

## Photochemical and Photocatalytic Behaviour of 'Flyover-bridge' Complexes

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The photochemical behaviour of a number of flyover-bridge complexes  $[\text{Fe}_2(\text{CO})_6\{(\text{RC}_2\text{R})_2\text{CO}\}]$  is discussed with regard to their electronic structure. In the case of  $[\text{Fe}_2(\text{CO})_6\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  the overall photochemical event is the formation of an unsaturated species upon CO loss, which evolves, in the absence of any Lewis bases, to the fragments  $[\text{Fe}(\text{CO})_3\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$ ,  $\text{C}_4\text{Ph}_4\text{CO}$ , and  $[\text{Fe}(\text{CO})_5]$ . Photosubstitution of CO by phosphine occurs very rapidly and proceeds stereospecifically in a pseudo-axial position as assessed by  $^{13}\text{C}$  n.m.r. studies. The title complexes exhibit photocatalytic activity toward olefin isomerization and, interestingly, this reaction can be activated simply by sunlight exposure. The dienone chain clasps the metal-metal bond, preventing complex decomposition and acts as a good sensitizer for the sunlight.

The reactions between acetylenes and iron carbonyls,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Fe}_2(\text{CO})_9]$ , and  $[\text{Fe}_3(\text{CO})_{12}]$ , give rise to a plethora of stable organometallic compounds.<sup>1,2</sup> Usually alkyne oligomerization takes place (with or without concomitant CO insertion) leading to interesting co-ordination modes of the organic chain to the metallic framework. Among the dimerization products, the diferracycloheptadiene or 'flyover-bridge' complexes,  $[\text{Fe}_2(\text{CO})_6\{C(\text{R})=C(\text{R}')C(\text{O})-C(\text{R}'')=C(\text{R}''')\}]$ , represent an important class since they are useful stoichiometric precursors in the syntheses of cyclopentadienones, quinones, hydroquinones, and their related six-membered heterocycles.<sup>3</sup> Solid-state structure investigations, carried out by Piron *et al.*<sup>4</sup> ( $\text{R} = \text{R}' = \text{R}'' = \text{R}''' = \text{Me}$ ), Cotton *et al.*<sup>5</sup> ( $\text{R} = \text{R}' = \text{R}'' = \text{R}''' = \text{Ph}$ ), and Pettersen and Cash<sup>6</sup> ( $\text{R} = \text{R}'' = \text{C}\equiv\text{CSiMe}_3$ ,  $\text{R}' = \text{R}''' = \text{SiMe}_3$ ), have shown a rather unusual arrangement of these molecules: the two  $\text{Fe}(\text{CO})_3$  units are symmetrically bridged by the twisted dienone chain (Figure 1). The equivalent environment of the two metallic moieties first suggested by i.r. analysis<sup>1</sup> has been confirmed by Mössbauer<sup>7</sup> as well as by variable-temperature  $^{13}\text{C}$  n.m.r. studies.<sup>5,8</sup> The interaction of the dienone chain with the  $\text{Fe}_2(\text{CO})_6$  unit has been described by Thorn and Hoffmann<sup>9</sup> and confirmed by a gas-phase u.v. photoelectron spectroscopic study coupled with *ab initio* calculations.<sup>10</sup> The dynamics<sup>11</sup> and electrochemistry<sup>12</sup> of such derivatives have been reported very recently.

We have been interested in the photochemical behaviour of transition-metal clusters,<sup>13,14</sup> especially in view of their potential use as homogeneous photocatalysts. However, one difficulty associated with cluster use in catalysis is their instability toward thermal or photochemical activation, which leads to irreversible decomposition to lower nuclearity fragments.<sup>15</sup> While this is particularly true for binary carbonyl derivatives, the co-ordination of polydentate ligands or organic chains provides an enhancement in their stability due to the multicentred interactions between such ligands and the metallic skeleton.<sup>16</sup> The 'flyover-bridge' complexes may be expected to fulfil this requirement: the dienone chain interacts with the  $\text{Fe}_2(\text{CO})_6$  moiety in a multicentred  $\sigma/\pi$  fashion and strongly clasps the iron-iron bond.

### Experimental

The title compounds were synthesized from  $[\text{Fe}_2(\text{CO})_9]$  and the

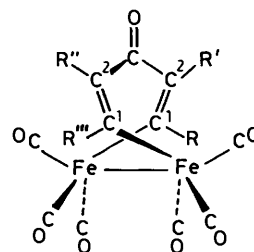


Figure 1. Structure of flyover-bridge complexes:  $\text{R} = \text{R}' = \text{R}'' = \text{R}''' = \text{Me}$ , (1);  $\text{R} = \text{R}' = \text{R}'' = \text{R}''' = \text{Et}$ , (2);  $\text{R} = \text{R}'' = \text{Me}$ ,  $\text{R}' = \text{R}''' = \text{Ph}$ , (3);  $\text{R} = \text{R}'' = \text{Ph}$ ,  $\text{R}' = \text{R}''' = \text{Me}$ , (4);  $\text{R} = \text{R}' = \text{Ph}$ ,  $\text{R}'' = \text{R}''' = \text{Me}$ , (5); and  $\text{R} = \text{R}' = \text{R}'' = \text{R}''' = \text{Ph}$ , (6)

appropriate alkyne according to the literature procedures.<sup>5,8</sup> After crystallization from *n*-hexane- $\text{CHCl}_3$  (4:1, v/v), their purity was checked by t.l.c., i.r., and mass spectrometry.

The  $^{13}\text{C}$ CO-enrichment of  $[\text{Fe}_2(\text{CO})_6\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  (6) was obtained by stirring a solution of (6) (200 mg) in toluene (20  $\text{cm}^3$ ) in a Pyrex Schlenk tube in the presence of gaseous  $^{13}\text{C}$ CO (Monsanto) ranging from 0.1 to 0.5 atm (depending on the desired degree of enrichment) exposed to sunlight for 8 h at room temperature.

U.v.-visible spectra were recorded on a Jasco Uviolet 650 spectrophotometer; i.r. spectra on a Perkin-Elmer 283 B machine with a Perkin-Elmer 3600 data station. N.m.r. spectra were obtained with a JEOL GX 270/89 spectrometer, mass spectra with a Kratos AEI MS 12 machine.

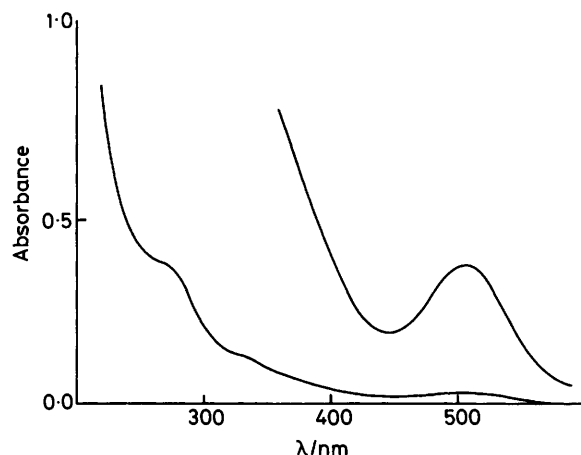
Solvents (Merck grade) were dried by standard procedures. Irradiation was performed using a Hanau medium-pressure mercury lamp equipped with the appropriate filters. Light intensity was determined by ferrioxalate actinometry.<sup>17</sup> Preparative photolysis was performed at ambient temperature with a 500-W Italquartz mercury lamp equipped with a water-cooled quartz finger and aqueous  $\text{NaNO}_2$  cut-off filter ( $\lambda > 390$  nm).

Thin-layer chromatography (t.l.c.) was carried out on commercial Merck plates (coated with a 0.25-mm layer of silica) eluting with *n*-heptane-diethyl ether (4:1, v/v).

For the photocatalytic experiments, deaerated solutions of the title compounds and pent-1-ene were introduced in sealed quartz vessels. These solutions were either irradiated with the

**Table 1.** Colours and  $\lambda_{\max}$  and  $\tilde{\nu}_{\max}$  values of the flyover-bridge complexes

Complex	Colour	$\lambda_{\max}/\text{nm}$	$\tilde{\nu}_{\max}/\text{cm}^{-1}$
(1) $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Me})=\text{C}(\text{Me})\text{C}(\text{O})\text{C}(\text{Me})=\text{C}(\text{Me})\}]$	Yellow	459	21 786
(2) $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Et})=\text{C}(\text{Et})\text{C}(\text{O})\text{C}(\text{Et})=\text{C}(\text{Et})\}]$	Dark yellow	453	22 075
(3) $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Me})=\text{C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Me})\}]$	Yellow-orange	463	21 598
(4) $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})=\text{C}(\text{Me})\text{C}(\text{O})\text{C}(\text{Me})=\text{C}(\text{Ph})\}]$	Red-orange	482	20 747
(5) $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})=\text{C}(\text{Me})\text{C}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Me})\}]$	Red	496	20 161
(6) $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Ph})\}]$	Red	502	19 920

**Figure 2.** Absorption spectrum of (6) in n-heptane at 300 K (upper line = expanded visible region)

filtered light of a Hanau Q-400 medium-pressure lamp or exposed to solar light. Aliquots of the solution were withdrawn with a gas-tight syringe through a port provided with a gas chromatography cap. The degree of *cis-trans* isomerization of the initial olefin was evaluated using a Perkin-Elmer F17 gas chromatograph using a Supelco 23% SP-1700 on 80/100 Chromosorb PAW.

## Results and Discussion

**Electronic Spectra and Photolysis of Flyover-bridge Complexes.**—The u.v.–visible spectrum of (6) in n-heptane is shown in Figure 2. This spectrum has a band at 502 nm ( $\epsilon$  2 500), a shoulder at 340 nm ( $\epsilon$  8 200), and a very intense band at 270 nm ( $\epsilon$  24 500  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ). The spectrum recorded at low temperature (78 K) shows a blue shift and a sharpening of the band at 502 nm, suggesting that this absorption is attributable to an electronic transition involving the metal–metal bond.<sup>18</sup> The u.v.–visible spectra of all the flyover-bridge derivatives (1)–(6) are qualitatively similar;  $\lambda_{\max}$  and  $\tilde{\nu}_{\max}$  values for the visible bands are collected in Table 1.

Irradiation of a n-heptane solution of (6) under  $\text{N}_2$  at  $\lambda \geq 400 \text{ nm}$  with light of intensity in the range  $10^{-7}$ – $10^{-6}$  einstein  $\text{min}^{-1}$  leads to slow decomposition of  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  (6) to  $[\text{Fe}(\text{CO})_3\{\text{C}(\text{PhC}_2\text{Ph})_2\text{CO}\}]$ ,  $\text{C}_4\text{Ph}_4\text{CO}$  (tetraphenylcyclopentadienone or tetracyclone), and  $[\text{Fe}(\text{CO})_5]$ . All these compounds have been isolated and identified from preparative photolysis {evidence of the presence of  $[\text{Fe}(\text{CO})_5]$  in the vapour phase has been obtained by mass spectrometry}. I.r. spectra recorded in the range 1 800–1 600  $\text{cm}^{-1}$  during the irradiation confirm the formation of  $[\text{Fe}(\text{CO})_3\{\text{C}(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  and tetracyclone; in fact, besides the decreasing band at 1 657  $\text{cm}^{-1}$  [typical of (6)], bands at

1 635 and 1 710  $\text{cm}^{-1}$  (corresponding to the C=O stretching mode of the two above mentioned compounds respectively) increase with irradiation time. This decomposition has precedents in the thermal behaviour of flyover-bridge complexes.<sup>1</sup>

Unfortunately, the determination of the disappearance quantum yield for complex (6) is problematic because of the formation of violet tetracyclone, which shows a visible band at 506 nm ( $\epsilon$  1 200  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) and which therefore overlaps with that of (6). The decrease in absorbance at 502 nm with irradiation time is not linear except for a short interval at the beginning of irradiation. This is too short ( $\leq 2 \text{ min}$ ) to calculate a disappearance quantum yield ( $\phi$ ) accurately. Extrapolation of this linear portion of the plot gives an estimated  $\phi_{\text{disapp.}} \cong 10^{-2}$ . When the irradiation is carried out under CO instead of  $\text{N}_2$ , the rate of disappearance of (6) decreases by at least one order of magnitude. On the contrary in  $\text{CCl}_4$  (a radical scavenger) the rate slightly increases.

On the basis of these experimental data, the photochemical behaviour of (6) seems to be consistent with the overall formation of an unsaturated species upon CO loss, which evolves, in the absence of any Lewis bases, to the above described decomposition products. The loss of CO as the final photochemical act is corroborated by the rapid incorporation of  $^{13}\text{CO}$  into (6) occurring when a solution of the complex is stirred in toluene under gaseous  $^{13}\text{CO}$  (0.2 atm) and exposed to sunlight. The reaction has been followed by the decrease in the i.r. highest frequency band (2 075  $\text{cm}^{-1}$ ) which represents the all- $^{12}\text{CO}$  molecules. This absorption completely disappears within a few hours. The same reaction carried out in the dark shows a negligible enrichment in  $^{13}\text{CO}$ . In an attempt to relate the observed photochemical behaviour of the flyover-bridge complexes with their electronic structure, it is worth considering the extended-Hückel molecular orbital scheme of the flyover-bridge system, first proposed by Thorn and Hoffmann<sup>9</sup> for the  $[\text{Fe}_2(\text{CO})_6\{(\text{HC}_2\text{H})_2\text{C}=\text{CH}_2\}]$  molecule in the hypothetical  $\text{C}_{2v}$  geometry and then modified for the  $[\text{Fe}_2(\text{CO})_6\{(\text{HC}_2\text{H})_2\text{CO}\}]$  molecule in the real  $\text{C}_2$  geometry.<sup>10</sup> The highest occupied molecular orbital (h.o.m.o.) (*a* symmetry) represents a direct metal–metal bond according to its parentage with the  $1a_1$  orbital of the  $\text{Fe}_2(\text{CO})_6$  fragment<sup>9</sup> ('sawhorse' geometry), and provides a stabilizing interaction with the empty pseudo- $\pi^* 3a$  orbital of the twisted dienone chain.<sup>10</sup> On the other hand, the lowest unoccupied molecular orbital (l.u.m.o.) (*b* symmetry) is metal–metal antibonding in character due to its parentage with the  $b_2$  orbital of the  $\text{Fe}_2(\text{CO})_6$  moiety.<sup>†</sup> In principle, the h.o.m.o.–l.u.m.o. electronic transition (metal–metal to  $\sigma$ – $\sigma^*$  type) is dipole allowed and is to be associated with the visible band at 502 nm.

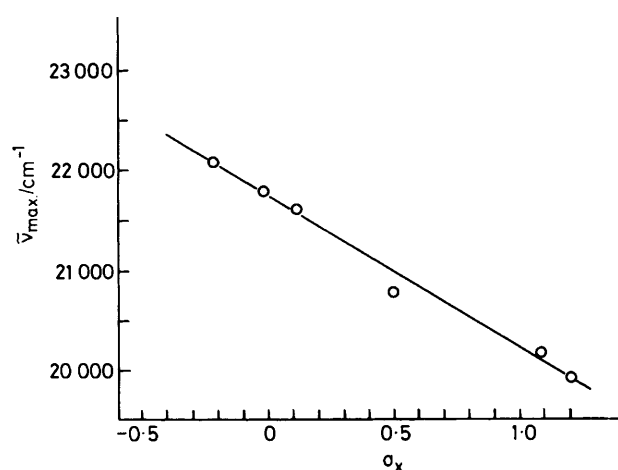
Thus irradiation at  $\lambda \geq 400 \text{ nm}$  should induce homolytic cleavage of the iron–iron bond. Generally, it is not easy to discriminate whether the rupture of this bond is the primary

<sup>†</sup> We gratefully thank Professor Granozzi and Dr. Casarin (University of Padova, Italy) for the extension of the previous extended-Hückel and *ab initio* calculations<sup>10</sup> to the l.u.m.o. of  $[\text{Fe}_2(\text{CO})_6\{(\text{HC}_2\text{H})_2\text{CO}\}]$ .

**Table 2.** Spectroscopic data of the compounds obtained from irradiation in the presence of phosphines

Complex	$\tilde{\nu}(\text{CO})^a/\text{cm}^{-1}$	$^{31}\text{P}$ N.m.r. <sup>b</sup>	$^{13}\text{C}$ N.m.r. <sup>c</sup> (carbonyl region)
(7) $[\text{Fe}_2(\text{CO})_5(\text{PPh}_3)\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$	2 056vs, 2 012vs, 1 997s, 1 994m, 1 657m br	51.7	211.4 (d, 1 C), 211.2 (d, 1 C), 210.4 (s, 1 C), 208.2 (s, 1 C), 207.6 (s, 1 C) <sup>d</sup>
(8) $[\text{Fe}_2(\text{CO})_5(\text{dppe-}P)\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$	2 057vs, 2 012vs, 1 998s, 1 993m, 1 650m br	46.7 (d, 1 P), -12.8 (d, 1 P) ( $^3J_{\text{PP}}$ 30.5 Hz)	212.6 (d, 1 C), 212.4 (d, 1 C), 210.9 (s, 1 C), 208.5 (s, 1 C), 207.8 (s, 1 C) <sup>d</sup>
$[\text{Fe}(\text{CO})_3\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$	2 068s, 2 016s, 1 995s, 1 635m br		208.5
$[\text{Fe}(\text{CO})_2(\text{PPh}_3)\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$	1 994s, 1 947s, 1 631m br	56.9 <sup>e</sup>	216.4 (d, $^2J_{\text{CP}}$ 14.3 Hz)

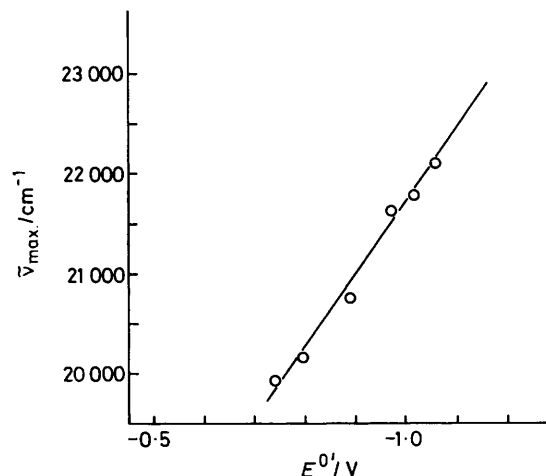
<sup>a</sup> In n-hexane. <sup>b</sup> At 109.6 MHz,  $\text{CDCl}_3$ , chemical shifts are reported positive downfield with respect to external  $\text{H}_3\text{PO}_4$  (85%). <sup>c</sup> At 67.9 MHz,  $\text{CDCl}_3$ . <sup>d</sup> At  $-30^\circ\text{C}$ . <sup>e</sup> Since the sample is highly (ca. 40%)  $^{13}\text{C}$ -enriched,  $^{13}\text{C}$  satellites are detectable and give a  $^2J_{\text{PC}}$  (14.5 Hz) in good accord with that directly found in the  $^{13}\text{C}$  n.m.r. spectrum.



**Figure 3.** Plot of  $\tilde{\nu}_{\text{max}}$  against the abscissa function  $\sigma_x$  obtained from the Taft  $\sigma^*$  values of the R substituents of the flyover-bridge complexes according to equation (1). The least-squares slope is  $-1\,535\text{ cm}^{-1}$  and the correlation coefficient 0.998

photochemical act.<sup>19</sup> Often, the proposed mechanism involves the cleavage of the metal-metal bond as the initial step. In dinuclear species this process leads directly to fragmentation, but we have no experimental evidence that this process occurs in our case. We have evidence, instead, that loss of CO occurs upon irradiation. This does not necessarily imply that the detachment of CO is the primary photochemical act; rupture of the metal-metal bond might still be the initial step. The falling apart of the biradical fragment would be, however, impeded by the 'clamping' effect of the dienone chain which should favour the reformation of the metal-metal bond. Part of the energy absorbed during irradiation would then be dissipated through the ejection of the co-ordinated carbonyl group.

It is already apparent from the colour of the flyover-bridge complexes synthesized (Table 1) that the visible band mainly depends upon the electronic characteristics of the  $\text{C}^1$  substituents of the dienone chain. Indeed,  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})=\text{C}(\text{Me})\text{C}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Me})\}]$  (5) has the same colour (red) as  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Ph})\}]$  (6) and  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Me})=\text{C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Me})\}]$  (3) the same colour (yellow) as  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Me})=\text{C}(\text{Me})\text{C}(\text{O})\text{C}(\text{Me})=\text{C}(\text{Me})\}]$  (1). This obviously indicates that the R and R' substituents deeply influence the energy gap of the  $\sigma\text{-}\sigma^*$  transition. In more quantitative terms, the wavenumbers ( $\tilde{\nu}_{\text{max}}$ ) of the visible bands, which represent the transition energies, depend on the field effect of the  $\text{C}^1$  substituents. As a matter of fact, a good linear correlation ( $r = 0.990$ ) is obtained by plotting the  $\tilde{\nu}_{\text{max}}$  values against the sum of the Taft  $\sigma^*$  values of



**Figure 4.** Plot of  $\tilde{\nu}_{\text{max}}$  against the formal potentials  $E^0$  for the reduction step (0/1-) in complexes (1)-(6); mercury working electrode, acetonitrile solution containing  $0.1\text{ mol dm}^{-3}\text{ NBU}_4\text{ClO}_4$ .<sup>12</sup> The least-squares slope is  $-7\,115\text{ cm}^{-1}\text{ V}^{-1}$  and the correlation coefficient 0.998

the  $\text{C}^1$  substituents only. The best correlation ( $r = 0.998$ ) is observed using, as abscissa parameter, the optimized function  $\sigma_x$  obtained from equation (1). This relationship (Figure 3)

$$\sigma_x = 0.9(\sigma_{\text{R}}^* + \sigma_{\text{R}''}^*) + 0.1(\sigma_{\text{R}'}^* + \sigma_{\text{R}'''}^*) \quad (1)$$

unambiguously indicates that the transmission of the electronic effect from the substituents to the metallic frame is mainly brought about through the  $\text{Fe}-\text{C}^1$   $\sigma$  bonds, in agreement with the previous theoretical<sup>10</sup> and electrochemical<sup>12</sup> studies.

A second free-energy linear correlation can be found when the  $\tilde{\nu}_{\text{max}}$  values are plotted against the formal electrode potential  $E^0$  for the monoreduction process (0/1-) of the flyover complexes<sup>12</sup> (Figure 4). A naïve picture of the reduction process consists of one-electron transfer from the metal electrode Fermi level to the l.u.m.o. of the flyover-bridge complex, which becomes the singly occupied m.o. in the radical anion  $[\text{Fe}_2(\text{CO})_6\{\text{RC}_2\text{R}_2\text{CO}\}]^{\cdot-}$ . Electron-withdrawing substituents decrease the h.o.m.o.-l.u.m.o. gap (then lower the  $\tilde{\nu}_{\text{max}}$  values) and make the reduction easier (in other words at less negative potentials).

*Photolysis of (6) in the Presence of  $\text{PPh}_3$  and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ .*—Irradiation at  $\lambda \geq 400\text{ nm}$  of a toluene solution of  $[\text{Fe}_2(\text{CO})_6\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  (6) and  $\text{PPh}_3$  (1:3 mol ratio) with light of intensity  $10^{-7}\text{ einstein min}^{-1}$  leads to a fast reaction affording the monosubstituted derivative  $[\text{Fe}_2(\text{CO})_5(\text{PPh}_3)\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  (7) (Table 2).

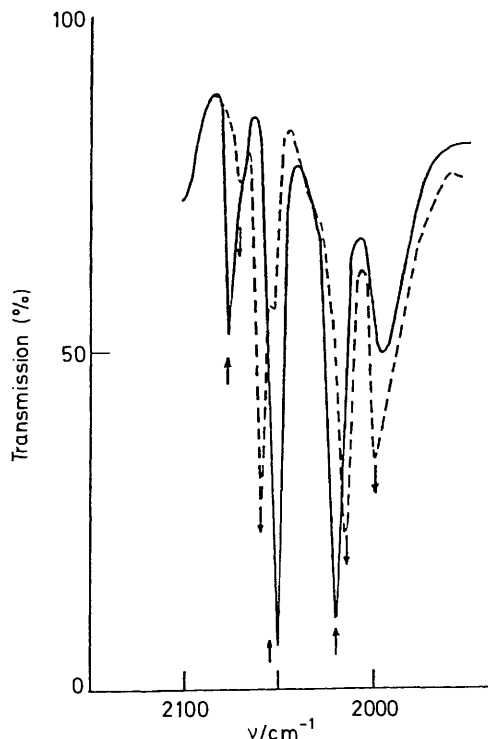


Figure 5. I.r. spectral changes during irradiation of complex (6) in the presence of excess of  $\text{PPh}_3$

This clean substitution reaction confirms that dissociative loss of CO is the overall photochemical process. The reaction can be easily followed by i.r. (Figure 5) and u.v.-visible spectroscopy, where a red shift is evident on passing from (6) ( $\lambda_{\text{max}}$ , 502 nm) to (7) ( $\lambda_{\text{max}}$ , 510 nm;  $\epsilon$  1 150  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ). There is precedent in the electronic spectra of  $[\text{Mn}_2(\text{CO})_{10}]$  and  $[\text{Co}_2(\text{CO})_8]$ <sup>20</sup> dimers where phosphine substitution leads to a decrease in energy for the  $\sigma$ - $\sigma^*$  transition and then to a red shift.

Preparative photolysis ( $\lambda$  390 nm) and t.l.c. separations show that (7) is the only isolable product obtained in ca. 80% yield within a few hours. It is important to recall that the thermal reaction (toluene at reflux) is extremely slow and the yield of (7) is poor. Prolonged irradiation does not give the bisubstituted derivative; on the contrary extensive decomposition is observed. In fact,  $[\text{Fe}_2(\text{CO})_5(\text{PPh}_3)\{\text{(PhC}_2\text{Ph)}_2\text{CO}\}]$  (7) is quite light and heat sensitive: prolonged irradiation or heating at  $T \geq 80^\circ\text{C}$  causes its irreversible fragmentation to  $[\text{Fe}(\text{CO})_3\{\text{(PhC}_2\text{Ph)}_2\text{CO}\}]$  and  $[\text{Fe}(\text{CO})_2(\text{PPh}_3)\{\text{(PhC}_2\text{Ph)}_2\text{CO}\}]$  (mol ratio ca. 1:1, total yield 40%), identified by i.r.,  $^{13}\text{C}$ , and  $^{31}\text{P}$  n.m.r. spectroscopy, and by t.l.c. comparison with authentic samples.<sup>21</sup>

The iron-iron bond is clearly destabilized in (7) with respect to the parent complex (6), according to the decrease in the h.o.m.o.-l.u.m.o. ( $\sigma$ - $\sigma^*$ ) energy gap, although steric constraints between the phenyl group of the organic chain and the phosphine ligand may have a role. In order to assess the solution structure of (7), a  $^{13}\text{C}$  n.m.r. study has been carried out on samples of the parent complex  $[\text{Fe}_2(\text{CO})_6\{\text{(PhC}_2\text{Ph)}_2\text{CO}\}]$  (6) at different degrees of  $^{13}\text{C}$  enrichment. A solution of (6) (15%  $^{13}\text{C}$ -enrichment) in  $\text{CDCl}_3$  at  $-30^\circ\text{C}$  exhibits three signals of integrated intensity 1:1:1 at 209.7, 206.9, and 206.2 p.p.m. as previously reported.<sup>5,8</sup> At this level of enrichment no  $^{13}\text{C}$ - $^{13}\text{C}$  couplings are detectable. When a higher  $^{13}\text{C}$ -enriched sample (ca. 40%) is employed, the two high-field resonances become apparent triplets, where the sidebands are

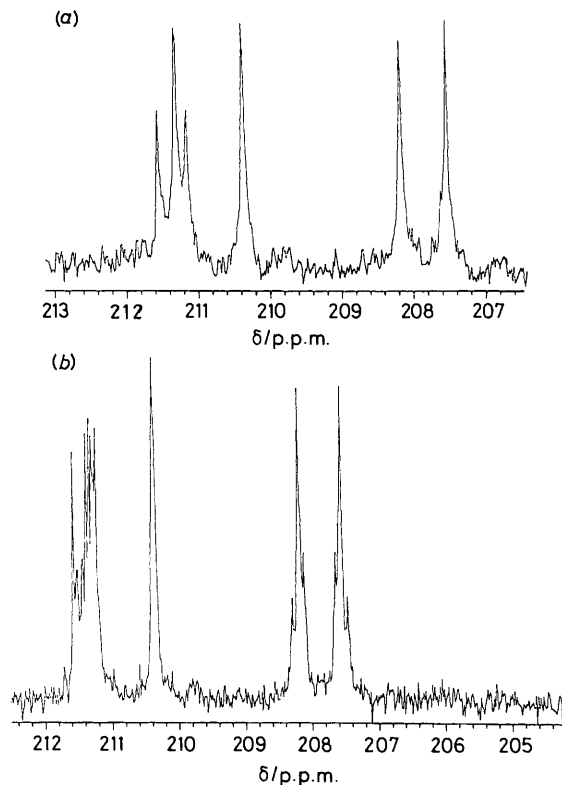


Figure 6.  $^{13}\text{C}$  N.m.r. spectrum (67.9 MHz) of  $[\text{Fe}_2(\text{CO})_5(\text{PPh}_3)\{\text{(PhC}_2\text{Ph)}_2\text{CO}\}]$  (7) in  $\text{CDCl}_3$  at  $-30^\circ\text{C}$  for (a) 15%  $^{13}\text{C}$  enrichment and (b) 40%  $^{13}\text{C}$  enrichment

due to  $^{13}\text{C}$ - $^{13}\text{C}$  coupling ( $^2J_{\text{CC}}$  ca. 10 Hz), which is in the range observed for carbonyls in a *cis* arrangement.<sup>22</sup> On the contrary, the peak at 209.7 p.p.m. remains virtually unchanged. These features lead to the assignment of the downfield resonance to the two carbonyls approximately *trans* to the iron-iron bond (pseudo-axial position).<sup>5</sup> Then the two samples of (6) are directly transformed to (7) by light-assisted reaction with  $\text{PPh}_3$ . The spectrum of the 15%-enriched sample in  $\text{CDCl}_3$  at  $-30^\circ\text{C}$  exhibits three singlets at 210.4, 208.2, and 207.6 p.p.m., easily assigned by analogy to chemical shift values of the unsubstituted  $\text{Fe}(\text{CO})_3$  moiety, and two partially overlapping doublets, centred at 211.4 and 211.2 p.p.m. ( $^2J_{\text{CP}}$  ca. 16 and 10 Hz respectively) attributed to the  $\text{Fe}(\text{CO})_2(\text{PPh}_3)$  unit [Figure 6(a)].

The 40%-enriched sample gives a more complex spectrum: the two high-field peaks appear again as pseudo-triplets with an identical  $^2J_{\text{CC}}$  coupling constant, the downfield signal becomes an entangled multiplet due to the  $^{31}\text{P}$ - $^{13}\text{C}$  and  $^{13}\text{C}$ - $^{13}\text{C}$  splittings, but, importantly, the peak at 210.4 p.p.m., is affected neither by  $^{31}\text{P}$  nor by  $^{13}\text{C}$  couplings and can be unambiguously assigned to the unique carbonyl *trans* to the iron-iron bond [Figure 6(b)]. Precedents of stereospecific substitution of CO by phosphine in a pseudo-axial position have been found in nitrogen,<sup>23</sup> phosphorus,<sup>24</sup> sulphur,<sup>25</sup> and cumulene<sup>26</sup> bridged di-iron complexes where the  $\text{Fe}_2(\text{CO})_6$  moiety has approximately the same sawhorse geometry. Also in  $[\text{Ru}_2(\text{CO})_5(\text{AsPh}_3)\{\text{C}(\text{Ph})=\text{C}(\text{Me})\text{C}(\text{O})\text{C}(\text{Me})=\text{C}(\text{Ph})\}]$  a similar solution structure has been suggested.<sup>11</sup> Finally, an attempt to obtain a disubstituted derivative has been performed using a chelating ligand such as 1,2-bis(diphenylphosphino)ethane (dppe). The photochemical activation, under the same experimental conditions employed for the work with  $\text{PPh}_3$ , affords  $[\text{Fe}_2(\text{CO})_5(\text{dppe-}P)\{\text{(PhC}_2\text{Ph)}_2\text{CO}\}]$  (8), in which the second

phosphorus donor atom is 'dangling' as unambiguously shown by the  $^{31}\text{P}$  spectrum: two doublets at 46.7 (region of transition-metal co-ordinated  $\text{PPh}_2$ ) and  $-12.8$  p.p.m. (region of free  $\text{PPh}_2$ ; Table 2). The i.r. and  $^{13}\text{C}$  n.m.r. spectra indicate that the solution structure of (8) is identical to that of (7), i.e. dppe-*P* co-ordinated *trans* to the iron-iron bond.

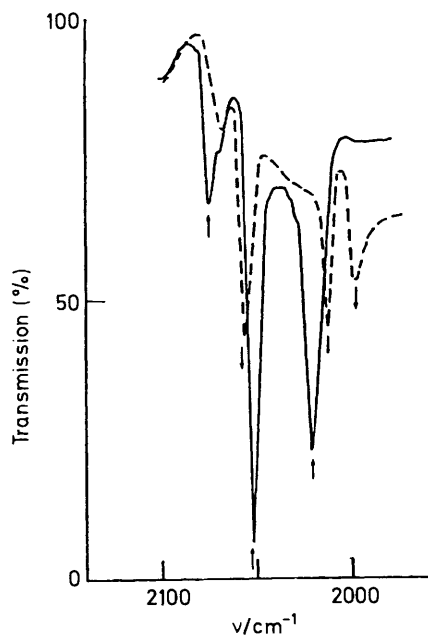


Figure 7. I.r. spectral changes following the irradiation of complex (6) in the presence of excess of pent-1-ene

**Photocatalysis.**—The irradiation ( $\lambda$  400 nm) of a n-heptane solution of (6) containing pent-1-ene in large excess has been performed in a sealed i.r. cell. Within few minutes spectral changes are apparent with the growth of new bands at 2 066, 2 054, 2 002, and 1 996  $\text{cm}^{-1}$  (Figure 7), a pattern similar to that of the monophosphine derivative (7). If, after the irradiation, the solution is left in the dark, the bands of the parent complex gradually reappear. Thus the  $\pi$ -co-ordination of the olefin,

Table 3. Conversion (%) obtained from gas chromatographic analyses during the isomerization of pent-1-ene photocatalysed by complex (6); the n-heptane solutions are  $0.3 \text{ mol dm}^{-3}$  in pent-1-ene and  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  in catalyst

Reaction time (h)	Transformation (%)	<i>cis-trans</i> Ratio (in pent-2-ene produced)	Activation condition
1	15	0.24	Hg lamp, $\lambda$ 500 nm
2	22	0.23	
3 <sup>a</sup>	28	0.25	
1	7	0.17	Sunlight
2	14	0.19	
5	22	0.21	
1	2	0.28	Thermal, $+68^\circ\text{C}$
2	4	0.30	
2	4	0.29	
1	3	0.31	Thermal, $+80^\circ\text{C}$
2	6	0.28	
3	8	0.29	
5 <sup>b</sup>	4	0.30	Sunlight

<sup>a</sup> At this time the catalyst is totally decomposed. <sup>b</sup>  $[\text{Fe}_2(\text{CO})_6\{(\text{EtC}_2\text{Et})_2\text{CO}\}]$  (2) is employed in place of  $[\text{Fe}_2(\text{CO})_6\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  (6) as photocatalyst.

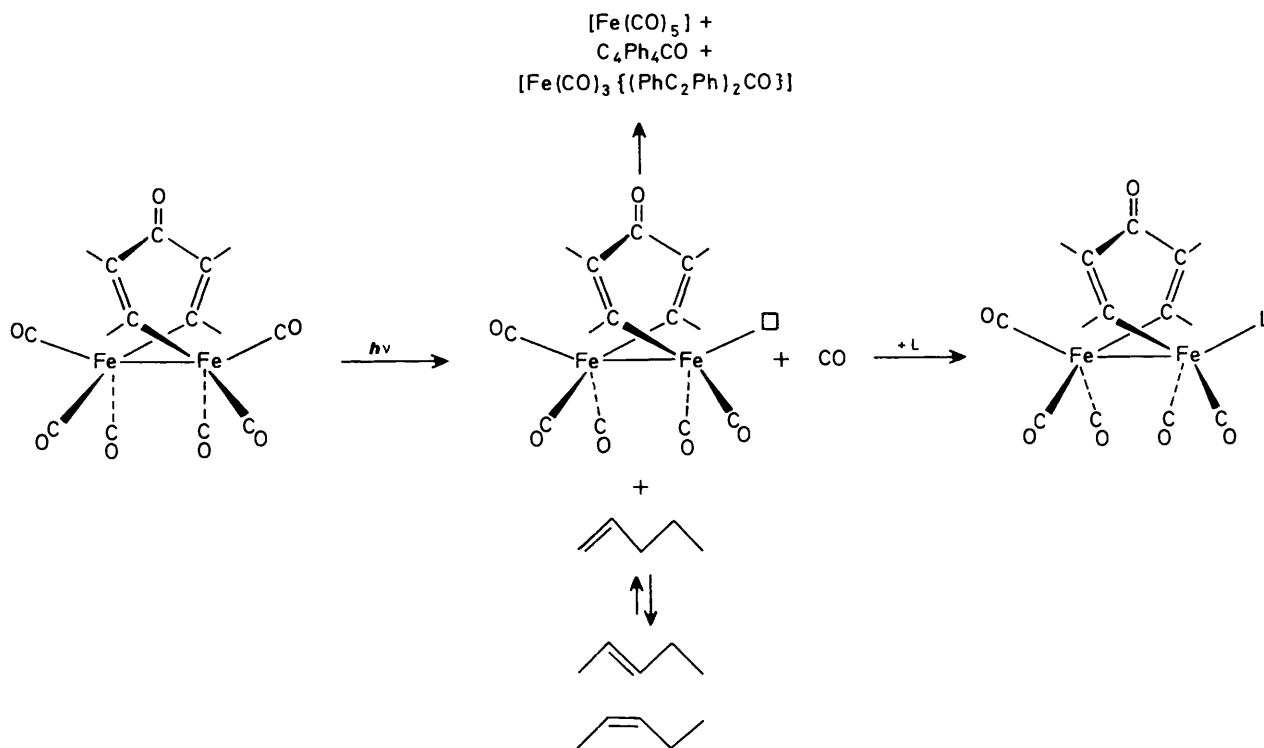


Figure 8. Schematic chart of the photochemical reactions of complex (6) under the various experimental conditions investigated; □ indicates a vacant site

likely in a pseudo-axial position, occurs in a reversible way and can obviously be inhibited by CO addition. A similar behaviour is observed upon exposure of the cell to sunlight; the reaction is identical but proceeds more slowly.

The reversible co-ordination of the double bond at a metal centre makes (6) (and the whole flyover-bridge series) a promising homogeneous photocatalyst for the isomerization of terminal alkenes. Indeed, irradiation of a solution of pent-1-ene at  $\lambda$  500 nm (light intensity of  $10^7$  einstein  $\text{min}^{-1}$ ) in the presence of (6) gives rise to an isomerization to pent-2-ene (Table 3). This photocatalytic process is initially fairly rapid, but drops after a few hours because of extensive decomposition of (6) to less active fragments. Decreasing the light intensity increases the life-time of the catalyst. Granted that the photochemical experiments have to be carried out with light of low intensity, and that the catalysts used are sensitive to visible light, it was natural to perform the experiments by exposing the samples to sunlight: the cheapest photochemical process. This leads to a slower but sizable isomerization with negligible decomposition of the catalyst. An inspection of Table 3 shows that the sunlight activation is also more convenient with respect to the thermal one. For all the catalytic isomerizations, the observed *cis-trans* ratio in pent-2-ene is *ca.* 1:4, indicating that the active isomerization site is not very crowded<sup>27</sup> as expected for a pseudo-axial co-ordination site.

Figure 8 summarizes the photochemical behaviour of (6) as an archetype of the flyover-bridge class under the various conditions investigated. Interestingly, when  $[\text{Fe}_2(\text{CO})_6\{(\text{EtC}_2\text{Et})_2\text{CO}\}]$  (2) ( $\lambda_{\text{max}}$ , 453 nm) is employed in lieu of  $[\text{Fe}_2(\text{CO})_6\{(\text{PhC}_2\text{Ph})_2\text{CO}\}]$  as a photocatalyst (sunlight activation), the isomerization rate decreases five fold, thus pointing out the role of the dienone chain as a sunlight sensitizer.

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