Inorganica Chimica Acta, 210 (1993) 33–37

Substitution photochemistry of bis(phosphido)-bridged diiron carbonyl complexes $[Fe_2(CO)_n(\mu\text{-}PBu^t_2)(\mu\text{-}PR_2)]$ ($n=5$, R = Bu^t, Cy; $n=6$, R = Cy, Me)

Helmut Knoll* and Horst Hennig
Fachbereich Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig (Germany)

Bernhard Walther and Hans-Christian Böttcher
Fachbereich Chemie, Martin-Luther-Universität Halle, Weinbergweg 16, D-06120 Halle (Germany)

Derk J. Stufkens
Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (Netherlands)

(Received January 7, 1993)

Abstract

Irradiation of the title complexes in THF in the presence of excess PBu^n_3 or $P(OMe)_3$ with 457.9 nm light resulted in a stepwise substitution of CO by the phosphine. With 351/363 nm light a substitution limit of products with remaining three CO ligands was found. The bis(phosphido)-bridging structure is maintained in the photoproducts, and also the coordinatively unsaturated iron center in the case of $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)_2]$.

Introduction

Very recently a new class of coordinatively unsaturated bis(phosphido)-bridged diiron carbonyl complexes with five CO ligands containing both tetrahedral and tetragonal pyramidal iron centers has been synthesized and characterized by IR, UV–Vis, NMR and MS spectroscopy [1–3]. The following abbreviations will be used throughout: Bu^t = tert-C_4H_9, Bu^n = n-C_4H_9, Cy = cyclo-C_6H_{11}, Me = CH_3, Ph = C_6H_5, OMe = OCH_3. Single crystal X-ray diffraction studies of $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PR_2)]$ (R = Bu^t (I) [1, 2], Cy (III) [3], and Ph [1]) revealed short iron–iron distances indicating the presence of double bonds. The existence of a double bond is further supported by EHMO calculations [1].

I appeared to be rather inert with respect to thermal substitution reactions. Excitation by light might enhance the reactivity at ambient temperature. Therefore we studied the photoreactivity of I and III and compared it with that of the coordinatively saturated complexes, $[Fe_2(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}PR_2)]$ (R = Cy (II), Me(IV)). In particular we were interested in the photochemical formation of new complexes. To scavenge short lived intermediates high concentrations of PR'_3 (R' = OMe, Bu^n) were added. To identify the products and to study the mechanism the photolysis of the complexes was followed by UV–Vis and IR spectroscopy, and in some cases by NMR spectroscopy. We report here on the first experiments on an analytical scale where the complexes were irradiated in the spectrometer cuvettes.

Experimental

Materials and preparations

Complexes **I**, **II** and **IV** were synthesized by treatment of $Na[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PBu^t_2)]$ with R_2PCl (R = Bu^t, Cy, Me); **III** was obtained by thermal CO elimination from **II** [3]. THF was dried, distilled and stored under nitrogen. All samples were prepared by means of the Schlenk technique, and all reactions were studied at room temperature.

Spectroscopy

IR spectra were recorded on a Nicolet 7199 B FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector (32 scans, resolution 1 cm^{-1}). Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV–Vis spectrometer connected to a model 3600 data station. NMR spectra were recorded on a Bruker AC 100 instrument.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

Photochemistry

A SP 2025 argon-ion laser was used as the light source for irradiation with the 351/363 and 457.9 nm lines, its 514.5 nm line was used for pumping a Coherent dye laser providing 620 nm. The flash photolysis apparatus with FWHM of 25 μs and 180 J/flash was home made.

Results and discussion

UV–Vis spectra of solutions of complex **I** in THF show bands at 657(659) and 463(465) nm (in parentheses band maxima in pentane [1]). The nearly complete coincidence of the band maxima in the polar and unpolar solvent indicates that these electronic transitions are not of the charge transfer type. **III** shows similar bands in the UV–Vis spectrum, see Table 1. According to the EHMO calculations for $[Fe_2(CO)_5(\mu\text{-PH}_2)_2]$ as a model for complexes **I** and **III** the lowest energy band is assigned to a low lying $\pi\pi^*$ transition [1].

Considering the above assignment of the lowest energy band of **I** and **III** the photochemical inertness of the complexes upon irradiation into this band is not surprising. They were stable upon continuous irradiation of 0.01 M solutions in THF in the whole range between 351 and 620 nm.

Complexes **II** and **IV** containing one CO ligand more than **I** and **III**, both with equivalent iron centers, exhibit their lowest energy bands just below 550 nm. Irradiation of **II** with 457.9 nm led to a decrease of the band at 538 nm where a band shows up at 656 nm. In a completely filled, tightly sealed cuvette there is a back reaction in the dark, Fig. 1. Following the decreasing absorbance at 700 nm during this thermal back reaction a second order rate constant of (22 ± 2) 10^{-3} M^{-1} s^{-1} was determined. From the UV–Vis spectral changes, and the IR product bands at 1902, 1950 and 2013 cm^{-1} (Table 2), it follows unambiguously that the reaction is a photolytic splitting of CO from **II** to form **III** which reacts back if the CO remains in the solution, reaction (1).

TABLE 1. UV–Vis spectral data of bis(phosphido)-bridged diiron carbonyl complexes in THF at room temperature

Complex	λ_{max} (nm)
$[Fe_2(CO)_5(\mu\text{-PBu}^t_2)_2]$ (**I**)	657, 463, 327
$[Fe_2(CO)_4(P(OMe)_3)(\mu\text{-PBu}^t_2)_2]$ (**VIa**)	690, sh, 330
$[Fe_2(CO)_4(PBu^n_3)(\mu\text{-PBu}^t_2)_2]$ (**VIb**)	680, sh, 330
$[Fe_2(CO)_5(\mu\text{-PBu}^t_2)(\mu\text{-PCy}_2)]$ (**III**)	656, 457, 321
$[Fe_2(CO)_5(\mu\text{-PBu}^t_2)(\mu\text{-PMe}_2)]$ (**V**)	660[a]
$[Fe_2(CO)_3(P(OMe)_3)_2(\mu\text{-PBu}^t_2)_2]$ (**VIIa**)	709, sh, 330
$[Fe_2(CO)_6(\mu\text{-PBu}^t_2)(\mu\text{-PCy}_2)]$ (**II**)	538, 321
$[Fe_2(CO)_6(\mu\text{-PBu}^t_2)(\mu\text{-PMe}_2)]$ (**IV**)	455, sh
$[Fe_2(CO)_5(P(OMe)_3)(\mu\text{-PBu}^t_2)(\mu\text{-PCy}_2)$ (**VIIIa**)	534, 323
$[Fe_2(CO)_5(PBu^n_3)(\mu\text{-PBu}^t_2)(\mu\text{-PCy}_2)]$ (**VIIIb**)	481, 343
$[Fe_2(CO)_5(P(OMe)_3)(\mu\text{-Pbu}^t_2)(\mu\text{-PMe}_2)]$ (**IXa**)	320
$[Fe_2(CO)_5(PBu^n_3)(\mu\text{-PBu}^t_2)(\mu\text{-PMe}_2)]$ (**IXb**)	334
$[Fe_2(CO)_4(P(OMe)_3)_2(\mu\text{-PBu}^t_2)(\mu\text{-PCy}_2)]$ (**Xa**)	530, 352
$[Fe_2(CO)_4(PBu^n_3)_2(\mu\text{-PBu}^t_2)(\mu\text{-PCy}_2)]$ (**Xb**)	sh, 376
$[Fe_2(CO)_4(P(OMe)_3)_2(\mu\text{-PBu}^t_2)(\mu\text{-PMe}_2)]$ (**XIa**)	350
$[Fe_2(CO)_4(PBu^n_3)_2(\mu\text{-PBu}^t_2)(\mu\text{-PMe}_2)]$ (**XIb**)	374
$[Fe_2(CO)_3(P(OMe)_3)_3(\mu\text{-PBu}^t_2)(\mu\text{-PMe}_2)]$ (**XIIa**)	500, sh, 310

[a] Short lived intermediate after flash photolysis.

$$[Fe_2(CO)_6(\mu\text{-PBu}^t_2)(\mu\text{-PR}_2)] \xrightleftharpoons{h\nu}$$

$$R = Cy\ (\textbf{II}),\ Me\ (\textbf{IV})$$

$$[Fe_2(CO)_5(\mu\text{-PBu}^t_2)(\mu\text{-PR}_2)] + CO \quad (1)$$

$$R = Cy\ (\textbf{III}),\ Me\ (\textbf{V})$$

Due to the thermal back reaction we could only estimate the initial quantum yield for the formation of **III** out of **II** to be of the order of 10^{-2}.

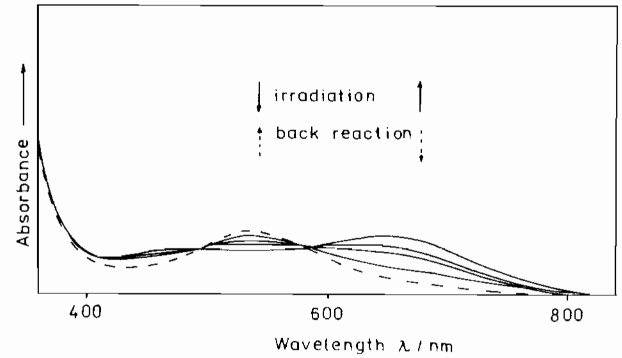

Fig. 1. UV–Vis spectral changes upon irradiation of 10^{-2} M **III** in THF in a 0.2 mm IR cell. – – – before, —— after irradiation at 457.5 nm.

TABLE 2. IR ν(CO) frequencies of bis(phosphido)-bridged diiron carbonyl complexes in THF at room temperature

Complex	ν(CO) (cm^{-1})
I	2011, sh 1949, 1900
VIa	1989, 1930, 1897, 1882
VIb	1978, 1921, 1875, 1864
III	2013, sh 1950, 1902
VIIa	1938, 1883, 1863
II	1991, 1949, sh 1934
IV	2034, 1994, sh 1954, 1938
VIIIa	1996, 1959, 1910, 1882
VIIIb	1990, 1949, 1904, 1877
IXa	1999, 1954, 1914
IXb	1990, 1948, 1908
Xa	1922, 1889
Xb	1903, 1870
XIa	1924, 1894
XIb	1909, 1878
XIIa	1923, 1894, 1860

With **IV** the dissociation of CO could not be detected by stationary UV–Vis or IR analyses. In a μs-flash photolysis experiment (λ_{exc} 320–500 nm, $c_0 = 3 \times 10^{-4}$ M) however we observed a transient difference absorbance with a maximum around 660 nm after the flash. It indicates the formation of $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PMe_2)]$ (**V**) as a short lived intermediate. 63% of its transient difference absorbance disappeared within 0.1 s. This behaviour is comparable to that of **II**, but the thermal back reaction is much faster obviously due to the smaller steric hindrance by the methyl groups.

The steric conditions around the iron cores seem to determine the stability of the hexa/pentacarbonyl complex pairs. While the hexacarbonyl compound with two bridging PBu^t_2 groups could not yet be prepared, **II** is stable in the dark. Up to now complex **III** has been prepared from **II** by refluxing in boiling toluene [1]. Our photochemical results show that **III** and probably other coordinatively unsaturated complexes with five CO ligands could also be synthesized by irradiation at lower temperatures, provided that the CO is efficiently removed by bubbling with an inert gas to prevent the back reaction of (1).

In order to scavenge such short lived intermediates we prepared mixtures of 10^{-2} M of the starting complexes with 0.3 M of PR'_3 ($R' = OMe, Bu^n$).

The photochemical substitution reactions of **I** will be discussed first. Just as in the absence of PR'_3, the mixtures of complex **I** with PR'_3 did not change upon irradiation at 620 nm. According to the EHMO calculations [1] the excited state is formed by a $\pi\pi^*$ transition which cleaves the Fe–Fe π-bond. Obviously this electronically excited complex or any intermediates derived from it are extremely short-lived and/or inert against PR'_3.

Irradiation with the laser line at 457.9 nm, however, gave rise to significant changes in the IR and UV–Vis spectra of mixtures of **I** with PR'_3. The UV–Vis spectra of the product mixtures of **I** showed a red shift of the lowest energy band of about 20–30 nm and other minor changes in the shape. The IR spectra of the products show four bands like the starting complex. Isosbestic points in the IR and UV–Vis spectra indicate a direct reaction from the starting complex to the product without an observable intermediate. These results, and in particular the remaining band > 650 nm, indicate that the structure of the starting complex with five monodentate ligands is maintained in the products, Fig. 2. The photolysis results in a substitution of one CO, reaction (2).

$$I + PR'_3 \xrightarrow{h\nu} [Fe_2(CO)_4(PR'_3)(\mu\text{-}PBu^t_2)_2] + CO \qquad (2)$$

VIa, VIb

$R' = OMe, Bu^n$

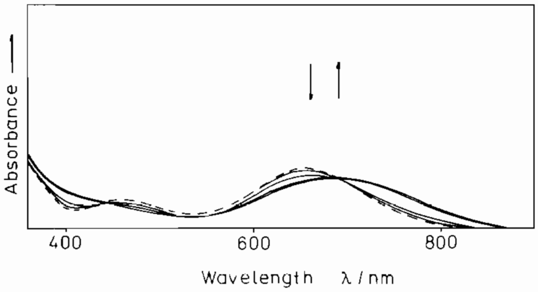

Fig. 2. UV–Vis spectral changes upon irradiation of 10^{-2} M **I** and 0.3 M PBu^n_3 in THF in a 0.2 mm IR cell. – – – before, —— after irradiation at 457.5 nm.

TABLE 3. ^{31}P NMR data of bis(phosphido)-bridged diiron carbonyl complexes in THF at room temperature

Complex	δ (ppm)			J (Hz)	
	$\mu\text{-}P_A$ [a]	$\mu\text{-}P_B$ [b]	PR'_3	$J(P_AP_B)$	$J(P_BP)$ [c]
I	364.0				
II	359.1	320.1		57.5	
IV	353.8	162.9		37.9	
VIIIb	331.7	239.4	49.4	52.2	12.3
IXb	330.8	174.8	52.8	46.0	9.8
Xb	268.5	198.8	46.4	79.6	14.2 [d]

[a] $\mu\text{-}PBu^t_2$. [b] $\mu\text{-}PR_2$. [c] $J(P_AP)$ not observed. [d] $J(P_AP) = 9.8$ Hz.

It remains unclear whether reaction (2) proceeds by an associative or dissociative mechanism, and whether the PR'_3 ligand ends up on the four- or five-coordinated iron centre.

Upon irradiation with the 351/363 nm lines a three band IR spectrum and a further shift of the band at 690 nm of **VIa** towards the red in the UV–Vis spectrum was obtained. These observations indicate continued substitution and formation of $[Fe_2(CO)_3(PR'_3)_2(\mu\text{-}PBu^t_2)_2]$ (**VII**) as the final products, reaction (3). The coordinatively unsaturated iron center was maintained.

$$VI + PR'_3 \xrightarrow{h\nu} [Fe_2(CO)_3(PR'_3)_2(\mu\text{-}PBu^t_2)_2] + CO \qquad (3)$$

VIIa

$R = OMe$

Whereas mixtures of **I** with PR'_3 are stable in the dark, solutions of **III** immediately turned red upon mixing with PR'_3 and the band at 656 nm disappeared. In accordance with the UV–Vis spectral changes accompanying reaction (1) the disappearance of the band at 656 nm indicates a structural change towards two tetragonal pyramidal iron centres with six monodentate ligands in the complex. The NMR spectrum gave an additional coupling of the PCy_2 bridge with a signal at higher field, Table 3. It can be assigned to the monodentate phosphine ligand [4]. Therefore we assign the spectroscopic effects accompanying the thermal reaction of **III** with PR'_3 to reaction (4).

$$\mathbf{III} + PR'_3 \longrightarrow$$

$$[Fe_2(CO)_5(PR'_3)(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)] \quad (4)$$

VIIIa, VIIIb

$R' = OMe, Bu^n$

Mixtures of **II** and **IV** with PR'_3 are stable in the dark and they showed another behavior upon irradiation with 457.9 nm, compared with **I**. The photolysis occurred in two steps as clearly indicated by the stepwise reduction of the number of ν(CO) bands in the products of reaction (5) derived from **II** and **IV**, see Table 2. The IR band patterns of the products of the two PR'_3 were consistent with respect to frequency and intensity, but the more basic PBu^n_3 gave rise to the formation of products having their CO vibrations at lower wavenumber than those formed from $P(OMe)_3$. In the UV–Vis spectra the bands of the starting complexes at 455 (**IV**) and 538 (**II**) nm disappeared and a band between 320 and 345 nm, in the second step between 350 and 380 nm showed up, see Fig. 3 and Table 1. CO ligands were substituted by PR'_3.

That our assignment of the products of the thermal reaction (4) is correct, is proven by the fact that the spectroscopic features of the products of the first step of reactions (5) with **II** and those of reactions (4) are identical. Separate photoreactions of **VIIIa, b** formed in the thermal reaction (4) gave the same products **Xa, b** as those in the second step of (5) starting with **II** in a purely photochemical reaction.

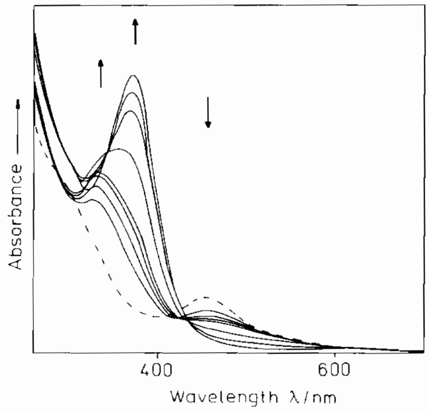

Fig. 3. UV–Vis spectral changes upon irradiation of 10^{-2} M **IV** and 0.3 M $P(OMe)_3$ in THF in a 0.2 mm IR cell. – – – before, —— after irradiation at 457.5 nm.

$$[Fe_2(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}PR_2)] + PR'_3 \xrightarrow{h\nu}$$

II
IV

$R' = OMe, Bu^n$

$$[Fe_2(CO)_5(PR'_3)(\mu\text{-}PBu^t_2)(\mu\text{-}PR_2)] + CO$$

VIIIa, VIIIb
IXa, IXb

$$[Fe_2(CO)_5(PR'_3)(\mu\text{-}PBu^t_2)(\mu\text{-}PR_2)] + PR'_3 \xrightarrow{h\nu}$$

VIII
IX

$R' = OMe, Bu^n$

$$[Fe_2(CO)_4(PR'_3)_2(\mu\text{-}PBu^t_2)(\mu\text{-}PR_2)] + CO \quad (5)$$

Xa, Xb
XIa, XIb

The coordination of the second PR'_3 ligand in the photoreaction (5) is accompagnied by changes in the NMR spectrum of **Xb** compared with **VIIIb**, see Table 3. The double bridge is maintained in the products. A comparable result has been obtained with the doubly bridged d7–d7 metal bonded complex $[Re_2(CO)_6$-(bis(dimethylphosphino)methane$)_2]$ [5].

Further substitution steps could not be observed upon irradiation with the 457.9 nm line due to side reactions at longer irradiation times.

Stationary irradiation with the combined 351/363 nm laser lines of a mixture of **IV** with $P(OMe)_3$, however, gave rise at first to the appearance of the two band IR spectrum of **XIa** while at a later stage a three band spectrum was observed, reaction (6). We assign it to $[Fe_2(CO)_3(P(OMe)_3)_3(\mu\text{-}PBu^t_2)(\mu\text{-}PMe_2)]$ (**XIIa**).

$$\mathbf{XIa} + P(OMe)_3$$

$$[Fe_2(CO)_3(P(OMe)_3)_3(\mu\text{-}PBu^t_2)(\mu\text{-}PMe_2)] + CO \quad (6)$$

XIIa

So in all cases the same stepwise substitution mechanism was observed upon irradiation with UV and visible light. The faster photoreactions upon UV irradiation with similar laser intensities as applied with the 457.9 nm line lend support to the following conclusion. UV transitions give rise to the occupation of the photoreactive states of the complexes studied and only tails of the UV bands are reached with the 457.5 nm line. At least in the case of complexes **II** and **IV** the first photochemical step was found to be CO loss.

Photochemistry on a preparative scale for isolation of the products at the substitution limit with the three remaining CO ligands would be necessary for NMR and/or X-ray studies in order to determine stereochemical features of the products.

Summarizing it can be concluded that differences in the photochemical and thermal behavior of the four complexes studied can be explained by the steric hindrance of the alkyl groups which increase in the order $Bu^t > Cy > Me$. Further studies are in progress.

Acknowledgement

The authors gratefully acknowledge the assistance of Wim J.G. de Lange in the NMR analyses.

References

1 B. Walther, H. Hartung, J. Reinhold, P.G. Jones, C. Mealli, H.-C. Böttcher, U. Baumeister, A. Krug and A. Möckel, *Organometallics, 11* (1992) 1982.
2 M.R. Adams, J. Galucci and A. Wojcicki, *Inorg. Chem., 31* (1992) 2.
3 B. Walther, H. Hartung, J. Reinhold, P.G. Jones, H.-C. Böttcher, U. Baumeister and A. Krug, *Chem. Ber., 125* (1992) 1379.
4 A.J. Carty, S.A. McLaughlin and D. Nuccione, in J.G. Verkade and L.D. Quin (eds.), *Methods of Stereochemical Analysis* (A.P. Marshal, Series ed.), Vol. 8, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis,* VCH, Deerfield Beach, FL, 1987.
5 S.J. Milder, M.P. Castellani, T.J.R. Weakley, D.R. Tyler, V.M. Miskowski and A.E. Stiegman, *J. Phys. Chem., 94* (1990) 6599.