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A Mechanistic Study of the Photochemistry of Fe(CO)$_3$(R-DAB) (R-DAB = 1,4-Diaza-1,3-butadiene), a Unique Group of Complexes with Two Close-Lying Reactive Excited States

Hans K. van Dijk, Derk J. Stufkens,* and Ad Oskam

*Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam,
J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam,
The Netherlands.* *Received January 15, 1988*

Abstract: The results are reported of a mechanistic study of the photosubstitution and low-temperature photolysis reactions of four complexes of the type Fe(CO)$_3$(R-DAB) (Ia–d: R = cHex (a), R = pTol (b), R = iPr$_2$Ph (c), R = tBu (d)). Although analogous photoproducts are obtained for these complexes at room temperature, flash photolysis shows that these reactions can proceed via one of two mechanisms. For complexes Ia–c loss of CO is the primary photoprocess, and complex Id reacts via breaking of a metal–nitrogen bond. For several phosphine ligands an intermediate in the reaction with Id could be stabilized and identified in low-temperature solution. For a photosubstitution reaction of the representative complex Ia the quantum yield was found to increase from 0.05 to 0.20 mol/einstein with the energy of irradation. Furthermore, an activation energy ΔE_a of 525 cm^{-1} was established for this reaction from the temperature dependence of ϕ upon low-energy excitation. Photolysis of Ia or Ib in *n*-pentane at 150 K in the absence of a substituting ligand affords two photoproducts, a binuclear CO-bridged complex IV and an isomeric form V of complex I in which the R-DAB ligand is η^4-CN,C′N′ coordinated to the metal. In agreement with the wavelength dependence of the photosubstitution quantum yield, the concentration of IVa increases at the expense of Va upon going to higher energy excitation. These results are rationalized in terms of an energy diagram with close-lying metal–ligand (ML) and ligand-field (LF) excited states. According to this model, the photosubstitution products as well as complexes IV are formed by reaction from the lowest ^{3}LF state, while complexes V are formed by reaction from the lowest ^{3}ML state.

From the group of α-diimines 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), pyridine-2-carbaldehyde imine ($C_5H_4NCH{=}NR$; R-PyCa), and 1,4-diaza-1,3-butadiene (RN=CH—CH=NR; R-DAB), the former two differ in their coordinating behavior from the R-PyCa and R-DAB ligands.[1] Bpy and phen only coordinate via their nitrogen lone pairs, either as a monodentate ligand (σ-N(2e), only for bpy[2]) or as a chelate (σ,σ-N,N′(4e)). R-PyCa and R-DAB can also coordinate η^2 via their CN bonds affording complexes in which they are σ-N(2e);[2b,3] σ,σ-N,N′(4e);[1] and σ-N, μ^2-N′, η^2-CN(6e),[4] or σ,σ-N,N′-η^4-CN,C′N′ (8e, only for R-DAB)[5] bonded. Only in one case[6] has a η^4-CN,C′N′(4e) coordinated R-DAB ligand been observed in inert gas matrices at 10 K. Not only are these ligands more versatile in their coordinating behavior than bpy and phen, also their σ,σ-N,N′(4e) bonded complexes differ already in their ground- and excited-state properties. This is due to the fact that the lowest π^* orbital has a lower energy for R-DAB (and to some extent also for R-PyCa) than for bpy and phen and has a much larger atomic contribution from the coordinating nitrogen atoms. As a result low-valence transition-metal complexes of R-DAB, e.g., W(CO)$_4$(R-DAB), show a much stronger mixing between this π^* orbital and one of the metal-d orbitals (π-back-bonding) than the corresponding bpy and phen complexes.[7] This change of π-back-bonding also has a large influence on the CT character of the strongly allowed electronic transition between these metal-d and ligand π^* orbitals. In W(CO)$_4$(bpy) and W(CO)$_4$(phen) these orbitals are hardly mixed and the transition between them in the visible region has a strong MLCT character and solvatochromic behavior. In the W(CO)$_4$(R-DAB) complexes on the other hand, this transition has no MLCT character since it takes place between strongly mixed orbitals.

This change of character of the electronic transitions can nicely be demonstrated with resonance Raman (RR) spectroscopy, which is a valuable tool for characterizing electronic transitions.[8] The RR spectra of W(CO)$_4$(bpy) and W(CO)$_4$(phen), excited into this electronic transition, show strong resonance enhancement of intensity for symmetrical ligand stretching modes confirming the MLCT character of these transitions.[7] The corresponding spectra of the W(CO)$_4$(R-DAB) complexes only showed RR effects for the symmetrical metal–nitrogen stretching and ligand deformation modes. Apparently, the transition has lost its MLCT character here and has become metal–ligand bonding to antibonding.

An even stronger interaction between metal and ligand orbitals occurs for the complexes Fe(CO)$_3$(R-DAB) (I) that have the structure shown in Figure 1. A MO calculation of Fe(CO)$_3$(H-DAB) showed that both the HOMO and LUMO have strongly mixed metal-d, ligand-π^* character and that the transition between these orbitals at about 500 nm (see Figure 2) hardly changes the electron distribution and bond characters of the complex.[9] This conclusion was confirmed by the results from the RR spectra.[9] These spectra were very weak, and they could only be measured for solutions with an optical density at 500 nm of about 15. This means that the bond characters indeed hardly change during this electronic transition. The lowest excited state will therefore not

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* Author to whom correspondence should be addressed.

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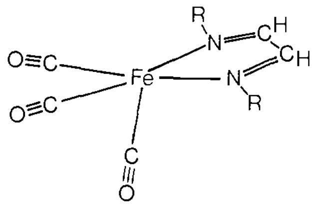

Figure 1. Molecular structure of $Fe(CO)_3$(R-DAB) (Ia–d): R = cHex (a), pTol (b), iPr_2Ph (c), tBu (d).

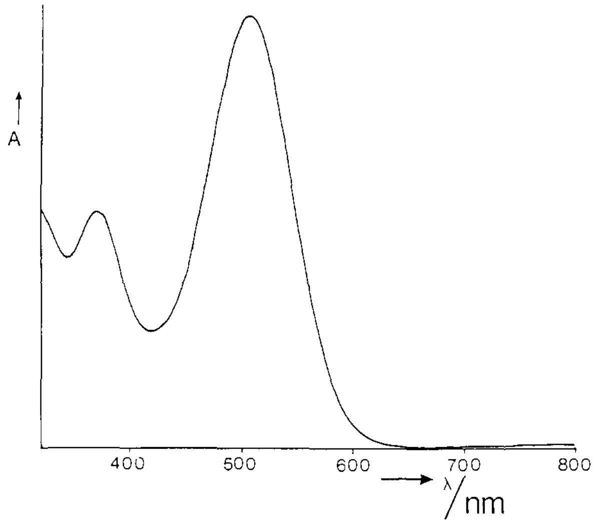

Figure 2. Electronic absorption spectrum of Ia at room temperature in toluene.

be reactive and irradiation of these complexes into the low-energy band is not expected to start a photochemical reaction. Contrary to these expectations, however, these complexes show efficient photosubstitution of CO ($\phi < 0.3$) by nucleophiles at room temperatures.[6b] The occurrence of these reactions from a nonreactive excited state has tentatively been explained with a strong vibronic coupling model, in analogy with the interpretation given by Trogler and co-workers for the corresponding tetraazadiene complex $Fe(CO)_3(MeN{=}NN{=}NMe)$.[10] In this model the energy of the lowest excited state is converted into vibrational motions within the molecule, giving rise to the breaking of a metal–ligand bond. Such a model can, however, not explain the occurrence of a completely different photochemical reaction of these complexes in inert gas matrices.[6] The R-DAB ligands of I then change their coordination to η^4-CN,C'N'(4e) giving rise to the formation of complex V (see Figure 9). This observation is more in line with a reaction scheme in which the above reactions take place from different, close-lying excited states. In order to establish the correctness of this assumption we studied in detail the temperature- and wavelength-dependent photochemistry of these complexes.

A second aspect of this work concerns the existing controversy about the primary photoprocess of the photosubstitution reaction. Cleavage of either a metal–CO or metal–nitrogen bond may lead to the formation of a photosubstitution product. In this article the results of a flash photolysis study are used to discriminate between these two mechanisms.

The complexes under study (Ia–d) have R-DAB ligands with the following substituents R at the coordinating nitrogen atoms: cyclohexyl (cHex) (Ia), *p*-tolyl (pTol) (Ib), 2,6-diisopropylphenyl (iPr_2Ph) (Ic), and *tert*-butyl (tBu) (Id).

Experimental Section

Materials. The R-DAB ligands and the complexes Ia–d were synthesized according to published methods.[11-13] All phosphines and solvents used were purified by distillation or sublimation and stored under nitrogen. Oxygen was carefully excluded from the reaction mixtures during the photochemistry experiments.

Equipment. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer and IR spectra on a Nicolet 7199 B FT-IR spectrophotometer with a liquid nitrogen cooled HgCdTe-detector (32 scans, resolution 0.5 cm^{-1}).

The home-made cryostat and setup for the liquid Xenon experiments has been described elsewhere.[14] Complex Ia was dissolved in this solvent at 230 K, and the solution was then cooled to 173 K and kept at a pressure of 150 psi.

Photochemical Procedures. For the photochemical reactions use was made of the following light sources: a CR 8 Argon-ion laser, a CR 490 tunable dye laser with Rhodamine 6G as a dye, pumped by a SP 171 Argon-ion laser and a CR 590 tunable dye laser with Rhodamine 6G as a dye, pumped by a SP 2020 Argon-ion laser.

The experimental setup for the flash photolysis experiments consisted of a Lambda Physik EMG-101 excimer laser as excitation source, filled with XeCl, thus providing 308-nm pulses of 10-ns duration. The output of the laser was typically 20 mJ/pulse. As monitoring beam a Xenon-flashlamp (EG&G, FX-42-C-3) was used (pulse duration 20 μs). The laser was fired when the Xe-lamp output had reached its maximum. For detection a crossed beam setup was applied and a Zeiss single quartz prism monochromator M4QIII with a RCA C-31025 C GaAs photomultiplier. The photomultiplier signal was fed to a Biomation Transient Digitizer 6500, with a 6 bits A/D converter coupled via a homemade interface to a TRS-80 microcomputer. The systems time resolution was 10 ns.

Quantum yields of product formation were derived from the electronic absorption spectral changes of a 2.5-mL stirred toluene solution (concentrations ca. 10^{-4} mol/dm^3) in a quartz cell with a 2–4 mW laser beam as irradiation source. The photon flux was calculated from the laser power, which was measured by a Coherent Model 212 power meter. Corrections were applied for reflections of the light within the cell and for transmission of the laser beam. The quantum yields, measured in duplicate, were accurate within 10%.

Results

Electronic Absorption Spectra. All complexes show a band at about 500 nm in toluene (room temperature) (Figure 2, Table I), which has been assigned to several electronic transitions within the metallacycle rather than to CT transitions from the metal to the R-DAB ligand.[9] As mentioned before, this assignment was based on the results from MO calculations and resonance Raman spectra. These transitions will be indicated as ML transitions.

Apart from this band a second one is observed at about 375 nm. Since no absorption spectra of analogous $Fe(CO)_3$(N—N) (N—N=N-donor chelate) or $Fe(CO)_3(N)_2$ complexes are known that could be of help for the assignment of this band, results from flash photolysis measurements have been used instead.

Flash photolysis of Id in CH_3CN causes within 10 ns of the flash the formation of $Fe(CO)_3$(σ-N-tBu-DAB)(CH_3CN) (IIId(CH_3CN)) (vide infra), which complex has the tBu-DAB ligand monodentately bonded to the metal. The reaction is accompanied by the disappearance of the 375- and 500-nm bands and by the growing in of a single band at 420 nm. This new band cannot be due to MLCT transitions since no such transitions occur for complexes with a monodentately bonded R-DAB ligand. For example, the transient absorption spectra of $Cr(CO)_5$(σ-N-tBu-DAB) and $Cr(CO)_5$(σ-N-en) (en = ethylenediamine) show the same LF band at 410 nm.[15] The 420-nm band of the above flash photolysis product is therefore assigned to a LF transition. Going to the starting complex Id this transition will shift to higher energy just as in the case of $W(CO)_4$(tmen) (tmen = tetramethylethylenediamine) and $W(CO)_4$(iPr-DAB) (iPr = isopropyl). For these latter two complexes the LF band shifts from 402 to 373 nm. The 375-nm band of Id and of all other complexes I under study is therefore assigned to a LF transition. The above electronic transitions of the complexes I, giving rise to the absorption bands

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Table I. CO Stretching Frequencies and UV/vis Data of All Complexes Studied

complex	notation	CO stretching freq (cm^{-1})	electronic absorption spectra (λ_{max}, nm)
$Fe(CO)_3$(cHex-DAB)	Ia	2024, 1945[a]	370, 507[c]
$Fe(CO)_3$(pTol-DAB)	Ib	2038, 1976, 1965[a]	370 (sh), 510[c]
$Fe(CO)_3$(iPr_2Ph-DAB)	Ic	2041, 1972, 1967[a]	390, 501[c]
$Fe(CO)_3$(tBu-DAB)	Id	2016, 1937[a]	378, 544[c]
$Fe(CO)_2$(cHex-DAB)($P(nBu)_3$)	IIa($P(nBu)_3$)	1950, 1890[a]	
$Fe(CO)_2$(cHex-DAB)(toluene)	IIa(toluene)		410, 580[c]
$Fe(CO)_2$(pTol-DAB)(toluene)	IIb(toluene)		435, 600[c]
$Fe(CO)_2$(tBu-DAB)(PPh_3)	IId(PPh_3)	1945, 1883[b]	
$Fe(CO)_2$(tBu-DAB)($P(cHex)_3$)	IId($P(cHex)_3$)	1928, 1867[b]	
$Fe(CO)_2$(iPr_2Ph-DAB)(toluene)	IIc(toluene)		430, 610[c]
$Fe(CO)_3$(σ-N-tBu-DAB)(toluene)	IIId(toluene)		450[c]
$Fe(CO)_3$(σ-N-tBu-DAB)(CH_3CN)	IIId(CH_3CN)		420
$Fe(CO)_3$(σ-N-tBu-DAB)($P(cHex)_3$)	IIId($P(cHex)_3$)	1974, 1908, 1866[b]	427[b]
$Fe(CO)_3$(σ-N-tBu-DAB)(PPh_3)	IIId(PPh_3)	1986, 1923, 1873[b]	
$Fe_2(CO)_5$(cHex-DAB)$_2$	IVa	1970, 1955, 1905 1893, 1744[a]	565, 740[a]
$Fe_2(CO)_5$(pTol-DAB)$_2$	IVb	1979, 1965, 1925 1911, 1779[a]	
$Fe(CO)_3$(η^4-CN,C'N'-cHex-DAB)	Va	2066/2060, 1999/1993 1971/1976[a]	
$Fe(CO)_3$(η^4-CN,C'N'-pTol-DAB)	Vb	2070, 2030, 2000[a]	

[a] Spectra taken from 150 K *n*-pentane solutions. [b] Spectra taken from 200 K *n*-pentane solutions. [c] Spectra taken from room temperature toluene solutions.

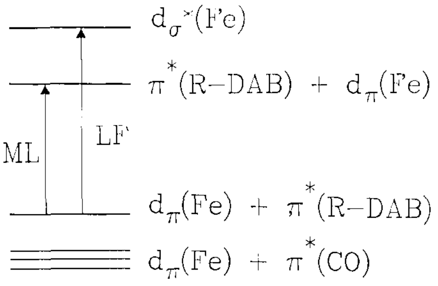
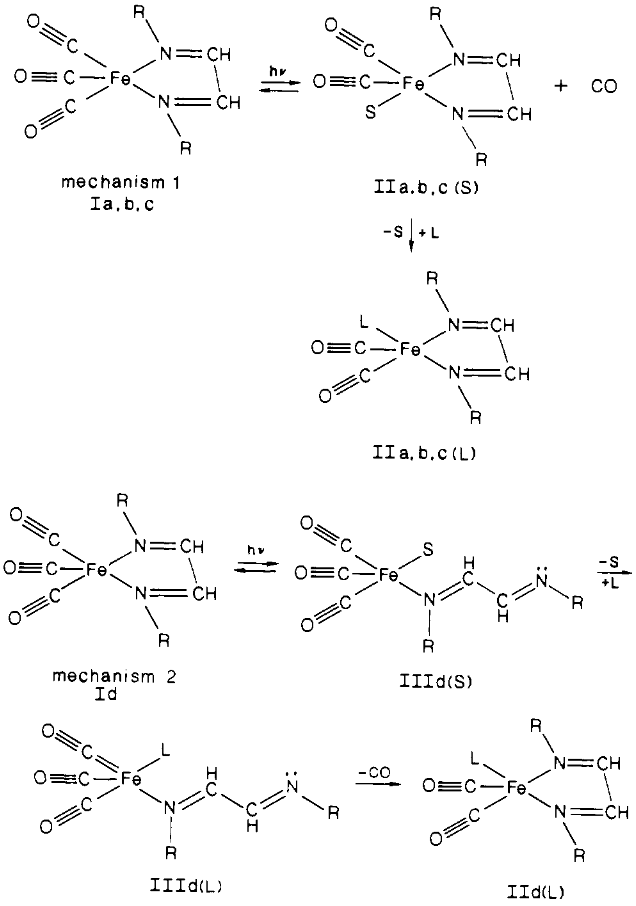


Figure 3. Qualitative MO diagram of Ia–d.

Scheme I. Two Possible Mechanisms for the Photosubstitution of CO by L in Ia–d



at 375 and 500 nm, have been indicated in the qualitative MO diagram of Figure 3.

Mechanism of the Photosubstitution Reaction. In a previous study on the photochemistry of these complexes,[6b] it has been shown that at least one CO group can readily be photosubstituted by nucleophiles at room temperature. Only in the case of small ligands with good π-accepting properties, such as $P(OMe)_3$, were two carbonyl groups substituted. All complexes appeared to be photostable when they were irradiated in the absence of a substituting ligand. This means that the primary photoproduct reacts back rapidly to the starting complex. Two mechanisms have been proposed for this reaction and they are presented in Scheme I. In the first mechanism, proposed by Trogler and co-workers,[16] the primary photoprocess is loss of CO. A solvent molecule (S) occupies the open site and is then replaced by a nucleophile L. The photostability of the complexes in the absence of L is due to the fast backreaction of CO with the primary photoproduct.

In the second mechanism, proposed by us,[6b] the primary photoprocess is breaking of a metal–nitrogen bond, followed by occupation of the open site by S, replacement of S by L, and rechelation of the R-DAB ligand with loss of CO. Flash photolysis can discriminate between these two mechanisms since the absorption spectral changes will be quite different in both cases. The primary photoproduct of mechanism 1 (II(S)) will show a low-energy absorption band since it still contains a metallacycle. In the spectrum of the corresponding primary photoproduct of mechanism 2 (III(S)) this band will have disappeared.

Solutions of the four complexes in toluene having an optical density of about 2 at the wavelength of irradiation were excited with the 308-nm line of an excimer laser, and the absorption spectra of the transients were measured by a pulsed Xe-monitoring beam with a pulse duration of 20 μs. The absorption maxima, measured 10 ns after the laser pulse, are collected in Table I. The transients formed out of the three complexes Ia–c exhibited two new bands at lower energy indicative of substitution of CO by a solvent molecule S (mechanism 1). Only in the case of complex Id, the transient absorption spectrum merely showed a single LF band, which means that in this case the reaction proceeds according to mechanism 2 with formation of the primary photoproduct IIId(S). The LF band shifts to higher energy when the reaction is performed in CH_3CN instead of toluene due to the stronger electron-donating properties of these solvent molecules.

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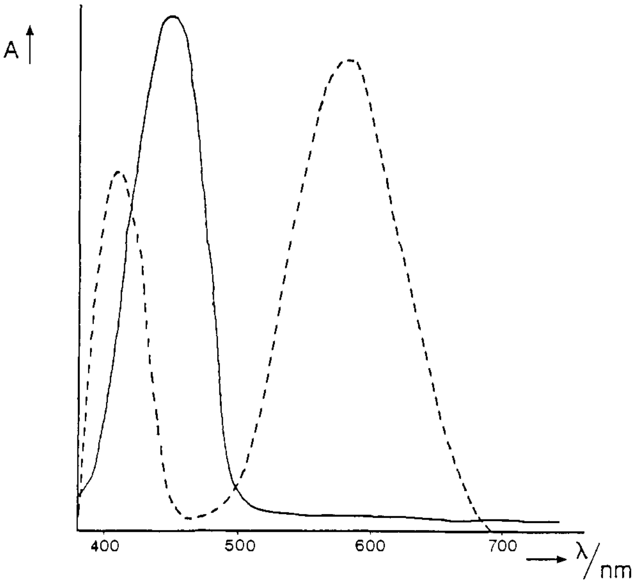

Figure 4. Transient absorption spectra of IIa(S) (---) and IIId(S) (—) at room temperature in toluene.

The above results are illustrated for two of these complexes in Figure 4. The lifetimes of the transients IIId(S) were longer than 20 μs (the pulseduration of the monitoring beam) and this observation prompted us to accomplish the stabilization of the corresponding IIId(L) intermediate at lower temperatures. For this purpose complex Id was irradiated into the 500-nm band in *n*-pentane at 200 K in the presence of $P(cHex)_3$. No free CO was then observed and the CO vibrations of Id shifted to lower frequencies (Figure 5a). At the same time the low-energy absorption band disappeared and a new LF band showed up at 427 nm. These spectroscopic data agree with the formation of IIId ($P(cHex)_3$) in which complex the tBu-DAB ligand is monodentately coordinated to the metal. The shift of the CO stretching modes to lower frequencies is accompanied by a frequency increase for $\nu_s(CN)$ of the tBu-DAB ligand from 1494 to 1613 cm^{-1} due to its change of coordination. Warming up the solution to room temperature resulted for 90% in a backreaction to the starting complex and for 10% in the formation of IId ($P(cHex)_3$). When this reaction at 200 K was performed in the presence of PPh_3 instead of $P(cHex)_3$, both IId(PPh_3) and IIId(PPh_3) were formed (Figure 5b). Note the frequency decrease of the CO stretching modes upon going from IIId(PPh_3) to IIId($P(cHex)_3$) due to the higher basicity of $P(cHex)_3$. Finally, performing the reaction in the presence of $P(nBu)_3$ did not result in the formation of an intermediate but instead in the instantaneous formation of the stable photoproduct IId($P(nBu)_3$).

This different behavior of the three phosphines can be explained as follows. Irradiation of Id leads to the formation of the intermediate IIId(L), which is apparently the final product in the case of $P(cHex)_3$ because of its large cone angle θ (170°). The bulkiness of this ligand prevents the formation of IId($P(cHex)_3$) and even at room temperature only a small amount of this complex is formed. For PPh_3 (θ = 147°) IIId(PPh_3) can still be observed at 200 K but IId(PPh_3) is also present here. Finally, $P(nBu)_3$ (θ = 132°) is too small to inhibit rechelation of the tBu-DAB ligand at 200 K and only IId($P(nBu)_3$) is observed. Under similar conditions, the other three complexes Ia–c only yielded the photoproducts IIa–c.

Thus, only complex Id reacts photochemically according to mechanism 2. This deviating behavior of the tBu-DAB complex is caused by the bulkiness of the tBu groups which have a weakening effect on the metal–nitrogen bonds. The weakness of these bonds is also reflected in the thermal substitution reactions of this complex at higher temperatures ($T > 50$ °C).[16] Trogler and co-workers observed the thermal replacement of the t-Bu-DAB ligand upon reaction of Id with PMe_3 affording $Fe(CO)_3(PMe_3)_2$. All other complexes, e.g. Ia, reacted differently and showed thermal substitution of CO yielding $Fe(CO)_2(R\text{-}DAB)(PMe_3)$ (II(PMe_3)). Complex IIId(L) (Scheme I) is then a common intermediate in the thermal and photochemical substitution reactions of Id. In the photochemical reactions, which were performed at $T < 20$ °C, this intermediate reacts further to give IId(L). In the thermal reactions at $T > 50$ °C the monodentately bonded tBu-DAB ligand is released instead and $Fe(CO)_3L_2$ is formed.[16] Thus, there is no inconsistency between mechanism 2 proposed for the photochemical reactions of Id and the results of its thermal reactions, as has been suggested by Trogler.[10b]

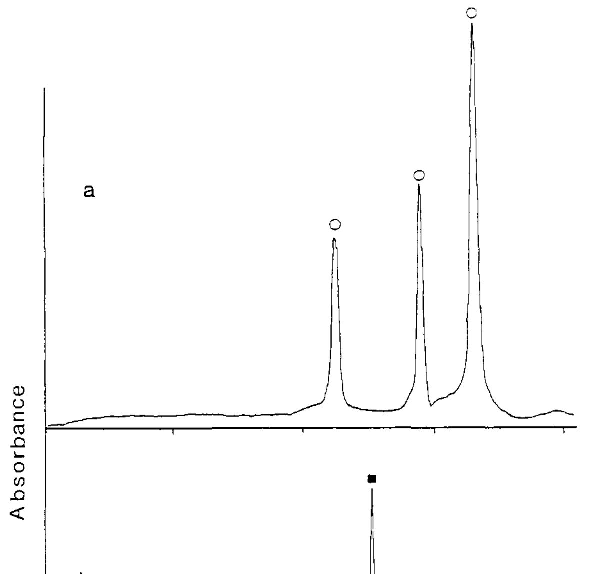

Figure 5. IR spectra in the CO-stretching region of the photoproducts obtained by irradiation of Id at 200 K in *n*-pentane in the presence of $P(cHex)_3$ (a) or PPh_3(b): (○) IIId($P(cHex)_3$), (●) IIId(PPh_3), (■) IId(PPh_3), (▲) Id.

Table II. Temperature and Irradiation Wavelength Dependence of the Quantum Yield of Product Formation ϕ for the Photosubstitution of CO by $P(nBu)_3$ (200-fold Excess) in Ia

	quantum yield ϕ (mol/einstein) × 10^2 at λ_{irr}(nm)[a]				
temp (K)	351/363[b]	458	488	514	565
293	20	15	7.1	6.0	5.0
283	20		6.5		
273	20		5.8		4.0
263	20		5.2		
253					3.2
233					2.6

[a] Estimated error: 10%. [b] Unresolved UV lines of argon-ion laser.

Photosubstitution Quantum Yields. Quantum yields for the photochemical reaction of complex Ia with $P(nBu)_3$ (200-fold excess) were measured in toluene at different wavelengths of irradiation and at several temperatures. These data are collected in Table II. The quantum yields show a regular increase throughout the low-energy band, from 0.05 mol/einstein at 560 nm to 0.07 mol/einstein at 488 nm. At 458 nm, however, ϕ suddenly obtains a much higher value of 0.15 mol/einsteins, close

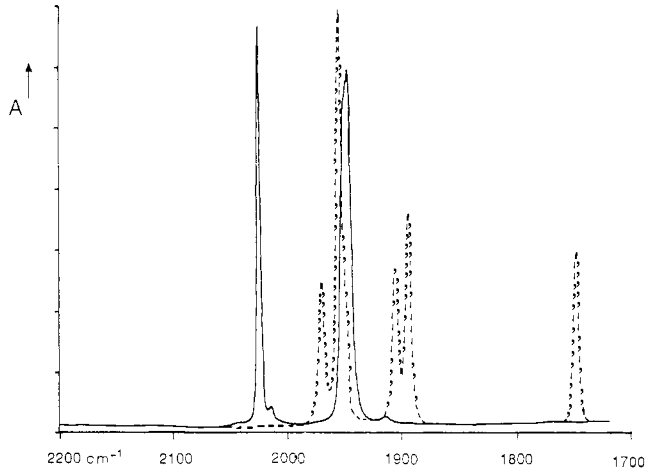

Figure 6. IR spectra in the CO-stretching region of Ia(—) and IVa(---) in *n*-pentane at 150 K.

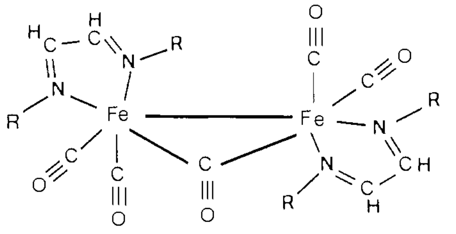

Figure 7. Proposed structure of IVa,b.

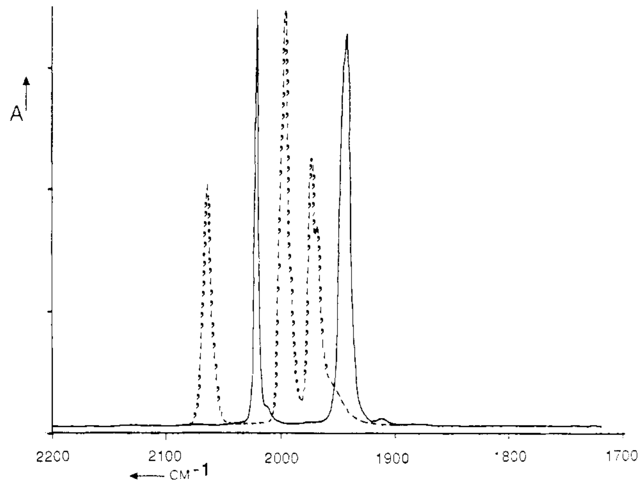

Figure 8. IR spectra in the CO-stretching region of Ia(—) and Va(---) in *n*-pentane at 150 K.

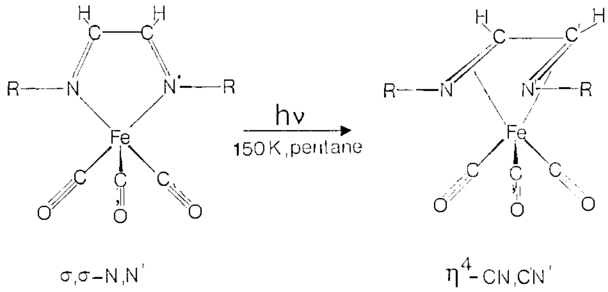

Figure 9. Photochemical conversion of Ia,b into Va,b.

to the limiting quantum yield of 0.20 mol/einstein measured at 351/363 nm. A similar wavelength dependence of ϕ has been observed before for several series of substituted pyridine (py-X) complexes,[17-20] which all possess close-lying MLCT and LF states. In the case of the complex ion Ru(bpy)$_3$$^{2+}$ and its derivates evidence for such a two-level scheme was obtained from the temperature dependence of the photophysical and photochemical quantum yields.[21] Similar temperature-dependent measurements were therefore performed for the reaction of complex Ia with P(nBu)$_3$ at three wavelengths of irradiation (Table II). From these data an apparent activation energy (ΔE_a) of 525 cm^{-1} was calculated for this reaction upon irradiation into the 500-nm band. In contrast with this, no activation energy was established for this reaction upon irradiation with the 351/363 nm laser lines into the LF band.

Low-Temperature Photolysis. Solutions of the complexes in *n*-pentane at 150 K were irradiated with different wavelengths in the absence of a substituting ligand. Contrary to the above photochemical reactions with nucleophiles two different photoproducts were obtained during these photolysis reactions, depending on the wavelength of irradiation. Excitation of complex Ia with 351/363 or 458 nm yielded a complex with a bridging CO ligand (ν = 1745 cm^{-1}, see Figure 6) and with an intense absorption band at 740 nm. These results point to the formation of a bridged dinuclear complex Fe$_2$(CO)$_5$(cHex-DAB)$_2$ (IVa) with a σ,σ-N,N'(4e) coordinated R-DAB ligand at each metal center. The formation of such a dinuclear complex, for which the structure of Figure 7 is proposed, is also evident from the observation that it is only formed at rather high concentrations of Ia. Otherwise decomposition occurs upon irradiation. This complex will be formed by reaction of the primary photoproduct IIa(S) with the parent compound Ia. A completely analogous complex Ru$_2$(CO)$_5$(iPr$_2$-CH-DAB)$_2$ (iPr$_2$-CH = diisopropylmethyl) has recently been obtained by irradiation of Ru(CO)$_3$(iPr$_2$-CH-DAB) under similar conditions.[22] Complex IVa could not be isolated or further characterized since it reacted back with CO from the solution to the parent compound upon raising the temperature. A similar photoproduct was obtained for Ib but not for Ic and Id. Complex Id did not show any reaction at all presumably due to a fast backreaction of intermediate IIId(S) to yield the starting complex Id. Complex Ic did not afford a binuclear complex IVc. Apparently, formation of IVc is inhibited by the bulky 2,6-diisopropylphenyl substituents at the coordinating nitrogen atoms of the R-DAB ligand.

A completely different reaction was observed when Ia was irradiated at longer wavelengths ($\lambda \geq 500$ nm). The IR spectrum obtained after 30 s of irradiation of Ia with the 565 nm laser line (20 mW) is shown in Figure 8. There is no correspondence between these CO vibrations and those of the binuclear complex IVa formed by irradiation of Ia with higher energy laser lines (351/363 or 458 nm, see Figure 6). Apparently, a completely different photoproduct is formed upon low-energy irradiation. This new complex (Va) consists of two isomers with CO stretching modes at 2066 (2060), 1999 (1993), and 1971 (1976) cm^{-1}. Raising the temperature to 180 K causes the disappearance of the second isomer. Complex Va is a monomeric species, since its formation does not depend on the concentration of the parent compound contrary to complex IVa (vide supra). The presence of three CO stretching modes and the absence of a band belonging to free CO point to the retention of the Fe(CO)$_3$ moiety. The CO vibrations are shifted to higher frequencies with respect to the parent compound which means that the metal to CO π-back-bonding has decreased and the metal to cHex-DAB π-back-bonding has increased. Such an increase of π-back-bonding will occur when the ligand changes its coordination from σ,σ-N,N' into η^4-CN,C'N' according to the reaction shown in Figure 9. The

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same photoproduct has been observed before by us upon low-energy excitation of several $Fe(CO)_3$(R-DAB) complexes in inert gas matrices at 10 K.[6b] This latter observation makes the alternative structure in which the R-DAB ligand is η^4-coordinated to the metal in its trans conformation highly improbable. The change of coordination of the cHex-DAB ligand is also evident from the disappearance of the 500-nm band and from the shift to lower frequency of ν_s(CN) of this ligand. In the parent compound Ia this vibration has a frequency of 1482 cm^{-1}, in a frequency region where *n*-pentane and most other solvents strongly absorb in the IR. An excellent alternative solvent is liquid xenon (LXe), which can be used over a temperature range 170–240 K when kept at a pressure of 150 psi.[23] Although most organometallic complexes do not dissolve well in LXe, sample cells with optical pathways as long as 5 cm can be used because of the complete transparency of this solvent in the IR. Reactions can therefore be studied at very low concentrations. A special high-pressure cryostat has been constructed in our laboratory to study photochemical reactions in LXe with IR and UV/vis spectroscopy.[14] The above photochemical reaction of complex Ia was also performed in LXe and followed in the 1300–2200 cm^{-1} region of the IR spectrum. During the reaction the temperature of the solution was kept at 173 K. Just as for the *n*-pentane solution irradiation with the 565 nm laser line led to the formation of complex Va with CO-stretching modes at 2066, 1999, and 1971 cm^{-1}. The formation of only one isomer here is understandable in view of the somewhat higher temperature of the solution compared with the *n*-pentane experiment. A small amount of the binuclear complex IVa is still formed under these conditions as evidenced by a shoulder at 1957 cm^{-1}. The parent compound shows a strong band at 1482 cm^{-1} belonging to ν_s(CN) which disappears upon irradiation. At the same time a new band shows up at 1364 cm^{-1}, which is assigned to ν_s(CN) of complex Va. A similar result had been obtained by us upon irradiation of this complex in a CO matrix.[6b] The formation of a small amount of complex IVa is evident from a new band at 1458 cm^{-1} (ν_s(CN)) which was not observed in the matrix. An analogous complex Vb was obtained by irradiation of Ib. Complexes Ic and Id, however, did not show this reaction probably due to the bulkiness of their N-substituents.

This is the first time that such η^4-coordinated R-DAB complexes have been obtained and characterized in solution. They are structurally related to the stable complexes $Fe(CO)_3(\eta^4$-2,3-Me_2-butadiene) and $Fe(CO)_3(\eta^4$-butadiene),[24] $Fe(CO)_3(\eta^4$-cyclobutadiene),[25] $Fe(CO)_3(\eta^4$-cyclooctatetraene),[26] and $Fe(CO)_3(\eta^4$-C_6H_4X CH=CHCHO),[27] and their CO-stretching frequencies closely agree. Contrary to these η^4-CC,CC coordinated complexes, the η^4-CN,C′N′ bonded complexes V are, however, very unstable since they already react back to the parent compound at 180 K. A similar backreaction is observed when these complexes are irradiated by the 313-nm line of a Hg-lamp.

Irradiation of Ia in *n*-pentane at 150 K with λ565 nm in the presence of a 1000-fold excess of $P(nBu)_3$ afforded both Va and the photosubstitution product IIa($P(nBu)_3$). The latter complex was not formed out of IVa since no such thermal or photochemical reaction between IVa and $P(nBu)_3$ occurred in the temperature range 150–180 K. This again shows that photochemical loss of CO according to mechanism 1 (Scheme I) still occurs at low temperatures upon low-energy excitation.

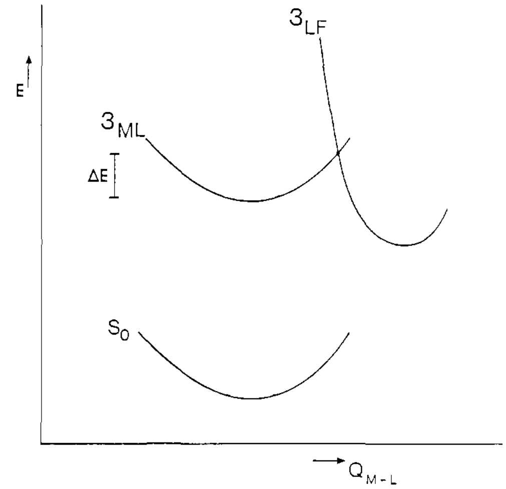

Figure 10. Potential energy diagram of I showing the lowest ^{3}ML and ^{3}LF states.

Discussion

All photochemical reactions reported in the preceding section have been performed by irradiating into the 500-nm band of these complexes. According to the MO calculations and resonance Raman spectra this band belongs to internal transitions (ML) of the Fe-(R-DAB) metallacycle, which hardly change the electron distribution and bond characters of the complex.[9] At about 375 nm a second band is observed which belongs to a LF transition (vide supra).

At first sight it seems contradictory that the photosubstitution quantum yields of these complexes are so high in view of the fact that irradiation into the 500-nm band will lead to population of a nonreactive excited state. A completely analogous behavior has, however, been observed for complexes having a lowest nonreactive MLCT state such as the substituted pyridine (py-X) complexes $Ru(NH_3)_5(py\text{-}X)^{2+}$,[17] $CpRe(CO)_2$(py-X),[18] $Fe(CN)_5(py\text{-}X)^{3-}$,[19] and $W(CO)_5$(py-X)[20] (see also Ford[28,29]). They all showed the presence of close-lying MLCT and LF states, and in the case that the MLCT states are lowest in energy still rather high photosubstitution quantum yields were obtained. These quantum yields increased upon going to higher energy irradiation, and the photochemical reactions were therefore proposed to occur from a reactive LF state at higher energy. The wavelength dependence of ϕ was explained with an energy-dependent competition between crossover into the manifold of LF states and internal conversion to the lowest MLCT state. No such wavelength dependence of ϕ was observed for py-X complexes having a lowest LF state.

For several of these py-X complexes with a lowest MLCT state an apparent activation energy has been estimated from the temperature dependence of the photosubstitution quantum yields. The activation energy was, at least in part, attributed to the energy difference ΔE between the MLCT and LF states. Van Houten and Watts[30] measured the temperature dependence of the photochemical quantum yield for the complex ion $Ru(bpy)_3^{2+}$, which also has a lowest MLCT state. They obtained values for both ΔE and the activation energy ΔE_a of the reaction from the LF levels. Meyer and co-workers[31] pointed out that this interpretation of ΔE in terms of an energy difference between the MLCT and LF states is only valid if there is a dynamic equilibrium between these states. In the case of an irreversible surface crossing between them, ΔE represents the energy of activation for this process. For all these py-X and bpy complexes activation energies were derived of several thousands of wavenumbers. A similar situation obtains for the complexes under study, the only difference being that they

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do not have low-energy MLCT transitions but instead internal transitions (ML) of the metallacycle. The photochemical reactions taking place for these complexes can then be explained with the qualitative energy vs Fe-L distortion diagram depicted in Figure 10. Irradiation into the 500-nm band causes population of a ^{1}ML state. Crossover to a LF state is not expected to occur directly from this state but rather from the corresponding ^{3}ML state after intersystem crossing as for the above-mentioned py-X and bpy complexes. The ^{3}LF state is reactive, showing loss of CO for complexes Ia–c (mechanism 1) or breaking of a metal–nitrogen bond for Id (mechanism 2). The energy barrier ΔE between the lowest ^{3}ML and ^{3}LF states is directly connected with the apparent activation energy ΔE_a for the photosubstitution reactions. For one of the reactions of complex Ia a value of only 525 cm^{-1} was obtained for ΔE_a, which is much smaller than the activation energies derived for the py-X and bpy complexes. Since no activation energy was found for the actual bond-breaking process from the ^{3}LF state (vide supra), ΔE_a mainly represents the energy barrier ΔE between ^{3}ML and ^{3}LF.

There is only a slight change of the photosubstitution quantum yield between 565 and 488 nm (0.05–0.07 mol/einstein) but a sudden increase (0.07–0.15 mol/einstein) upon going from 488- to 458-nm excitation. The latter effect may be due to excitation into a different electronic transition within the 500-nm band. Gaussian analysis of the absorption and magnetic circular dichroism spectra of Ic and resonance Raman excitation profiles of this complex indeed show the presence of three different electronic transitions within this band.[9] The observed wavelength dependence of ϕ is then due to differences in quantum yields for the internal conversion between the various ^{3}ML states and ^{3}LF.

In one respect the complexes under study differ from the py-X and bpy complexes which have completely nonreactive lowest MLCT states. In contrast with this, irradiation of complex Ia at 150 K causes the formation of two photoproducts IVa and Va. Complex IVa is formed out of Ia by a CO-loss reaction, which is also the primary photoprocess for the room temperature reactions of Ia at all wavelengths of irradiation. In both cases the reaction will occur from a ^{3}LF state. Complex Va is not a precursor of IVa since there is no thermal or photochemical interconversion between these photoproducts. Va will therefore be formed from a different excited state having either ^{3}ML or ^{3}LF character.

A reaction from a ^{3}LF state is, however, rather unlikely in view of the resonance Raman (RR) data.[9] These RR spectra, obtained by excitation into the ML band, do not show an antiresonance Raman effect. This means that there is no underlying LF transition and that the first LF transition occurs at about 370 nm. Just as for the corresponding py-X and bpy complexes,[17-20] which have their lowest-energy LF transitions at a similar position, the lowest ^{3}LF state of complex Ia will not easily be populated upon 565-nm irradiation, certainly not at such a low temperature. Besides, the RR spectra[9] are in favor of the ^{3}ML character of the excited state from which Va is formed. Resonance enhancements of Raman intensity are only observed for low-frequency vibrations and mainly for deformation modes of the $Fe(CO)_3$ moiety and the Fe-(R-DAB) metallacycle. The electronic transitions within the ML band are therefore accompanied by a change of bond angles rather than by a change of bond lengths. Such a distortion may then lead to the observed structural change upon going from Ia to Va.

The alternative explanation that IVa and Va are formed from the same lowest ^{3}LF state with different activation energies for the bond-breaking process is also improbable. Apart from the above arguments, this explanation is also unlikely in view of the fact that no such energy barrier was deduced from the temperature dependence of ϕ upon irradiation into the LF band.

A somewhat comparable change of structure as observed upon going from Ia to Va has been observed by Durante and Ford upon flash photolysis of the complex ions $Ru(NH_3)_5(py\text{-}X)^{2+}$.[32] The py-X ligands then changed their coordination from σ-N into η^2. However, in contrast to the formation of Va out of Ia, the $Ru(NH_3)_5(\eta^2\text{-pyridine})^{2+}$ photoproducts appeared to be transient intermediates of the photoaquation process taking place from the lowest ^{3}LF state.

There is a wavelength-dependent competition between the formation of complexes IVa and Va just as has been observed for the photosubstitution quantum yield at room temperature. Excitation at 565 nm causes a nearly complete conversion of Ia into Va while the yield of IVa increases with respect to that of Va upon going to higher energy irradiation. The nearly complete absence of complex IVa in the spectrum of the 565-nm excited solution is only partly due to the existing barrier between the lowest ML and LF states. One has also to take into account that the primary photoproduct IIa(S) partly reacts back with CO from the solution to give Ia instead of yielding complex IVa.

The influence of this backreaction becomes evident when Ia is irradiated with 565 nm at 150 K in the presence of a 1000-fold excess of $P(nBu)_3$. In that case still an appreciable amount of the substitution product IIa(P(nBu) is formed whereas IVa can hardly be observed in the 565 nm product spectrum when Ia is photolyzed in the absence of $P(nBu)_3$.

Conclusions

From the above results the following conclusions can be drawn.

1. The photosubstitution reactions of the complexes can proceed via one of two mechanisms, depending on the steric requirements of the R-DAB ligand. In the case that breaking of a metal–nitrogen bond is the primary photoprocess, one of the reaction intermediates is long-lived and can easily be detected in low-temperature solutions.
2. Photolysis at low temperature affords two different photoproducts. The main product upon high-energy ($\lambda < 500$ nm) excitation is a binuclear complex that is formed according to the same mechanism as the photosubstitution products. Upon irradiation with $\lambda > 500$ nm the main reaction is a change of coordination of the R-DAB ligand from σ,σ-N,N′ to η^4-CN,C′N′.
3. A model is proposed according to which the reactions take place from two different close-lying excited states. There is an energy-dependent crossover between these states as evidenced by a wavelength dependence of the photosubstitution quantum yields and of the product formation at low temperatures. This behavior is unique and has never been observed for any of the corresponding py-X and bpy complexes having close-lying MLCT and LF states.

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