kept constant along the reaction path.[68]

The a^3A' and b^3A' MLCT states that were quasi bound with respect to the metal−hydrogen bond homolysis are weakly bound with respect to the CO loss. The PEC corresponding to the $^3A''$ (yz → π^*) MLCT excited state is dissociative with respect to the loss of an axial carbonyl ligand in our model system $HMn(CO)_3(dab)$ and should be responsible for the CO loss observed upon irradiation of this family of molecules at low energy (500 nm).[21,22,69−71] The c^3A' ($\sigma \rightarrow \pi^*$) excited states responsible for the Mn−H bond breaking is not dissociative with respect to the CO loss. The shape of the PEC along the metal−CO_{ax} elongation is relatively simple, at least for the low-lying excited states, without any strong interactions between the different excited states, to be contrasted with the number of avoided crossings occurring along the metal−H bond elongation.

Qualitative Mechanism for the Photochemistry of the Model System $HMn(CO)_3(dab)$ and Related Complexes. From the set of PEC shown in Figures 1 and 2, it is possible to propose a qualitative mechanism for the photochemistry of the model system $HMn(CO)_3(dab)$ and related molecules.

(i) Irradiation into the MLCT band (around 500 nm or 20 000 cm^{-1}) will bring the molecule into vibrationally excited levels of the lowest singlet MLCT states calculated between 18 030 and 21 710 cm^{-1}. After intersystem crossing (ISC) to the corresponding triplet MLCT states, the system may either get trapped in the potential well of these long lifetime excited states and provide emission spectra or be able to overcome the energy barriers (of the order of 20.0 kcal mol^{-1} in our model system), yielding a fraction of the primary products H + $Mn(CO)_3(dab)$ in their ground states.

(ii) Irradiation into the UV domain (around 300 nm or 33 000 cm^{-1}) will bring the molecule in one of the singlet excited states corresponding to d → d or $\sigma \rightarrow \pi^*$ excitations and calculated between 28 980 and 37 980 cm^{-1}. After ISC to the C^3A' excited state, the system may evolve along the corresponding PEC until it reaches the potential well around 2.04 Å. After two successive internal conversions (IC) at 2.04 and 2.15 Å, the molecule will drop on the a^3A' PEC and dissociate to the primary products H + $Mn(CO)_3(dab)$ in their ground states.

From some of the low-lying MLCT excited states a part of the molecule may also dissociate with a low quantum yield to the carbonyl loss primary products (reaction 2). The branching ratio of the concurrent channels Mn−H homolysis vs carbonyl loss vs photophysics can be determined by photodissociation dynamics simulation.[72]

4. Conclusion

Potential energy curves for the homolysis of the metal−hydrogen bond as well as for the carbonyl loss in the model system $HMn(CO)_3(dab)$ have been computed for the ground and lowest triplet excited states from CASSCF/CCI calculations. The potential energy curves obtained for the photodissociation of this simple model system point to the complexity and the richness of the photochemistry of transition-metal complexes with low-lying MLCT states. This work represents the first theoretical evidence of the participation of the low-lying MLCT states in the photodissociation mechanism of these molecules. The observed photodissociation[21,22,69−71] of a carbonyl ligand at low irradiation energy will compete with the MLCT relaxation. It appears that the interaction between the two lowest $^3A'$(d → π^*) MLCT excited states and the $^3A'$ ($\sigma \rightarrow \pi^*$) LLCT dissociative state, which correlates with the primary products H + $Mn(CO)_3(dab)$ in their ground states, plays a key role in the photochemistry of this family of molecules. In a number of theoretical studies of the photochemistry of transition-metal compounds we have shown that the primary reaction was

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[68] A CASSCF geometry optimization of $HMn(CO)_3(dab)$ in the electronic ground state gives a $Mn-CO_{ax}$ bond distance of 1.892 Å for a Mn−H distance of 1.682 Å longer than the idealized one of 1.576 Å. In the optimization procedure, the CASSCF active space is limited to six active orbitals where six electrons are correlated and the basis sets used are of split valence quality for the second row atoms and of the type (13, 8, 6) contracted to [5, 3, 3] for the metal atom.[44] Increasing the CASSCF active space and the size of the basis sets should improve these preliminary results.

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oriented by the bonding and antibonding properties of the orbitals involved in the electronic excitation during the last stage of the reaction.[33] In the case of transition-metal hydrides, the triplet excited state corresponding to the $\sigma \rightarrow \sigma^*$ excitation was responsible for the metal−hydrogen bond breaking.[73] Here again, the b^{3}A′ PEC corresponds in its dissociative part (beyond 2.75 Å) to the $\sigma \rightarrow \sigma^*$ excitation, leading to the homolysis of the metal−hydrogen bond. However, in the family of molecules studied in the present work, this "photoactive excited state" is rejected in the upper part of the electronic spectrum due to the presence of low-lying MLCT and LLCT states. It is clear from the study reported here that the general mechanism proposed for the photochemistry of transition-metal hydrides does not apply to transition-metal complexes with low-lying MLCT and LLCT excited states. The presence of a ^{3}LLCT ($\sigma \rightarrow \pi^*$) photoactive excited state confirms the conclusion of recent experiments reported for this class of compounds,[69] namely a fast homolysis observed for Mn(benzyl)(CO)$_3$(iPr-dab) (dab = 1,4-diazabuta-1,3-diene) (τ < 10 ns) without any long-lived excited state. A similar behavior is observed when the manganese is replaced by rhenium. The interactionn between the MLCT states and the low-lying LLCT ($\sigma \rightarrow \pi^*$) dissociative excited state for the metal−hydrogen bond breaking and probably for the other primary reactions leading to a radical species (metal−alkyl or metal−metal bond homolysis) is the key of the photochemical behavior observed in this family of molecules. The quantum yield and the time scale of the homolysis will depend on the factors (wavelength of irradiation, nature of the radical species to be produced, metal center and π acceptor ligand) governing the facility for the system to overcome the energy barrier occurring at the avoided crossing points between this photoactive excited state and one of the lowest MLCT states. For instance, if the homolysis reaction of M(benzyl)(CO)$_3$(iPr-dab) (M = Mn, Re) is characterized by a high quantum yield close to one, the alkyl analogous M(alkyl)(CO)$_3$(iPr-dab) do not show any homolysis upon visible excitation into the MLCT band[69] indicating the presence of a high energy barrier. However, at this stage of the theoretical study it is rather difficult to explain some of the experimental features. For instance there is experimental evidence from transient absorption and emission data that the ^{3}LLCT states in some related rhenium complexes have a long lifetime (greater than the lifetime observed for the ^{3}MLCT), at least in apolar solvents and in glasses.[69] A significant solvent effect in this class of molecules is a shift of the MLCT states to higher energies with a change in the shape of the PEC. As a consequence all the dynamics of the photodissociation will be affected. From the shape of the PEC calculated for the Mn−H elongation it is clear that two different opposite channels are open from the ^{3}LLCT state: (i) an ultrafast direct dissociation (in less than 100 fs) with 100% of the system dissociating toward the diradicals and (ii) a nonradiative transition to the vibrationally excited levels of the ^{3}MLCT states at the avoided crossing points followed by emission. The study of the role of the singlet excited states in the mechanism of photodissociation as well as a detailed analysis of the photodissociation dynamics in the ideal gas phase conditions is in progress.

Acknowledgment. The authors are grateful to Prof. D. J. Stufkens and to Dr. B. Rossenaar for helpful discussions and for providing preliminary results prior to publication. K. F. acknowledges the Fond der Chemischen Industrie. This work was supported by the Euronetwork "Quantum Chemistry on Transition Metal Complexes" N° ERBCHRXCT 930156. The calculations were carried out on the C98 computer of the IDRIS (Orsay, France) through a grant of computer time for the Conseil Scientifique de l'Institut du Développement et des Ressources en Informatique Scientifique.

JA9518033

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