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Low temperature photochemistry of [$Fe_2(CO)_6$(bipy)-($P(n\text{-}Bu)_3$)]. Stabilization of an intermediate photoproduct in a decomposition reaction

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Abstract

The complex [$Fe_2(CO)_6$(bipy)($P(n\text{-}Bu)_3$)] (I), a photoproduct from [$Fe_2(CO)_7$(bipy)], is itself photolabile. The UV, IR, resonance Raman spectra of I are described and used for the interpretation of its photochemical behaviour. Irradiation of I in its low-energy MLCT band in the presence of PR_3 or a N-donor ligand (L) causes photosubstitution of the last CO ligand of the Fe(1)-bipy moiety, giving the thermally unstable complex [$Fe_2(CO)_5$(bipy)($P(n\text{-}Bu)_3$)(L)] (II). Because of this thermal lability of the primary photoproduct, the photochemical reactions were performed in 2-Me-THF at 133 K. The complexes II with L = PR_3 decomposed thermally above 200 K, but when L was an N-donor ligand, partial decomposition took place at 133 K. The nature of these decomposition products depend on L. It is suggested that the photochemical reactions occur from a reactive ^{3}LF state after intersystem crossing from the ^{1}MLCT state. Evidence for a close lying ^{1}LF state comes from the resonance Raman spectrum upon 458 nm excitation, which shows anti-resonance Raman effects for all the vibrations.

Introduction

The complexes [$Fe_2(CO)_7$(L)] (L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)), in which L is σ,σ-N,N′(4e) coordinated to one of the Fe atoms, contain a symmetrically bridging and a semi-bridging carbonyl ligand [1]. We have recently shown that irradiation of these complexes into their low-energy MLCT-band causes the photosubstitution of the CO ligand of the Fe$(CO)_2$(L) moiety *trans* to the semi-bridging carbonyl [2]. In the substitution products the bridging character of

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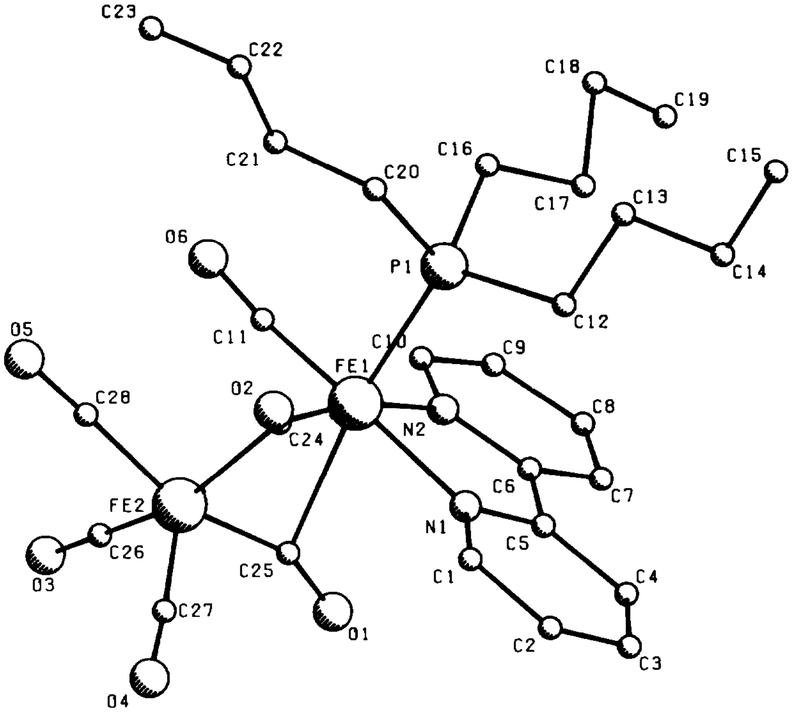

Fig. 1. Crystal structure (PLUTO-drawing) of $[Fe_2(CO)_6(bipy)P(n\text{-}Bu)_3)]$ (I).

this latter carbonyl was shown to depend on the nucleophilic properties of the substituting ligand. For hard bases, such as 2-Me-THF, CH_3CN, pyridine and n-propylamine, a symmetrical bridge was formed; for soft bases, such as phosphines, the relevant CO ligand remained semi-bridging as in the parent compound, although it became more bent-semi bridging [20a*].

For one of these photoproducts, $[Fe_2(CO)_6(bipy)(P(n\text{-}Bu)_3)]$ (I) the molecular structure, which was determined crystallographically [2], is shown in Fig. 1. We present below the results of a spectroscopic and photochemical study of this complex I.

Results

I. Spectroscopic characterization of the compound I

Figure 2 shows the electronic absorption spectrum of I in 2-Me-THF at 133 K. The band at 630 nm is red-shifted with respect to the corresponding band of $[Fe_2(CO)_7(bipy)]$ as the result of replacement of an electron-withdrawing carbonyl group by $P(n\text{-}Bu)_3$. As in the case of this latter complex [2], the 630 nm band of I is assigned to MLCT transitions to the lowest π^* orbital of bipy. The second band at 400 nm is assigned to MLCT transitions to the second π^* orbital of bipy, as for other bipy complexes [3]. Support for these assignments is given by the resonance

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* A reference number with an asterisk indicates a note in the list of references.

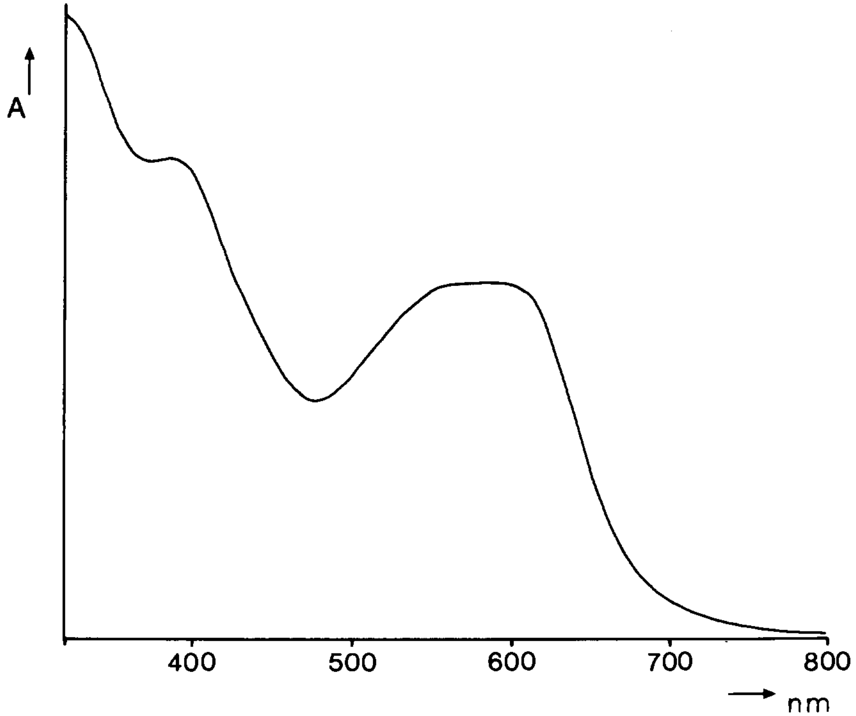


Fig. 2. Electronic absorption spectrum of $[Fe_2(CO)_6(bipy)(P(n\text{-}Bu)_3)]$ in 2-Me-THF at 133 K.

Raman (rR) spectra, obtained by excitation into these bands; such spectra give valuable information about the changes of normal coordinates and bond characters during allowed electronic transitions [4–9].

Figure 3 shows the rR spectra of I obtained by excitation at 458, 514.5 and 600 nm. The most pronounced bands in these spectra (recorded for 3 mg of complex I in a KNO_3 pellet of 200 mg) at 110 K are at 1605, 1560, 1488, 1322, 1272, 1172, 1023 and 661 cm^{-1}. They all belong to bipy modes [10,11], and were found in the rR spectra of $Ru(bipy)_3^{2+}$ [12–14] and of other carbonyl-bipy complexes [9–15]. As for these latter complexes, both absorption bands of I therefore belong to metal to bipy MLCT transitions. A common feature of all these complexes is the presence of several MLCT transitions from various metal orbitals. For complex I this feature is evident from the appearance of a structured lowest-energy band in 2-Me-THF at 133 K. The most strongly allowed electronic transition within this band takes place between the metal d_π and bipy π^* orbitals that have the same symmetry and are responsible for the π-backbonding from the metal to the bipy ligand. Of the highest frequency rR bands, those at 1605 and 1560 cm^{-1} belong to the in-plane ring-stretching vibrations [16], while the 1488 cm^{-1} band can be assigned to a ring-stretch/CH-bending mode. The main difference between the rR spectra excited with λ 600 nm and λ 458 nm into the first and second absorption band of complex I, respectively, is a change in intensities of the 1605 and 1560 cm^{-1} bands relative to that of the 1488 cm^{-1} band. The first two bands increase in intensity upon going to higher energy excitation into the second absorption band; a similar effect was

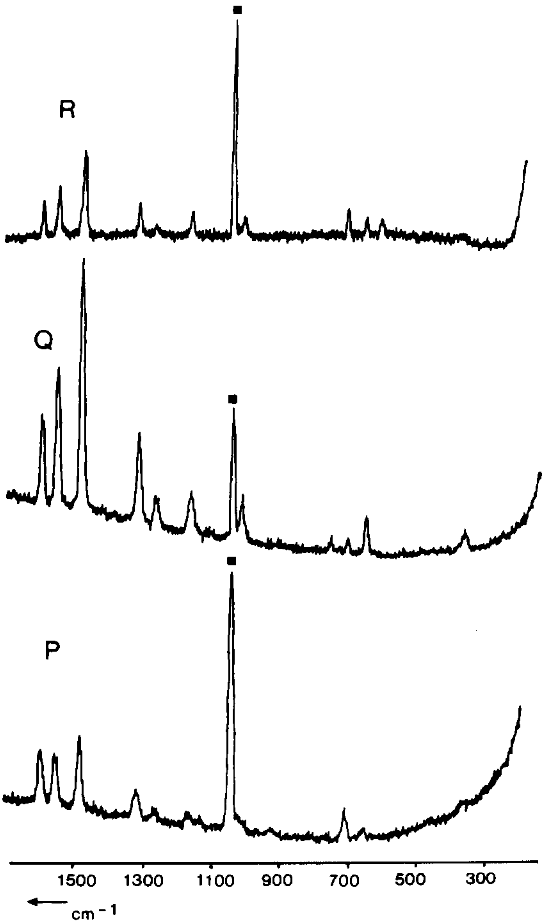


Fig. 3. Resonance Raman spectra of $[Fe_2(CO)_6(bipy)(P(n\text{-}Bu)_3)]$ recorded from KNO_3 pellets at 110 K. P: λ_{exc} 458 nm; Q: λ_{exc} 514.5 nm; R: λ_{exc} 600 nm (■ = NO_3^-).

observed by Poizat and Sourisseau for $Ru(bipy)_3^{2+}$ [11]. Since these two highest frequencies are pure ring-stretch vibrations, excitation into the second MLCT-band evidently leads to a more pronounced lengthening of the C=C and C=N bonds of the bipy ligand.

The rR spectrum excited with λ 458 nm shows a decrease of intensity for all the Raman bands relative to those in the other spectra. This is probable due to the near coincidence of the second MLCT state with a LF state, which gives rise to an anti-resonance Raman effect [17]. Thus according to the rR data both absorption bands belong to MLCT transitions to bipy, although there may be an underlying LF transition at shorter wavelengths.

For the α-diimine (L) complexes $M(CO)_4L$ (M = Cr, Mo, W) [18] and $Ph_3SnMn(CO)_3L$ [7] an extra rR effect was observed for the (symmetrical) stretching mode of the carbonyl ligand(s) in the *cis* position with respect to L. This effect was attributed to a delocalization of the lowest MLCT state over the carbonyl(s) by through-space overlap between the π^*-orbitals of L and CO. In the rR spectrum of

I no such rR effect is observed. This is consistent with the structure of the complex, in which the CO ligand is *trans* to bipy (see Fig. 1), and through-space overlap between the π^*-orbitals of these ligands thus precluded. The CO-stretching modes of complex I in 2-Me-THF at 133 K are shown in Fig. 4. The band at 1815 cm^{-1} belongs to the stretching mode of the bent semi-bridging C(25)O(1) ligand (Fig. 1) *trans* to $P(n\text{-}Bu)_3$, and the 1739 cm^{-1} band to that of the symmetrically-bridged C(24)O(2) group *trans* to one of the N atoms of the bipy ligand. The other bands at higher frequencies belong to the terminal carbonyls of I.

II. Photochemistry

Under the conditions of the photochemical experiments complex I did not react thermally with phosphines or N-donor ligands. All reactions discussed hereafter are therefore photochemical in nature, although secondary thermal reactions were observed. For all the experiments 2-Me-THF, was used as a solvent, since it readily dissolves this type of organometallic complexes and has a low glass-point ($T \simeq 130$ K). It also has the great advantage over, e.g., alkanes (in addition to giving higher solubilities), that it is a weakly coordinating solvent at low temperatures. Thus, whereas coordinatively unsaturated species formed in the photochemical event readily decompose, dimerize, or revert to the parent compound in alkanes, they are stabilized by coordination of 2-Me-THF molecules at low temperatures. When the temperature is raised above 170 K these solvent molecules are readily replaced by nucleophilic ligands.

Prolonged irradiation at room temperature in the presence of a nucleophile resulted in the photodecomposition of I into two mononuclear complexes. When, however, the complex was irradiated for only a few seconds, an intermediate was observed in the IR spectrum and decomposed thermally into the mononuclear complexes. This intermediate was stable enough for observation only for phosphines as substituting ligands, and in the case of N-donor ligands were apparently too short-lived to be detected by standard IR techniques. Lowering the temperature of the solution caused an increase of stability of the intermediate, and at 133 K in 2-Me-THF it was the only product formed for most nucleophiles. Only in the case of pyridine and n-propylamine mononuclear complexes were then observed as side-products. Since the nature of these photochemical reactions does not vary with temperature, only those at lower temperatures are discussed below.

Initially a solution of I in 2-Me-THF was irradiated at 133 K into the MLCT-bands in the absence of a substituting ligand. No reaction was observed, which is a very remarkable in view of the fact that this solvent has been shown to take part in photosubstitution reactions at this temperature [2,19]. Thus, even the analogous complex $[Fe_2(CO)_7(bipy)]$ reacts under these conditions to give $[Fe_2(CO)_6(bipy)(2\text{-}Me\text{-}THF)]$, which is stable up to about 170 K. Apparently, the back-reaction of the primary photoproduct of I with CO is much more efficient than complex formation with a solvent molecule. Both steric and electronic effects are expected to contribute to this stability of the solvent-coordinated complex.

In a second experiment, complex I was irradiated under the same conditions in the presence of various PR_3 (R = c-Hex, OPh, Ph, n-Bu, OMe) and N-donor (pyridine, n-propylamine, acetonitrile) ligands. Variation of the wavelength of the laser line from 458 to 580 nm had no effect on the nature of the reaction. Figure 4 shows the CO-stretching region of the IR spectrum of the parent compound and the

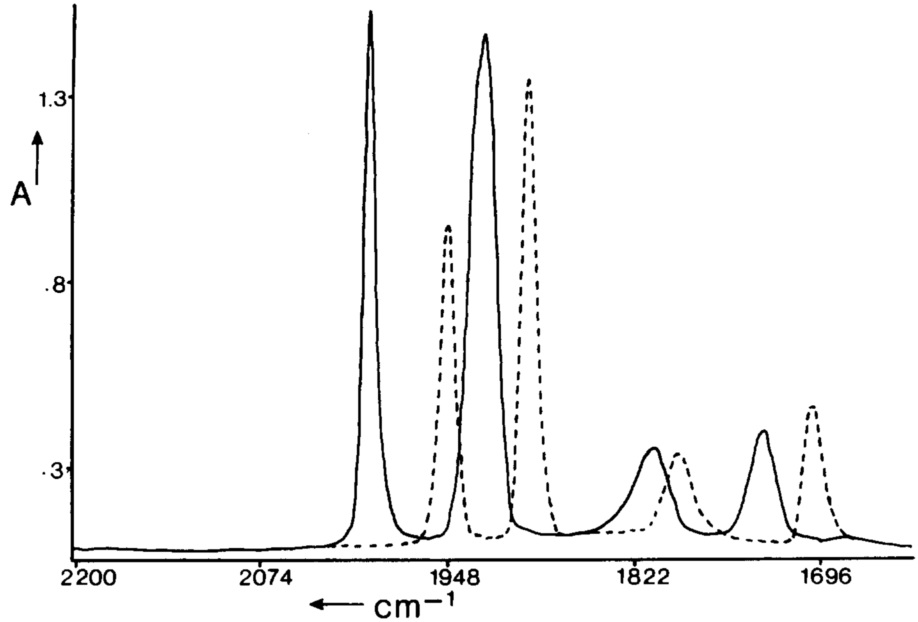


Fig. 4. The CO-stretching region of the IR spectra of [$Fe_2(CO)_6$(bipy)(P(n-Bu)$_3$)] (drawn) and [$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(PPh_3)] (dashed) at 133 K in 2-Me-THF.

product of its reaction with PPh_3 and Fig. 5 shows the corresponding spectral changes for the reaction with pyridine. The figures indicate that similar species are formed as the photoproduct in the two cases although extra bands from thermal decomposition products are observed for the reaction with pyridine.

In both cases the photoproduct is suggested to be the binuclear complex [$Fe_2(CO)_5$(bpy)(P(n-Bu)$_3$(L)] (L = P- or N-donor ligand) (II), formed by substitution of the last CO ligand of the Fe(CO)(bipy)(P(n-Bu)$_3$) moiety in I by L. Support for this proposal comes from the following observations. First, both reactions result in the appearance of a weak band due to free CO at 2132 cm^{-1}; comparison of the intensity of this band with those of the photoproduct and parent compound, taking into account the extinction coefficients of the bands, shows that only one CO ligand is photosubstituted by L. Secondly, two stretching modes of bridging carbonyls appear in the IR spectrum, which means that the binuclear CO-bridged structure is retained. The question arises as to whether a CO ligand of the Fe(1)-bipy fragment or of the Fe(2)(CO)$_3$-moiety is displaced. Because of the tendency of the products to decompose at higher temperatures, no reliable ^{31}P NMR spectra could be obtained for them, and structural information could only be derived from the IR spectra. All the photoproducts show only two IR bands for the remaining three terminal carbonyls (see Table 1). Since accidental coincidence of CO-stretching modes can be rejected in this case in view of the large number of photoproducts studied, these two bands can only be assigned to the vibrations of an Fe(CO)$_3$ moiety having local C_{3v} symmetry. This means that the last CO ligand of the Fe(1)-bipy fragment has been photosubstituted.

The appearance of only two bands for the terminal carbonyls in the case of substitution of a CO ligand of the Fe(CO)$_3$ fragment cannot be easily rationalized.

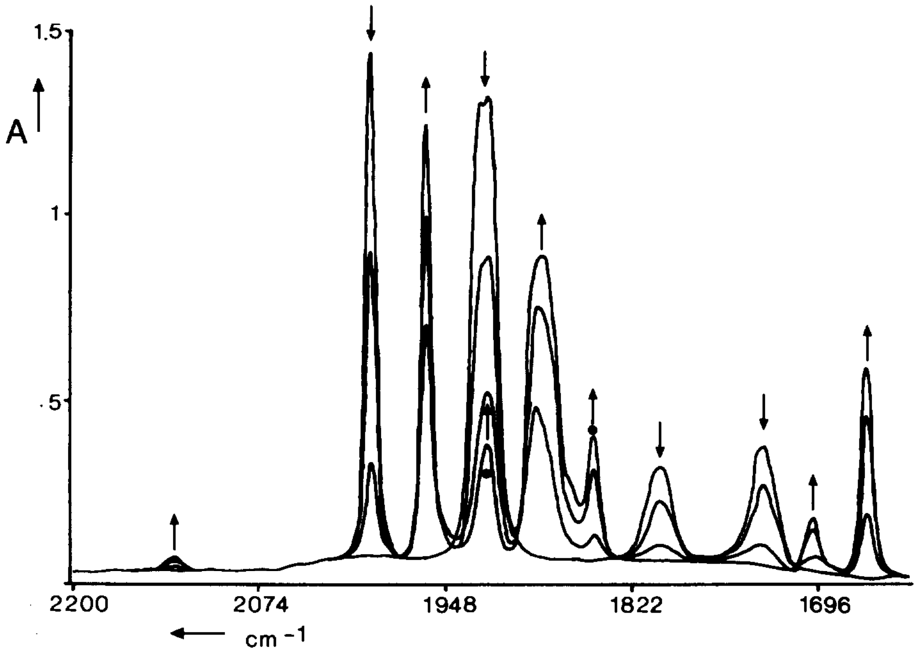


Fig. 5. IR-spectral changes in the CO-stretching region during the photochemical reaction of [$Fe_2(CO)_6$(bipy)(P(n-Bu)$_3$)] with pyridine at 133 K in 2-Me-THF (● = decomposition product).

Substitution of CO by PPh_3 causes a shift of all the CO-stretching modes to lower frequencies, and just as in the parent compound two different bridging carbonyls are observed, one symmetrically bridging (ν(CO) 1702 cm^{-1}) and the

Table 1

CO-stretching frequencies of all PR_3 and N-donor substituted photoproducts at 133 K in 2-Me-THF

Complex	CO-stretching frequencies (cm^{-1})
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(pyridine)]	1961(s), 1884(s) 1701(w), 1664(m)
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(n-propylamine)]	1956(s), 1866(s) 1708(w), 1673(m)
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(CH_3CN)]	1953(s), 1888(s) 1791(w), 1724(w)
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)$_2$]	Isomer 1 1956(s), 1886(s) 1701(w), 1668(m)
	Isomer 2 1940(s), 1888(s) 1777(w), 1699(m)
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(PPh_3)]	1949(s), 1893(w) 1791(w), 1702(m)
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(P(OPh)$_3$)]	1962(s), 1915(s) 1794(w), 1716(m)
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(P(OMe)$_3$)]	1958(s), 1899(s) 1795(w), 1707(m)
[$Fe_2(CO)_5$(bipy)(P(n-Bu)$_3$)(P(c-Hex)$_3$)]	1936(s), 1884(s) 1792(w), 1696(m)

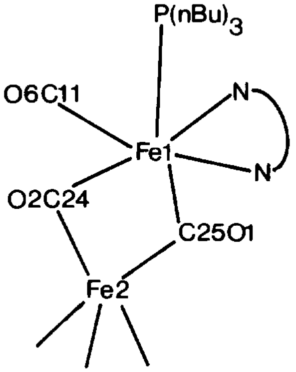
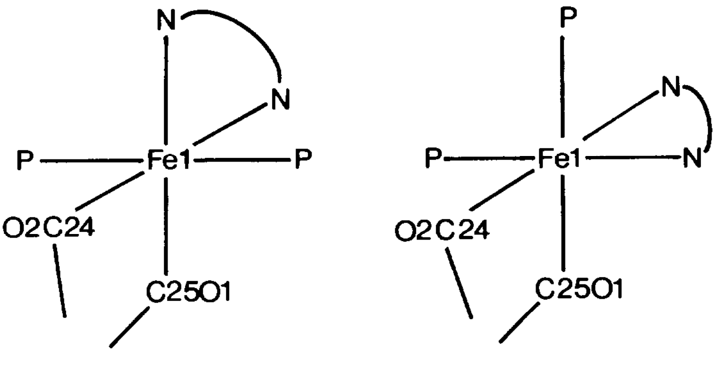


Fig. 6. Schematic representation of the local structure around Fe(1) in complex I.

other bent-semi bridging (ν(CO) 1791 cm^{-1}) [20a*]. None of the vibrations is more affected than the others, and this holds for all the PR substituted products (Table 1). This feature can best be explained by taking into account the local structure of the Fe(1)-bipy moiety (Fig. 1) in the parent compound, which is shown schematically in Fig. 6. In a discussion of the photochemistry of [$Fe_2(CO)_7$(bipy)] [2] we have shown that the bridging character of C(25)O(1) in the photoproduct [$Fe_2(CO)_6$(bipy)(L)] strongly depends on the electron donating properties of the ligand L *trans* to it (L = $P(n\text{-}Bu)_3$ in Fig. 6). Whereas C(24)O(2) is symmetrically bridging in [$Fe_2(CO)_7$(bipy)] and all its photosubstitution products, C(25)O(1) is semi-bridging in the unsubstituted product but it becomes more and more symmetrically bridging (bent semi-bridging) with increasing electron-donating character of the substituted ligand. This behaviour is reflected in the stretching mode of the C(25)O(1) ligand, which gradually decreases for the complexes [$Fe_2(CO)_6$(bipy)(L)] (L = CO, PR_3, N-donor ligand) from 1855 cm^{-1} for L = CO to 1775 cm^{-1} for L = pyridine.

Since C(11)O(6) is not *trans* to one of the bridging carbonyls in this case photosubstitution of this ligand by PPh_3 or by any other PR_3 ligand (except $P(n\text{-}Bu)_3$, vide infra) does not particularly influence C(24)O(2) or C(25)O(1). It merely causes an increase of electron density at Fe(1) that is in turn transferred to both bridging carbonyls and to the $Fe(CO)_3$ moiety. The reaction with pyridine is quite different. The frequency shifts of the terminal CO groups are similar to those of the PR_3-substituted complexes. C(25)O(1), however, changes its bond character rather dramatically from bent-semi bridging in complex I (ν(C(25)O(1)) 1805 cm^{-1}) to symmetrically bridging in the pyridine substituted complex (ν(C(25)O(1)) 1701 cm^{-1}). Such a large shift for ν(C(25)O(1)) can only result from a change of electron-donating capacity of the ligand *trans* to C(25)O(1). This means that pyridine having replaced C(11)O(6) changes position with $P(n\text{-}Bu)_3$. Such a conformation of the complex will, of course, be more stable. *N*-Propylamine behaves similarly, but the CH_3CN complex has a frequency pattern which is closely analogous to that of the PR_3-substituted complexes.

An exception is also the $P(n\text{-}Bu)_3$-substituted complex, [$Fe_2(CO)_5$(bipy)($P(n\text{-}Bu)_3)_2$]. Upon irradiation of complex I in 2-Me-THF at 133 K, a complex (isomer 1) is formed with two symmetrically bridging carbonyls (ν(CO) 1701 and 1668

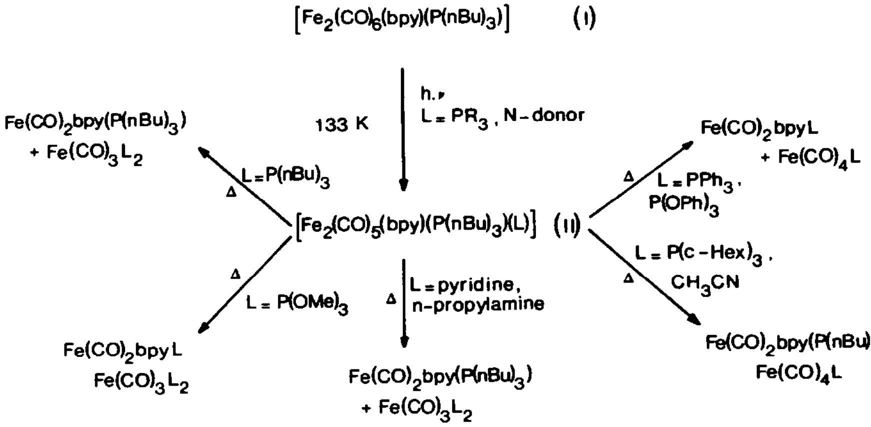


isomer 1 isomer 2

Fig. 7. Schematic representation of the two isomers of [$Fe_2(CO)_5(bipy)(P(n\text{-}Bu)_3)_2$].

cm^{-1}, respectively) just as in the pyridine substituted complex. Raising the temperature to about 170 K causes isomerization to a complex (isomer 2) with bridging carbonyl frequencies close to those of the other phosphine-substituted complexes. These isomers probably differ in the position of one of the $P(n\text{-}Bu)_3$ ligands. In isomer 1 one of the nitrogen atoms of bipy will be *trans* to C(25)O(1), giving rise to a similar low frequency for this ligand as in the pyridine substituted complex. Isomer 2, on the other hand, has the same structure as the other PR_3-substituted complexes, with one of the $P(n\text{-}Bu)_3$ ligands *trans* to C(25)O(1). Possible structures for these isomers are shown in Fig. 7.

Raising the temperature causes a thermal decomposition of the photoproducts into mononuclear complexes, the N-donor-substituted complexes being most sensitive to this reaction. Even at 133 K these latter compounds have partly decomposed (see Fig. 5), whereas the phosphine-substituted complexes start decomposing above 200 K. The decomposition products are shown in Scheme 1 and their CO-stretching frequencies are collected in Table 2.



Scheme 1

Table 2

CO-stretching frequencies of all the decomposition products

Product	ν(CO) (cm^{-1})
$Fe(CO)_2bipy(P(n\text{-}Bu)_3)$	1923, 1852
$Fe(CO)_2bipy(PPh_3)$	1925, 1868
$Fe(CO)_2bipy(P(OMe)_3)$	1929, 1872
$Fe(CO)_2bipy(P(OPh)_3)$	1927, 1873
$Fe(CO)_3(P(n\text{-}Bu)_3)_2$	1871
$Fe(CO)_3(P(OMe)_3)_2$	1907
$Fe(CO)_4PPh_3$	2047, 1971, 1941
$Fe(CO)_4P(OPh)_3$	2064, 1988, 1952
$Fe(CO)_4P(c\text{-}Hex)_3$	2040, 1961, 1928
$Fe(CO)_4CH_3CN$	2058, 1961, 1948
$Fe(CO)_3(pyridine)_2$	1968, 1876/1867
$Fe(CO)_3(n\text{-}propylamine)_2$	1956, 1869/1858

The formation of these decomposition products can be explained as follows. As a result of the large increase of π-backbonding from Fe(1) to the bridging carbonyls in the photosubstitution reaction, the bonds of these ligands to Fe(2) are weakened and easily broken upon raising of the temperature. At the same time the Fe(1) moiety looses the substituted ligand, giving the decomposition product $[Fe(CO)_2(bipy)(P(n\text{-}Bu)_3]$. In the case of $L = PPh_3$, $P(OPh)_3$ or $P(OMe)_3$ in II, $[Fe(CO)_2(bipy)(L)]$ is formed instead, since these ligands are better electron acceptors than $P(n\text{-}Bu)_3$. The other decomposition products $Fe(CO)_4L$ and $Fe(CO)_3L_2$ are formed by reaction of the $Fe(CO)_3$ fragment with L in competition with CO still present in the solution.

This mechanism for the decomposition is similar to that proposed by Cotton and Troup [1] for the reaction between $Fe_2(CO)_9$ and bipy. In $Fe_2(CO)_9$, consisting of two $Fe(CO)_3$ groups linked by three bridging carbonyls, two terminal carbonyl ligands are replaced by bipy to give the intermediate shown in Fig. 8a. As a result of the large electron density at the Fe atom bonded to bipy, one of the bridging carbonyls becomes terminal and another semi-bridging, as shown in Fig. 8b.

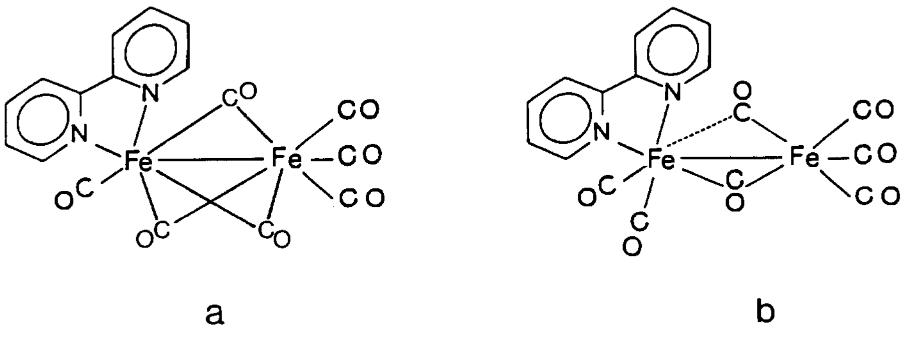


Fig. 8. (a) Intermediate formed in the reaction between $[Fe_2(CO)_9]$ and bipyridine. (b) Structure of $[Fe_2(CO)_7(bipy)]$.

The photochemical mechanism

The photosubstitution reactions are dissociative in character, since the quantum yields do not depend on the cone-angle, the concentration, or the basicity of the substituting ligand. The question remains from which excited state these reactions take place. The complexes were irradiated into the lowest energy bands, which belong, as indicated by the resonance Raman spectra, to MLCT transitions. Usually such MLCT states are not reactive, since the decrease of π-backbonding to L with respect to the ground state is normally compensated by an increase of ionic interaction. Reactions can, however, take place from a close-lying reactive LF state as e.g. in the case of $[Ru(bipy)_3{}^{2+}]$ [21]. This latter complex is relatively photostable at room temperature, but photodecomposes with increase in temperature because of thermal population of a reactive LF state. Similar close-lying MLCT and LF states have been shown to be present in the complexes $[Ru(NH_3)_5(py\text{-}X)^{2+}]$ [22,23] and $[M(CO)_5(L)]$ (M = Cr, Mo, W; L = py-X, pyridazine) [24].

The absorption spectrum of I does not allow identification of LF transitions in the visible region because of the presence of intensive MLCT bands. In the resonance Raman spectra, however, the presence of such a LF transition around 450 nm is evident from an anti-resonance Raman effect observed at this excitation wavelength (vide supra).

At 133 K, however, the photosubstitution reaction takes place by irradiation into the lowest-energy MLCT band even at about 600 nm, far away from the lowest LF transition. So, internal conversion from the lowest ^{1}MLCT state into the ^{1}LF state can be excluded here, and the reaction will proceed from the lowest ^{3}LF state after direct intersystem crossing from the ^{1}MLCT state.

A reaction from a low-lying metal–metal antibonding $^3\sigma\sigma^*$ state, as has been observed for the non-bridged metal–metal bonded complexes $[M_2(CO)_{10}]$ and $[M_2(CO)_8(bipy)]$ (M = Mn, Re) [25], can be rejected here. A reaction from such a state, if it took place at all, would lead to splitting of the metal–metal bond, and therefore to photodecomposition of complex I into mononuclear complexes.

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