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The influence of substitution of CO by PR_3 on the photochemistry of $Fe(CO)_3$(i-Pr_2Ph-DAB) and $Ru(CO)_3$(i-Pr_2CH-DAB) (DAB = 1,4-diaza-1,3-butadiene); a flash-photolysis and low-temperature study

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Abstract

The results are presented of a photochemical study of the complexes $Fe(CO)_3$(i-Pr_2Ph-DAB) and $Ru(CO)_3$(i-Pr_2CH-DAB) and of some of their PR_3-containing derivatives. The reactions were studied by flash-photolysis with 308 nm laser light and by irradiation at various temperatures and exciting wavelengths. Both tricarbonyls show release of CO from the ^{3}LF state but no reaction from the ^{3}ML state of the metal R-DAB metallacycle at lower energy. In contrast, $Fe(CO)_2$(i-Pr_2Ph-DAB)($P(OPh)_3$) undergoes breaking of a metal–nitrogen bond from the ^{3}LF state, but this reaction is followed by a fast back-reaction to regenerate the parent compound. As a result only a reaction from the ^{3}ML state is observed, in which the i-Pr_2Ph-DAB ligand changes its coordination from σ,σ-N,N′ into η^4-CN,C′N′. For the complexes $Ru(CO)_2$(i-Pr_2CH-DAB)(PR_3) breaking of the metal–nitrogen bond from the ^{3}LF state leads to release of the i-Pr_2CH-DAB ligand and formation of $Ru(CO)_2(PR_3)_3$ and $Ru(CO)_3(PR_3)_2$. Low-energy irradiation into the ML band gives rise to the formation of $Ru(CO)_2$(η^4-i-Pr_2CH-DAB)(PR_3) from the ^{3}ML state. These differences in photochemical behaviour between the tricarbonyl complexes and their PR_3-derivates are discussed in detail.

Introduction

In recent years we have studied in detail the spectroscopic and photochemical properties of a series of α-diimine (L) complexes of the type d^6-$M(CO)_4L$ (M = Cr,

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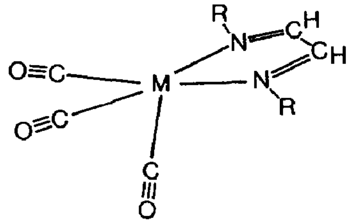


Fig. 1. Molecular structure of the complexes $M(CO)_3(R\text{-}DAB)$ (I: M = Fe, R = i-Pr_2Ph; III: M = Ru, R = i-Pr_2CH).

Mo, W) [1–5]; d^7-$(CO)_5MM'(CO)_3L$ (M, M' = Mn, Re) [6–10]; d^8-$M(CO)_3L$ (M = Fe, Ru) [11–13] and d^{10}-$Ni(CO)_2L$ [14]. The α-diimines not only included 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) but also two less well known representatives of this group, pyridine-2-carbaldehyde imine (R-PyCa; $C_5H_4NCH{=}NR$) and 1,4-diaza-1,3-butadiene (R-DAB; RN=CHCH=NR). The resonance Raman (rR) spectra showed, especially for the R-DAB complexes that the character of the main metal-to-α-diimine charge transfer (MLCT) transition can differ appreciably from one complex to another. This transition has a strong MLCT character in the case of e.g., $ClRe(CO)_3(R\text{-}DAB)$ [15], but it is metal–ligand bonding to antibonding in the case of the $W(CO)_4(R\text{-}DAB)$ [15] and some $Ni(CO)_2(R\text{-}DAB)$ [14] complexes. This change of character is mainly caused by the increase in mixing between one of the metal-*d* orbitals and the lowest π^* orbital of the R-DAB ligand upon going from Re^+ to W^0 to Ni^0.

An extreme situation was observed for the d^8-complexes $Fe(CO)_3(R\text{-}DAB)$ (Fig. 1), which gave only very weak rR spectra upon excitation into the lowest-energy absorption band ($\lambda_{max} \simeq 500$ nm) [11]. From this observation and from the MO calculations performed on these complexes, it was concluded that the central metal atom and the R-DAB ligand form a metallacycle in which the HOMO and LUMO have very similar electron density distributions. Irradiation into the low-energy metal-ligand (ML) transition between these orbitals was therefore not expected to cause an efficient photochemical reaction, but such a reaction (photosubstitution of CO) was observed, with quantum yields varying from 0.05 to 0.20 mole/einstein [12,13]. From the temperature and wavelength dependence of ϕ if appeared that the reaction occurred from a reactive ^{3}LF state after energy transfer from the lowest ^{3}ML state (Fig. 2) [13].

A remarkable, wavelength dependent, photochemistry was observed for some of these complexes upon irradiation in n-pentane at 150 K in the absence of a substituting ligand. Irradiation at the high-energy side of the ML band ($\lambda_{irr} < 500$ nm) under these conditions caused a slow photodecomposition at low concentrations and formation of a dimer $Fe_2(CO)_5(R\text{-}DAB)_2$ at high concentrations. Irradiation with $\lambda > 500$ nm, at the low-energy side of the ML band (n-pentane, 150 K), led to formation of a completely different photoproduct in which the R-DAB ligand had changed its coordination from σ,σ-N,N' to η^4-CN,C'N' (see Fig. 3).

These η^4-coordinated R-DAB complexes appeared to be much less thermally stable than the corresponding η^4-diene complexes [16–20], since they revert to the parent compound even at about 200 K. Furthermore, they could only be formed for the complexes of c-Hex-DAB and *p*-Tol-DAB, and not for those of the much bulkier ligands t-Bu-DAB and i-Pr_2Ph-DAB.

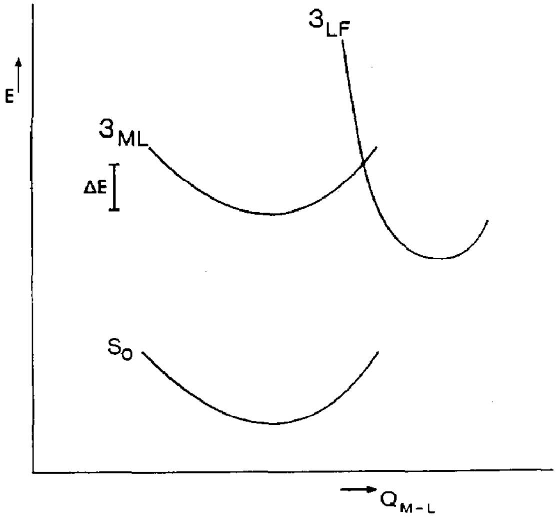


Fig. 2. Potential energy diagram for the complexes $M(CO)_3(R\text{-}DAB)$ (M = Fe, Ru) showing their lowest ^3ML and ^3LF states.

This wavelength dependent photochemistry can also best be explained in terms of the energy level diagram shown in Fig. 2, in which a surface crossing can take place between the lowest ^3ML and ^3LF states. According to the temperature dependent quantum yield data the barrier between these states is low (ca. 500 cm^{-1}), which implies that the reaction from the ^3LF state can take place readily at RT (room temperature). At low temperatures the reaction from the ^3LF state will only occur upon higher-energy excitation. Irradiation with $\lambda > 500$ nm leads to population of the ^3ML state and to the rather inefficient isomerization reaction (σ,σ-N,N′ → η^4-CN,C′N′) from this state.

As mentioned above a η^4-coordinated complex was formed only when the R-DAB ligand was not too bulky. We show below, however, that the PR_3-substitution products of such complexes in which the group R is bulky can readily be transformed photochemically into a η^4-coordinated product. This behaviour was observed for Fe- as well as Ru-$(CO)_3$(R-DAB) complexes. The complexes studied were $Fe(CO)_3(i\text{-}Pr_2Ph\text{-}DAB)$ ($i\text{-}Pr_2Ph$ = 2,6-diisopropylphenyl) (I) and $Ru(CO)_3$(i-

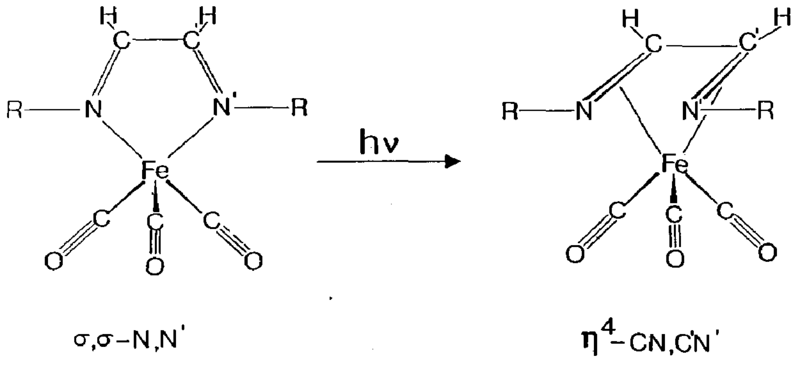


Fig. 3. Photochemical conversion of $Fe(CO)_3(\sigma,\sigma\text{-}R\text{-}DAB)$ into $Fe(CO)_3(\eta^4\text{-}R\text{-}DAB)$.

Pr_2CH-DAB) (i-Pr_2-CH=diisopropylmethyl) (III) and their PR_3-containing derivatives II and IV, respectively. The following PR_3 ligands were used: R = n-butyl (n-Bu); phenyl (Ph); cyclohexyl (c-Hex); methoxy (OMe); phenoxy (OPh).

Experimental

Materials and syntheses. All solvents and phosphines were carefully purified by distillation or sublimation, and stored under nitrogen. Oxygen was carefully excluded from the reaction mixtures during the photochemical experiments.

$Fe(CO)_3$(i-Pr_2Ph-DAB) (I) was synthesized by known procedures [21–23]. $Fe(CO)_2$(i-Pr_2Ph-DAB)($P(OPh)_3$) (IIb). A mixture of 4.5×10^{-5} mol of complex I and 4.5×10^{-5} mol. $P(OPh)_3$ in 100 ml n-pentane was irradiated for 3 h (λ_{irr} 488 nm, P 50 mW), after which 93% of the parent compound had been converted into the substitution product. The solvent was evaporated and the red solid residue stored at −20 °C in the dark.

$Ru(CO)_3$(i-Pr_2CH-DAB) (III). n-Heptane (30 ml) was added to a mixture of 377.7 mg (1.509 mmol) i-Pr_2CH-DAB (synthesized according to ref. 21–23) and 322.5 mg (0.505 mmol) $Ru_3(CO)_{12}$ in a Schlenk tube. The solution was refluxed for 3 h at 130 °C, during which it became dark red. The solution was cooled to room temperature and the n-heptane was evaporated off in vacuo. n-Pentane (5 ml) was added to the solid residue and the solution was kept for two days at −80 °C, during which crystals were formed. The exact yield could not be determined because the crystals were very air- and light-sensitive. They had to be stored at −20 °C in the dark.

Spectroscopic measurements. Electronic absorption spectra were recorded on a Perkin–Elmer Lambda 5 UV/Vis spectrophotometer, IR spectra on a Nicolet 7199 B FT-IR interferometer with a liquid nitrogen cooled HgCdTe-detector (32 scans, resolution 0.5 cm^{-1}). Resonance Raman spectra were recorded on a Jobin–Yvon HG 2S Ramanor using a SP model 171 argon ion laser as the excitation source. For wavelengths outside the argon ion laser region ($\lambda > 514.5$ nm) use was made of a CR 590 dye-laser with Coumarin 6 or Rhodamine 6G as dyes.

Photochemical procedures. A SP model 2020 argon ion laser was used as irradiation source for the photochemical reactions. For wavelengths above 514.5 nm the same apparatus used for the Raman measurements was employed.

The flash-photolysis apparatus, which has been described before [13], consisted of XeCl-filled Lambda Physik EMG-101 excimer laser as excitation source, providing 308 nm pulses of 10 ns duration. The output of the laser was 20 mJ/pulse and the time resolution was 10 ns.

Results and discussion

Before discussing the photochemistry of complexes II-IV, we first recall our earlier results for $Fe(CO)_3$(i-Pr_2Ph-DAB) (I) [13]. The absorption spectrum of this complex in n-pentane at RT shows a LF band at 393 nm and a ML band at 497 nm. Irradiation of a RT solution of I into either of these bands in the presence of a nucleophile L produced $Fe(CO)_2$(i-Pr_2Ph-DAB)(L) (II). By use of flash photolysis it was shown that release of CO is the primary photoprocess in this reaction. Upon irradiation of I in n-pentane at 150 K neither $Fe_2(CO)_5$(i-Pr_2Ph-DAB$)_2$ nor

$Fe(CO)_3(\eta^4$-i-Pr_2Ph-DAB) were formed, in keeping with the behaviour of the corresponding c-Hex-DAB and *p*-Tol-DAB complexes. This behaviour was attributed to the bulk of the i-Pr_2Ph group.

A different photochemistry was observed for the $P(OPh)_3$-substituted complex $Fe(CO)_2$(i-Pr_2Ph-DAB) ($P(OPh)_3$) (IIb), which has its LF and ML transitions at 396 and 497 nm, respectively. Irradiation of a RT solution of IIb in the absence or presence of a nucleophile gave no photoproduct. A flash photolysis study showed, however, that a photochemical reaction did in fact occur. For this purpose a RT toluene solution of IIb was irradiated with 10 ns pulses of an excimer laser (λ_{irr} 308 nm). The absorption spectrum recorded 200 ns after the laser pulse showed one band in the visible region at 420 nm. After 1500 ns the same spectrum was obtained. This result shows that the ML band had disappeared and that only a LF band had remained. This could in principle result from a change of coordination of the i-Pr_2Ph-DAB ligand from σ,σ-N,N′ (4e) to η^4-CN,C′N′ (4e) or to σ-N (2e). Formation of a η^4-coordination complex is, however, very unlikely, since such complexes start to absorb in the near UV (ca. 350 nm) (vide infra). It is much more likely that a metal–nitrogen bond is broken and a solvent coordinated complex $Fe(CO)_2(\sigma$-N-i-Pr_2Ph-DAB)($P(OPh)_3$)(S) is formed. This conclusion is supported by the close correspondence with the behaviour of the complexes $Fe(CO)_3(\sigma$-N-t-Bu-DAB) (L) (L = PR_3, CH_3CN), which also have their lowest-energy LF transition at about 420 nm [13]. This cleavage of the metal–nitrogen bond is also evident from the photochemical reaction of complex I with P(c-Hex)$_3$ in n-pentane at 200 K. Again the first photoproduct was $Fe(CO)_2$(i-Pr_2Ph-DAB) (P(c-Hex)$_3$) (IIc). Prolonged irradiation led to transformation of IIc into a complex with two low-frequency CO-vibrations (1955 and 1881 cm^{-1}). At the same time the ML band disappeared. These CO-stretching frequencies, which correspond closely to those of e.g. $Fe(CO)_2$(t-Bu-DAB) (PPh_3) (1945 and 1883 cm^{-1}), are assigned to the complex $Fe(CO)_2(\sigma$-N-i-Pr_2Ph-DAB) (P(c-Hex)$_3)_2$ formed from IIc by photochemical cleavage of a metal–nitrogen bond. Increase of the temperature to 240 K led to a complete reconversion of this photoproduct into I.

This breaking of metal–nitrogen bond in the case of complex IIb will be followed by a fast rechelation of the i-Pr_2Ph-DAB ligand, and this is responsible for the photostability of IIb under continuous irradiation. In respect of this reaction, the behaviour of IIb differs from that of I, which undergoes release of CO as the primary photoprocess. This effect, which has also been observed for the corresponding Ru complexes (vide infra), will be discussed later.

Complexes I and IIb also differred in their photochemical behaviour upon irradiation at 200 K in n-pentane. In the case of complex I no photoproduct was formed in the absence of a nucleophile, whereas complex IIb was transformed into a photoproduct with CO-stretching vibrations at 2080, 2029 and 2009 cm^{-1} (see Fig. 4). These frequencies are very close to those of $Fe(CO)_3(\eta^4$-*p*-Tol-DAB) in the same medium (2070, 2030 and 2000 cm^{-1}) [13], and they are therefore assigned to $Fe(CO)_3(\eta^4$-i-Pr_2Ph-DAB). The reaction was accompanied by the complete disappearance of absorption bands above 350 nm. Raising the temperature of the solution to 260 K caused a complete conversion of this photoproduct into I. It is very remarkable that $Fe(CO)_3(\eta^4$-i-Pr_2Ph-DAB) is formed in this way, whereas irradiation of I into its ML band does not give such a product under similar conditions. A second important aspect of this reaction is that $Fe(CO)_3(\eta^4$-i-Pr_2Ph-

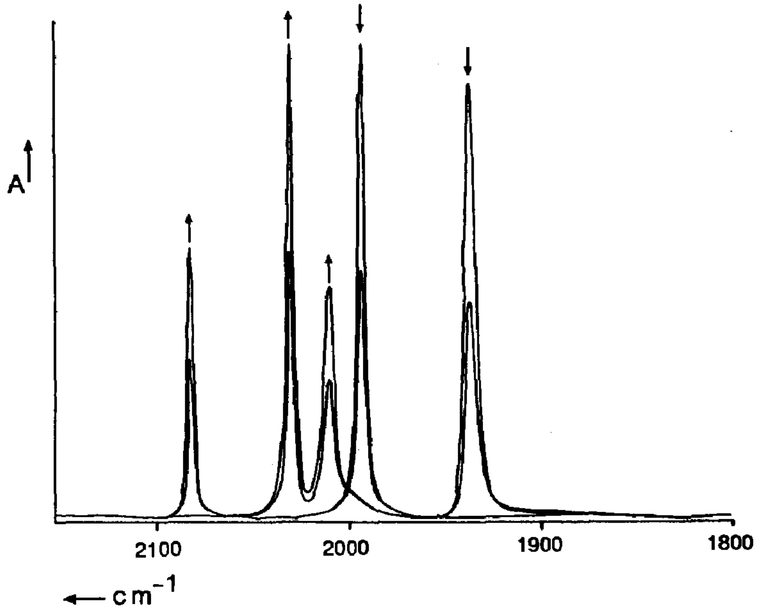


Fig. 4. IR spectral changes (CO-stretching region) accompanying the photochemical conversion of complex IIb into Fe(CO)$_3$ (η^4-i-Pr$_2$Ph-DAB) (n-pentane, 200 K).

DAB) was formed at all irradiation wavelengths (351–560 nm) and that no Fe(CO)$_2$(η^4-i-Pr$_2$Ph-DAB)(P(OPh)$_3$) was produced.

A somewhat different photochemistry was observed for Ru(CO)$_3$(i-Pr$_2$CH-DAB) (III) and its PR$_3$-containing derivatives Ru(CO)$_2$(i-Pr$_2$CH-DAB)(PR$_3$) (IV). The absorption spectrum of complex III in n-pentane, shown in Fig. 5, contains a ML band at 479 nm. Resonance Raman spectra, obtained by excitation of a solution of III in benzene with λ 458 and 575nm, respectively, are presented in Fig. 6.

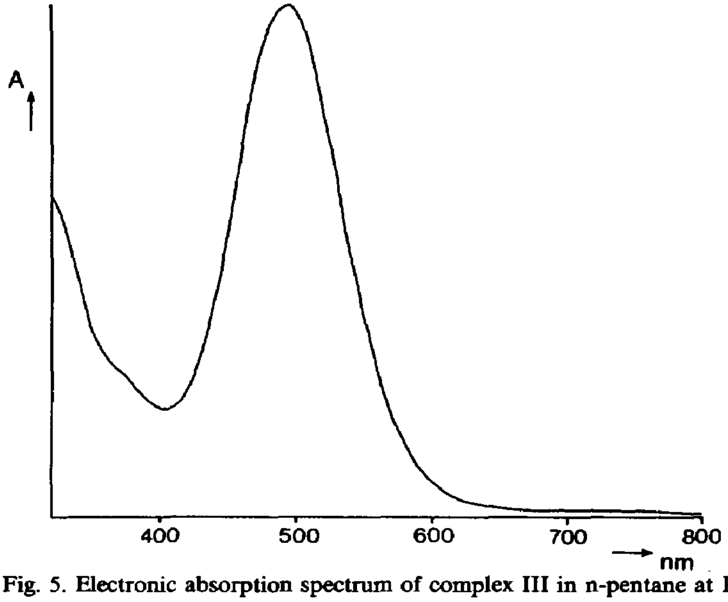


Fig. 5. Electronic absorption spectrum of complex III in n-pentane at RT.

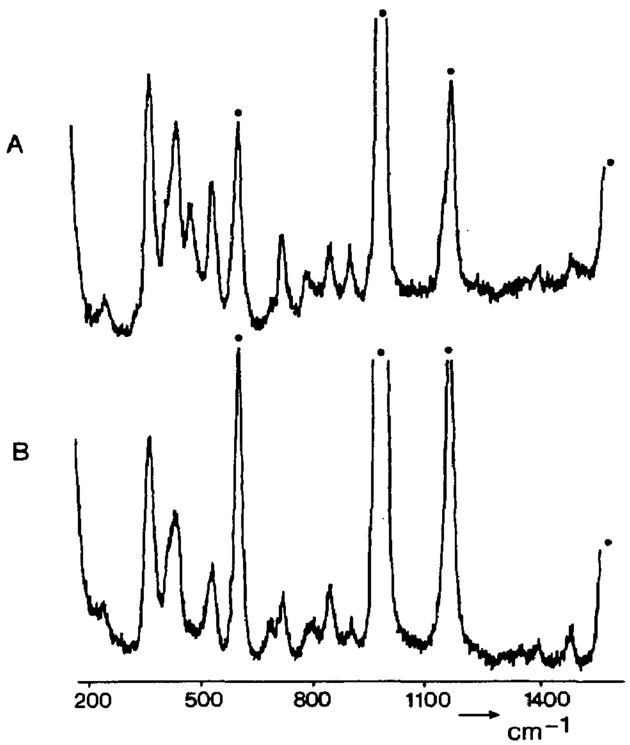


Fig. 6. Resonance Raman spectra of complex III excited with $\lambda = 458$ nm (A) and $\lambda = 575$ nm (B) (benzene, RT)• = C_6H_6.

These spectra are very weak, since they could only be recorded for a solution with an optical density of about 20 at the maximum of the ML band. Similar weak rR effects had been observed for the corresponding Fe complex of this ligand [11]. These weak rR spectra imply the presence of a Ru-DAB metallacycle in complex III, with only minor changes in bond character during the lowest-energy ML transitions. Resonance enhancement of Raman intensity is observed for ν_s(Ru–N) at 242 cm^{-1}, for ν_s(Ru–C) at 372 cm^{-1} and for (Ru-CO) and (Ru-DAB) deformation modes at 445, 480, 538, 723, 850 and 905 cm^{-1}. ν_s(CN) of the i-Pr_2CH-DAB ligand is only observed as a very weak band at 1490 cm^{-1}. This means that the ML transition has no CT character but causes only a weakening of the metal–ligand bonds and a weak distortion of the metallacycle. In the case of the Fe complexes these vibronic couplings of the Fe–C and Fe–DAB deformation modes to the ML transition have been related to the observed formation of the complexes $Fe(CO)_3(\eta^4$-R-DAB) from the lowest ^{3}ML state [11–13]. In the case of complex III, the deformation modes above 600 cm^{-1} are, however, much weaker than those for the corresponding Fe complex.

When a room temperature solution of complex III in n-pentane was irradiated with light at wavelengths in the range 313 to 514.5 nm no photochemical reaction was observed, but flash-photolysis proved that this photostability was due to a fast back-reaction of the photoproduct to regenerate the parent compound. Irradiation of a RT solution of III in toluene with the 308 nm line of an excimer laser caused the disappearance of the ML band of III, while two new bands showed up at *t* 200

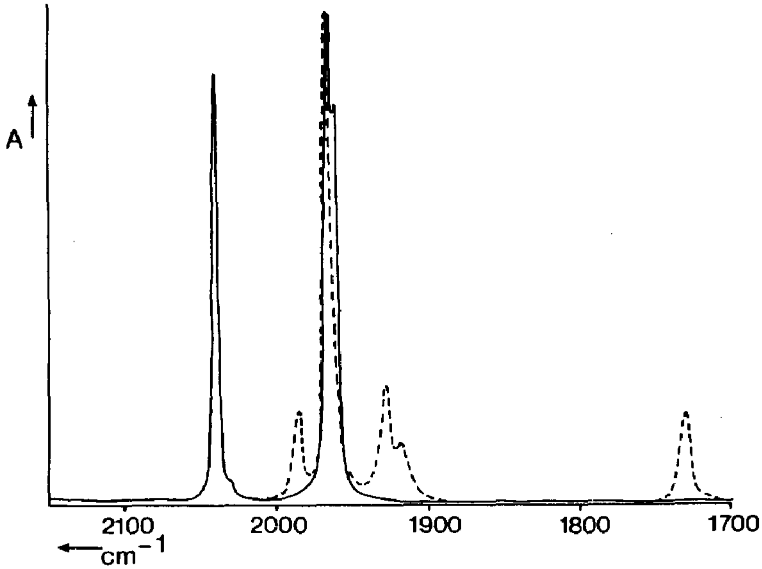


Fig. 7. IR spectra (CO-stretching region) of complex III (drawn) and its photoproduct $Ru_2(CO)_5$(i-Pr_2CH-DAB)$_2$ (dashed) (n-pentane, 150 K).

ns with their maxima at 425 and 605 nm, respectively. Again the 425 nm band is assigned to a LF transition and the band at 605 nm to the ML transition. The shift of this band to lower energy with respect to the parent compound is caused by the replacement of the electron-withdrawing CO group by a solvent molecule (S). The same spectrum was obtained at *t* 1750 ns after the laser pulse, and it points to the formation of $Ru(CO)_2$(i-Pr_2CH-DAB)(S) (IVa). This means that release of CO is the primary photoprocess of III, just as it is for complex I.

This CO-loss reaction of complex III is also evidenced by its photolysis reaction in n-pentane at 150 K. The IR spectral changes in the CO-stretching region accompanying this reaction are shown in Fig. 7. The photoproduct has a bridging carbonyl ligand (ν(CO) 1729 cm^{-1}), and its proposed structure is shown in Fig. 8.

Similar binuclear complexes had been formed by irradiation of several $Fe(CO)_3$(R-DAB) complexes [13], the only difference being that $Ru_2(CO)_5$(i-Pr_2CH-DAB)$_2$ is the only product at all irradiation wavelengths ($\lambda_{irr} = 351-600$ nm), whereas the Fe dimers were only formed by irradiation at $\lambda < 500$ nm. Raising the temperature of the solution induced the back-reaction of CO with the dimer to regenerate the parent compound.

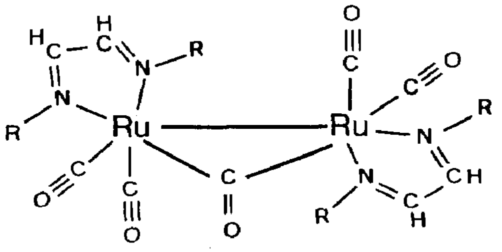


Fig. 8. Proposed structure of $Ru_2(CO)_5$(i-Pr_2CH-DAB)$_2$.

Irradiation of a 150 K solution of complex III in n-pentane in the presence of one of several PR_3 ligands (R = n-Bu, c-Hex, Ph, OMe or OPh) yielded the substitution products $Ru(CO)_2$(i-Pr_2CH-DAB)(PR_3) (IVb–IVf) (b: R = n-Bu; c: R = c-Hex; d: R = Ph; e: R = OMe; f: R = OPh). The CO-stretching frequencies of these complexes, listed in Table 1, nicely reflect the differences in nucleophilic character of the PR_3 ligands. In the case of $P(OMe)_3$ three isomers of its complex IVe could be detected, two of which are clearly seen in Fig. 9. Just as in the case of the Fe complexes I and II, the Ru complex III and its PR_3-containing derivatives IV differ in their photochemical behaviour. Whereas no η^4-coordinated i-Pr_2CH-DAB complex was formed for complex III, such products were obtained by irradiation of the complexes IV. Prolonged irradiation of the n-pentane solution of III in the presence of PR_3 first yielded IV, which then reacted further to give various photoproducts depending on the wavelength of irradiation. Irradiation at $\lambda > 458$ nm into the ML band produced with low quantum yield a photoproduct having two CO-stretching frequencies shifted to higher frequencies with respect to those of the parent compounds IVb–IVf. At the same time the ML band disappeared. The shift

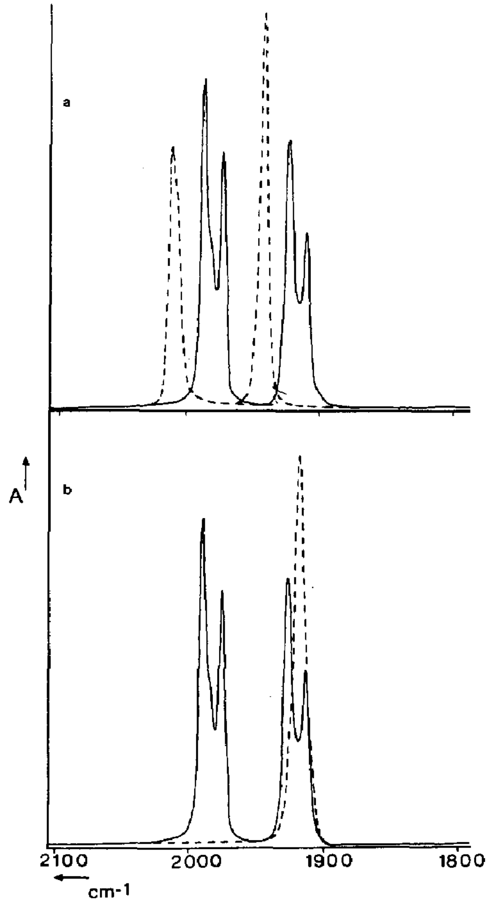


Fig. 9. IR spectra (CO-stretching region) of complex IVe (drawn) and of its photoproducts (dashed) $Ru(CO)_2(\eta^4$-i-Pr_2CH-DAB)($P(OMe)_3$) (a, $\lambda_{irr} > 458$ nm) and Ru(CO)(i-Pr_2CH-DAB)$(P(OMe)_3)_2$ (b, $\lambda_{irr} < 350$ nm) (n-pentane, 150 K).

Table 1

CO-stretching frequencies and UV/Vis data of the complexes studied

Complex	Notation	CO-stretching frequencies (cm^{-1})	Electronic absorption maxima (nm)
$Fe(CO)_3(i\text{-}Pr_2Ph\text{-}DAB)$	I	2032 1973 1967 ^{a}	393 497 ^{a}
$Fe(CO)_3(\eta^4\text{-}i\text{-}Pr_2Ph\text{-}DAB)$		2080 2029 2009 ^{b}	
$Fe(CO)_2(i\text{-}Pr_2Ph\text{-}DAB)(toluene)$	IIa		430 610 ^{c}
$Fe(CO)_2(i\text{-}Pr_2Ph\text{-}DAB)(P(OPh)_3)$	IIb	1992 1936 ^{b}	396 497 ^{b}
$Fe(CO)_2(i\text{-}Pr_2Ph\text{-}DAB)(P(c\text{-}Hex)_3)$	IIc	1966/1959 1906/1900 ^{d}	
$Fe(CO)_2(\sigma\text{-}N\text{-}i\text{-}Pr_2Ph\text{-}DAB)(P(c\text{-}Hex)_3)_2$		1955 1881 ^{d}	
$Fe(CO)_2(\sigma\text{-}N\text{-}i\text{-}Pr_2Ph\text{-}DAB)(P(OPh)_3)$ (toluene)			420 ^{c}
$Fe(CO)_3(PEt_3)_2$ ^{e}		1875	
$Fe(CO)_2(PEt_3)_3$ ^{e}		1880 1820	
$Ru(CO)_3(i\text{-}Pr_2CH\text{-}DAB)$	III	2041 1968 1965 ^{a}	368 479 ^{a}
$Ru(CO)_2(i\text{-}Pr_2CH\text{-}DAB)(toluene)$	IVa		425 605 ^{c}
$Ru(CO)_2(i\text{-}Pr_2CH\text{-}DAB)(P(n\text{-}Bu)_3)$	IVb	1970 1907 ^{b}	387 481 ^{b}
$Ru(CO)_2(i\text{-}Pr_2CH\text{-}DAB)(P(c\text{-}Hex)_3)$	IVc	1966 1901 ^{b}	
$Ru(CO)_2(i\text{-}Pr_2CH\text{-}DAB)(PPh_3)$	IVd	1979 1915 ^{b}	395 489 ^{b}
$Ru(CO)_2(i\text{-}Pr_2CH\text{-}DAB)(P(OMe)_3)$	IVe	1995/1990/1981 1931/1918 ^{b}	368 479 ^{b}
$Ru(CO)_2(i\text{-}Pr_2CH\text{-}DAB)(P(OPh)_3)$	IVf	1997 1941 ^{d}	382 485 ^{d}
$Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(P(n\text{-}Bu)_3)$		2005/2000/1986 1938/1932/ 1927 ^{b}	328 ^{b}
$Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(P(c\text{-}Hex)_3)$		1998 1928 ^{b}	
$Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(PPh_3)$		2007 1941 ^{d}	353 ^{d}
$Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(P(OMe)_3)$		2019 1952 ^{b}	341 ^{b}
$Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(P(OPh)_3)$		2026 1965 ^{d}	350 ^{d}
$Ru(CO)(i\text{-}Pr_2CH\text{-}DAB)(P(OMe)_3)_2$		1923 ^{b}	373 469 ^{b}
$Ru_2(CO)_5(i\text{-}Pr_2CH\text{-}DAB)_2$		1984 1965 1927 1918 1729 ^{b}	
$Ru(CO)_3(P(n\text{-}Bu)_3)_2$		1878 ^{b}	
$Ru(CO)_3(P(c\text{-}Hex)_3)_2$		1882 ^{b}	
$Ru(CO)_3(PPh_3)_2$		1897 ^{d}	
$Ru(CO)_2(P(n\text{-}Bu)_3)_3$		1889 1838 ^{b}	

[a] Spectra taken from RT n-pentane solution. [b] 150 K n-pentane solution. [c] RT toluene solution (flash-photolysis). [d] 200 K n-pentane solution. [e] From ref. 25.

of the CO-vibrations, which is shown in Fig. 9a for the photoproduct of $Ru(CO)_2(i\text{-}Pr_2CH\text{-}DAB)(P(OMe)_3)$ (IVe), is typical for a change of coordination of the $i\text{-}Pr_2CH\text{-}DAB$ ligand from σ,σ-N,N′ to η^4-CN,C′N′ [12,13] to give $Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(P(OMe)_3)$.

The shifts to higher frequencies reflect the decrease in π-backbonding to the carbonyls accompanying the increase of π-backbonding to the $i\text{-}Pr_2CH\text{-}DAB$ ligand. Complexes of the type $Fe(CO)_2(\eta^4\text{-}diene)(P(OMe)_3)$ are known, and have been characterized by IR spectroscopy [24].

Similar photoproducts $Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(PR_3)$ were obtained for all complexes IVb–IVf and their CO-stretching frequencies are listed in Table 1. Raising the temperature of the solution above 200 K led to thermal backreaction of these complexes to give their parent compounds IVb–IVf. In the case of the complex containing $P(n\text{-}Bu)_3$ three isomers $Ru(CO)_2(\eta^4\text{-}i\text{-}Pr_2CH\text{-}DAB)(P(n\text{-}Bu)_3)$ were formed (see Table 1). Raising the temperature to 200 K caused the conversion of two of these isomers into the third one with CO-stretching frequencies at 2000 and 1932 cm^{-1}. A further increase in temperature then induced the thermal backreaction to give IVb. Up to now the attempts to isolate these η^4-coordinated R-DAB complexes have failed. Attempted isolation and further characterization of the compounds is in progress.

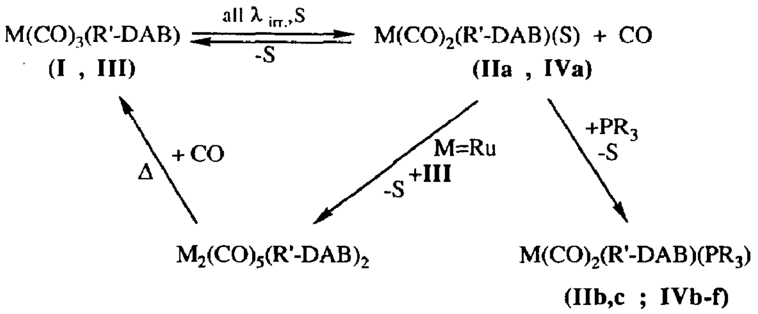
A completely different reaction was observed upon irradiation of the complexes IV into the LF band (λ_{irr} 351, 364 nm). In this case the complexes IV, except for the $P(OMe)_3$-derivative IVe gave $Ru(CO)_3(PR_3)_2$, and in some cases $Ru(CO)_2(PR_3)_3$, as evidenced by their CO-stretching frequencies, which agree with those for the corresponding Fe-complexes [25] (see Table 1). The conversion of the dicarbonyl into a tricarbonyl complex is possible in this case because of the presence of free CO in the solution. During this reaction the ML bands disappeared. Raising the temperature of the solution from 150 to 200 K resulted in thermal conversion of $Ru(CO)_3(PR_3)_2$ and $Ru(CO)_2(PR_3)_3$ into $Ru(CO)_3$(i-Pr_2CH-DAB) (III) and $Ru(CO)_2$(i-Pr_2CH-DAB)(PR_3) (IV), respectively, by replacement of two PR_3 groups by the i-Pr_2CH-DAB still present in the solution.

The $P(OMe)_3$-containing complex reacted differently by giving Ru(CO)(i-Pr_2CH-DAB)$(P(OMe)_3)_2$ instead of $Ru(CO)_2(P(OMe)_3)_3$ and $Ru(CO)_3(P(OMe)_3)_2$. The single CO vibration of this photoproduct can be seen in Fig. 9b. At the same time the ML band shifted to 469 nm. This different behaviour of the $P(OMe)_3$ complex can be explained as follows. The formation of $Ru(CO)_3(PR_3)_2$ and $Ru(CO)_2(PR_3)_3$ from the complexes IV points to a cleavage of a metal–nitrogen bond as the primary photoprocess. A PR_3 ligand then occupies the open site, and rechelation of the i-Pr_2CH-DAB ligand is prevented by the presence of two bulky PR_3 ligands on the metal. Only in the case of $P(OMe)_3$ can such a rechelation process occur, leading to loss of another CO ligand and formation of Ru(CO)(i-Pr_2CH-DAB)$(P(OMe)_3)_2$. This influence of the size of the PR_3 ligand on the rechelation of the R-DAB ligand has also been observed for the photochemical reactions of $Fe(CO)_3$(t-Bu-DAB) with different PR_3 ligands [13]. In this latter case, also, breaking of a metal–nitrogen bond is the primary photoprocess upon irradiation into the LF band.

The photochemical mechanism

The unsubstituted complexes I(Fe) and III(Ru) behave similarly in undergoing release of CO both at RT and at 150 K independent of the wavelength of irradiation. For irradiation with λ 308 nm the occurrence of this CO-loss reaction is clearly demonstrated by the flash-photolysis results. The only difference between the two complexes is the formation of the dimer $Ru_2(CO)_5$(i-Pr_2CH-DAB$)_2$ upon irradiation of III in n-pentane at 150 K. Complex I is photostable under these conditions, although analogous photoproducts $Fe_2(CO)_5$(R-DAB$)_2$ were produced by irradiation of $Fe(CO)_3$(R-DAB) complexes with less bulky substituents R [13]. Apparently, formation of a dimer from complex I is inhibited by the bulky i-Pr_2Ph groups. These reactions of I and II, shown in Scheme 1, probably occur from the lowest ^{3}LF state, as in the case of the corresponding $Fe(CO)_3$(R-DAB) (R = c-Hex, *p*-Tol) complexes [13].

The question remains of why complexes I and III do not give rise to the formation of photoproducts with a η^4-coordinated R-DAB ligand, whereas their PR_3-derivatives II and IV do. In the case of the Fe-complex I, thermal instability of the photoproduct $Fe(CO)_3(\eta^4$-i-Pr_2Ph-DAB), due to the bulk of the i-Pr_2Ph groups,



Scheme 1. The photochemical reactions of complexes I and III (S = solvent).

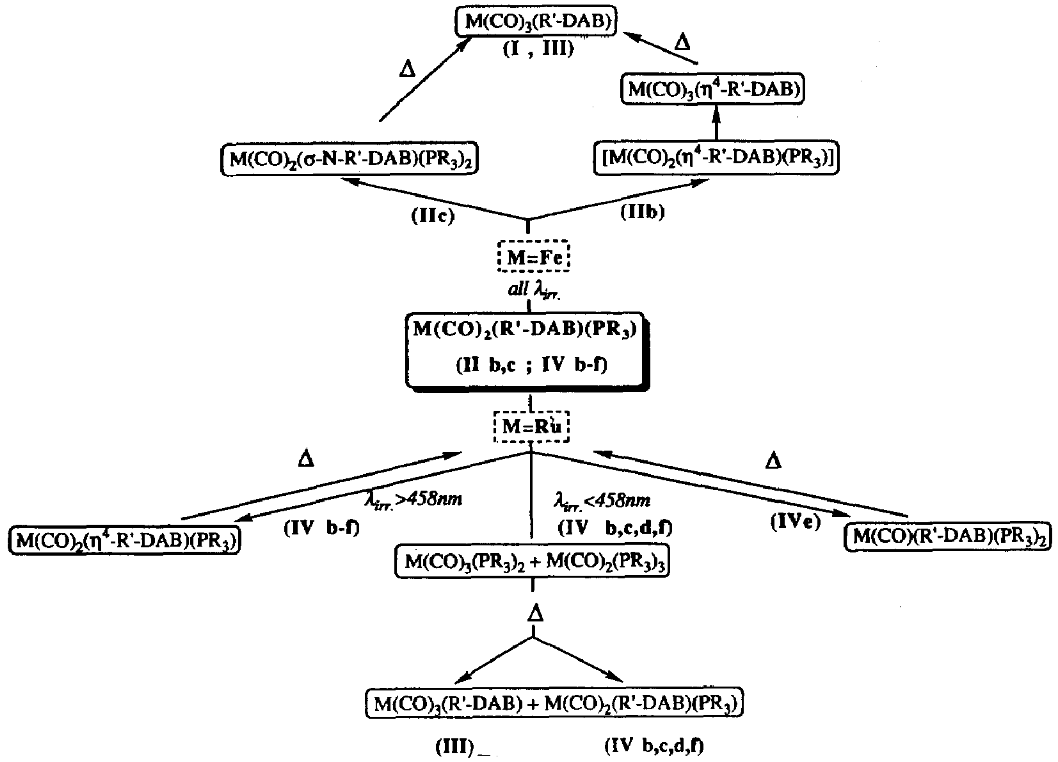
can be excluded since this complex was formed as a stable photoproduct up to 200 K by irradiation of IIb. Yet the formation of $Fe(CO)_3(\eta^4\text{-i-Pr}_2\text{Ph-DAB})$ is probably inhibited by these bulky $\text{i-Pr}_2\text{Ph}$ groups, since this isomerization reaction, involving the change of coordination of the R-DAB ligand from σ,σ-N,N′ to η^4-CN,C′N′, occurs readily in the case of the closely analogous complex $Fe(CO)_3(p\text{-Tol-DAB})$ [13]. The latter complex and complex I differ significantly in the size of their R-DAB substituents but hardly at all in their electronic properties. A similar influence of steric effects has been observed for the complexes $Fe(CO)_3$(R-DAB) (R = c-Hex, t-Bu), of which only the c-Hex-DAB complex undergoes the isomerization reaction. In contrast, the complex $Fe(CO)_2(\text{i-Pr}_2\text{Ph-DAB})(P(OPh)_3)$ (IIb) undergoes isomerization, although steric interactions are even more important here than in the case of complex III. Thus the difference in behaviour between the various Fe complexes can certainly not be due to steric effects alone. Such a difference is even more pronounced for the Ru complexes, which undergo the isomerization even in the case of $Ru(CO)_2(\text{i-Pr}_2\text{CH-DAB})(P(\text{c-Hex})_3)$ (IVc), but not in the case of complex III. Two major electronic effects can influence the reactions of these complexes. Substitution of CO by PR_3 may influence both the relative energies and the characters of the ^{3}ML and ^{3}LF states, and thus also the crossing between these states. If this crossing becomes less efficient, reactions from the ^{3}ML state can more easily occur upon low-energy, low-temperature excitation. The relative energies of the ^{3}LF and ^{3}ML states will hardly change when CO is replaced by PR_3, since both the LF and ML transitions are observed at nearly the same position. The characters of these states will however, change, appreciably. This is clearly demonstrated for the ^{3}LF states, which undergo release of CO in the parent compounds I and IV but breaking of a metal–nitrogen bond in the case of the substituted complexes II and VI (vide infra). The character of the ^{3}ML state is of crucial importance for the occurrence of an isomerization reaction from this state. Up to now this reaction has only been observed for this type of complexes $Fe(CO)_3$(R-DAB) possessing a chracteristic ML transition within the metallacycle [12,13]. According to the rR spectra this ML transition is accompanied by a distortion of the metallacycle, apparently leading to the isomarization of a complex [11,12]. The rR spectrum of the corresponding Ru-complex III (Fig. 6) only shows very weak rR effects for the deformation modes of the $\text{i-Pr}_2\text{CH-DAB}$ ligand, which means that distortion of the metallacycle is less likely to occur for complex III. Substitution of CO by PR_3 will, however, change the electron density distribution within the metallacycle and also affect the character of the ML transition. Unfortunately, such a change of character could not be verified by rR spectroscopy because of the photolability of the PR_3-containing complexes IV.

The same effect may be responsible for the difference in behaviour between complexes I and IIb. Because of the steric requirements of the bulky i-Pr_2Ph groups the weak distortion of the metallacycle by the ML transition may not give the $Fe(CO)_3(\eta^4$-i-Pr_2Ph-DAB) isomer. Substitution of CO by $P(OPh)_3$ may lead to an increase of the distortion of the metallacycle during the ML transition and so to formation of the isomer from the ^{3}ML even though the steric interactions have increased. Again, this change of character of the ML transition could not be proved by rR spectroscopy owing to the photolability of IIb.

Irradiation of the $P(cHex)_3$-substituted complex IIc did not produce $Fe(CO)_3(\eta^4$-i-Pr_2Ph-DAB). Apparently, this phosphine ligand is too bulky to permit such an isomerization.

In summary it can be said that formation of a η^4-coordinated R-DAB complex may depend on both the efficiency of the surface crossing between the ^{3}ML and ^{3}LF states, and on the extent to which the metallacycle is distorted in the ^{3}ML state. More information about the relative importance of steric and electronic effects on the isomerization reactions of the Ru complexes may be obtained by varying the R-substituent. Unfortunately, Ru complexes with smaller R-DAB ligands are thermally much less stable than the corresponding Fe compounds since they easily form binuclear complexes after loss of CO [26]. Irradiation of the $P(OPh)_3$ containing complex IIb did not give $Fe(CO)_2(\eta^4$-i-Pr_2Ph-DAB)$(P(OPh)_3$, but instead $Fe(CO)_3(\eta^4$-i-Pr_2Ph-DAB), formed by reaction of the former photoproduct with CO from the solution.

It is noteworthy that in the case of complex IIb the isomerization reaction occurred at all wavelengths of irradiation whereas for the corresponding Ru-complexes IVb–IVf it took place only upon ML excitation. This difference in behaviour can be explained as follows. According to the flash-photolysis data, complexes I and III undergo release of CO from their lowest ^{3}LF state. Substitution of one CO group by a PR_3 ligand changes this primary photoprocess. Flash-photolysis shows that in the case of complex IIb a metal–nitrogen bond is broken instead, and this is confirmed by the formation of the photoproduct $Fe(CO)_2(\sigma$-N-i-Pr_2Ph-DAB)(P(c-Hex$)_3)_2$ upon irradiation of complex IIc in the presence of P(c-Hex$)_3$. Although no flash-photolysis experiments could be performed on the PR_3-containing Ru complexes (IVb–IVf), LF excitation clearly showed release of the i-Pr_2CH-DAB ligand for all the PR_3 complexes except that with R = OMe. This points to cleavage of a metal–nitrogen bond as the primary photoprocess in this case also. Thus the primary photoprocesses from the ^{3}LF states are release of CO for the tricarbonyls and breaking of a metal–nitrogen bond for their PR_3 derivatives. This change in the reaction of the ^{3}LF state is closely connected with the change of relative metal–ligand bond-strengths upon substitution of CO by PR_3. This substitution causes a strengthening of the remaining metal–CO bonds and a weakening of the metal–nitrogen bond *trans* to the PR_3 ligand. The breaking of the metal–nitrogen will be followed by occupation of the open site by the PR_3 ligand. In the case of the Fe complex this intermediate apparently loses the PR_3 ligand again, with simultaneous rechelation of the i-Pr_2Ph-DAB ligand to give the parent compound. Thus LF excitation of complex IIb did not yield any photoproduct other than the parent compound. This explains why this complex undergoes the isomerization at all



Scheme 2. The photochemical reactions of complexes II and IV.

irradiation wavelengths. The corresponding Ru complexes IVb–IVf also undergo breaking of a Ru–N bond from the lowest ^{3}LF state. Again the open site will be occupied by a PR_3 ligand. In contrast with the Fe-complex IIb, however, the i-Pr_2CH-DAB ligand did not take part, in rechelation, but was released with formation of $Ru(CO)_2(PR_3)_3$ and $Ru(CO)_3(PR_3)_2$. Only in the case of the small $P(OMe)_3$ ligand was rechelation of the i-Pr_2CH-DAB ligand observed, with formation of Ru(CO)(i-Pr_2CH-DAB)$(P(OMe)_3)_2$. Since LF excitation of these complexes IV gives photoproducts different from those from the parent compounds, the isomerization reaction will only be observed upon excitation into the ML band. All the reactions of the PR_3-containing complexes II and IV reported in this paper are shown schematically in Scheme 2.

Conclusion

We conclude that replacement of CO by PR_3 in the complexes $M(CO)_3$(R-DAB) (M = Fe, Ru) (I, III) facilitates the photochemical change of coordination of bulky R-DAB ligands from σ,σ-N,N′ into η^4-CN,C′N′. This effect is probably due to a larger distortion of the MR-DAB metallacycle in the lowest excited state of the PR_3 substituted complexes, which results in this change of coordination. It is evident that small changes in the electron density distributions in the Fe- and Ru-metallacycles can strongly affect their photochemical behaviour.

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