Photochemical and Photocatalytic Behaviour of 'Flyover-bridge' Complexes

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The photochemical behaviour of a number of flyover-bridge complexes $[Fe_2(CO)_6\{(RC_2R)_2CO\}]$ is discussed with regard to their electronic structure. In the case of $[Fe_2(CO)_6\{(PhC_2Ph)_2CO\}]$ 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 $[Fe(CO)_3\{(PhC_2Ph)_2CO\}]$, C_4Ph_4CO , and $[Fe(CO)_5]$. Photosubstitution of CO by phosphine occurs very rapidly and proceeds stereospecifically in a pseudo-axial position as assessed by ¹³C 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, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, and $[Fe_3(CO)_{12}]$, give rise to a plethora of stable organometallic compounds.1,2 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, $[Fe_2(CO)_6 C(R)=C(R')C(O)-$ C(R'')=C(R'''), represent an important class since they are useful stoicheiometric precursors in the syntheses of cyclopentadienones, quinones, hydroquinones, and their related six-membered heterocycles.³ Solid-state structure investigations, carried out by Piron *et al.*⁴ ($\mathbf{R} = \mathbf{R}' = \mathbf{R}'' = \mathbf{M}''$), Cotton et al.⁵ ($\mathbf{R} = \mathbf{R}' = \mathbf{R}'' = \mathbf{R}''' = \mathbf{Ph}$), and Pettersen and Cash⁶ $(R = R''' = C \equiv CSiMe_3, R' = R'' = SiMe_3)$, have shown a rather unusual arrangement of these molecules: the two Fe(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. analysis¹ has been confirmed by Mössbauer⁷ as well as by variable-temperature ¹³C n.m.r. studies.^{5,8} The interaction of the dienone chain with the Fe₂(CO)₆ unit has been described by Thorn and Hoffmann⁹ and confirmed by a gas-phase u.v. photoelectron spectroscopic study coupled with ab initio calculations.¹⁰ The dynamics¹¹ and electrochemistry¹² of such derivatives have been reported very recently.

We have been interested in the photochemical behaviour of transition-metal clusters,^{13,14} 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.¹⁵ 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.¹⁶ The 'flyover-bridge' complexes may be expected to fulfil this requirement: the dienone chain interacts with the Fe₂(CO)₆ moiety in a multicentred σ/π fashion and strongly clasps the iron-iron bond.

Experimental

The title compounds were synthesized from $[Fe_2(CO)_9]$ and the



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

appropriate alkyne according to the literature procedures.^{5,8} After crystallization from n-hexane–CHCl₃ (4:1, v/v), their purity was checked by t.l.c., i.r., and mass spectrometry.

The ¹³CO-enrichment of $[Fe_2(CO)_6\{(PhC_2Ph)_2CO\}]$ (6) was obtained by stirring a solution of (6) (200 mg) in toluene (20 cm³) in a Pyrex Schlenk tube in the presence of gaseous ¹³CO (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 Uviolec 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.¹⁷ Preparative photolysis was performed at ambient temperature with a 500-W Italquartz mercury lamp equipped with a water-cooled quartz finger and aqueous NaNO₂ 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	I. Colours	and λ_{max}	and \tilde{v}_{max}	values of the	flyover-bridge	complexes
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Complex	Colour	$\lambda_{max.}/nm$	\tilde{v}_{max}/cm^{-1}
(1) $[Fe_2(CO)_6 \{C(Me)=C(Me)C(O)C(Me)=C(Me)\}]$	Yellow	459	21 786
(2) $[Fe_2(CO)_6 \{C(Et)=C(Et)C(O)C(Et)=C(Et)\}]$	Dark yellow	453	22 075
(3) $[Fe_2(CO)_6{C(Me)=C(Ph)C(O)C(Ph)=C(Me)}]$	Yellow-orange	463	21 598
(4) $[Fe_2(CO)_6 \{C(Ph)=C(Me)C(O)C(Me)=C(Ph)\}]$	Red-orange	482	20 747
(5) $[Fe_2(CO)_6 \{C(Ph)=C(Me)C(O)C(Ph)=C(Me)\}]$	Red	496	20 161
(6) $[Fe_2(CO)_6 \{C(Ph)=C(Ph)C(O)C(Ph)=C(Ph)\}]$	Red	502	19 920



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.

400

λ/nm

500

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 (ε 2 500), a shoulder at 340 nm (£ 8 200), and a very intense band at 270 nm (ϵ 24 500 dm³ mol⁻¹ 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.¹⁸ The u.v.-visible spectra of all the flyover-bridge derivatives (1)-(6) are qualitatively similar; λ_{max} and $\tilde{\nu}_{max}$ values for the visible bands are collected in Table 1.

Irradiation of a n-heptane solution of (6) under N₂ at $\lambda \ge 400$ nm with light of intensity in the range 10^{-7} — 10^{-6} einstein min⁻¹ leads to slow decomposition of $[Fe_2(CO)_6 \{(PhC_2Ph)_2CO\}\]$ (6) to $[Fe(CO)_3\{(PhC_2Ph)_2CO\}\], C_4Ph_4CO$ (tetraphenylcyclopentadienone or tetracyclone), and [Fe- $(CO)_5$]. All these compounds have been isolated and identified from preparative photolysis {evidence of the presence of $[Fe(CO)_5]$ in the vapour phase has been obtained by mass spectrometry. I.r. spectra recorded in the range 1 800-1 600 cm⁻¹ during the irradiation confirm the formation of [Fe- $(CO)_{3}{(PhC_{2}Ph)_{2}CO}]$ and tetracyclone; in fact, besides the decreasing band at 1657 cm⁻¹ [typical of (6)], bands at

1 635 and 1 710 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.¹

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 (ϵ 1 200 dm³ mol⁻¹ 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 ($\leq 2 \min$) to calculate a disappearance quantum yield (φ) accurately. Extrapolation of this linear portion of the plot gives an estimated $\varphi_{disapp.} \cong 10^{-2}$. When the irradiation is carried out under CO instead of N_2 , the rate of disappearance of (6) decreases by at least one order of magnitude. On the contrary in CCl₄ (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 CO into (6) occurring when a solution of the complex is stirred in toluene under gaseous ¹³CO (0.2 atm) and exposed to sunlight. The reaction has been followed by the decrease in the i.r. highest frequency band (2 075 cm⁻¹) which represents the all-¹²CO molecules. This absorption completely disappears within a few hours. The same reaction carried out in the dark shows a negligible enrichment in ¹³CO. 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 flyoverbridge system, first proposed by Thorn and Hoffmann⁹ for the $[Fe_2(CO)_6{(HC_2H)_2C=CH_2}]$ molecule in the hypothetical C_{2v} geometry and then modified for the [Fe₂(CO)₆{(HC₂H)₂-CO}] molecule in the real C_2 geometry.¹⁰ 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 Fe₂(CO)₆ fragment⁹ ('sawhorse' geometry), and provides a stabilizing interaction with the empty pseudo- π^* 3a orbital of the twisted dienone chain.¹⁰ 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 Fe₂(CO)₆ moiety.[†] In principle, the h.o.m.o.-l.u.m.o. electronic transition (metal-metal to σ - σ * type) is dipole allowed and is to be associated with the visible band at 502 nm.

Thus irradiation at $\lambda \ge 400$ 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

[†] We gratefully thank Professor Granozzi and Dr. Casarin (University of Padova, Italy) for the extension of the previous extended-Hückel and ab initio calculations¹⁰ to the l.u.m.o. of $[Fe_2(CO)_6\{(HC_2H)_2CO\}]$.

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

Complex	$\tilde{v}(CO)^{a}/cm^{-1}$	³¹ P N.m.r. ^b	¹³ C N.m.r. ^c (carbonyl region)
(7) $[Fe_2(CO)_5(PPh_3){(PhC_2Ph)_2CO}]$	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) ^d
(8) [Fe ₂ (CO) ₅ (dppe- P){(PhC ₂ Ph) ₂ CO}]	2 057vs, 2 012vs, 1 998s, 1 993m, 1 650m br	46.7 (d, 1 P), -12.8 (d, 1 P) (3 L= 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) ^d
$[Fe(CO)_{3}{(PhC_{2}Ph)_{2}CO}]$ $[Fe(CO)_{2}(PPh_{3}){(PhC_{2}Ph)_{2}CO}]$	2 068s, 2 016s, 1 995s, 1 635m br 1 994s, 1 947s, 1 631m br	56.9°	208.5 216.4 (d, ² J _{CP} 14.3 Hz)

^a In n-hexane.^b At 109.6 MHz, CDCl₃, chemical shifts are reported positive downfield with respect to external H₃PO₄ (85%).^c At 67.9 MHz, CDCl₃. ^d At -30 °C.^c Since the sample is highly (*ca.* 40%) ¹³CO-enriched, ¹³C satellites are detectable and give a ²J_{PC} (14.5 Hz) in good accord with that directly found in the ¹³C n.m.r. spectrum.



Figure 3. Plot of \tilde{v}_{max} , against the abscissa function σ_x obtained from the Taft σ^* values of the R substituents of the flyover-bridge complexes according to equation (1). The least-squares slope is -1535 cm^{-1} and the correlation coefficient 0.998

photochemical act.¹⁹ 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 goes 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 C¹ substituents of the dienone chain. Indeed, $[Fe_2(CO)_6 \{ C(Ph) =$ C(Me)C(O)C(Ph)=C(Me)] (5) has the same colour (red) as $[Fe_2(CO)_6 C(Ph)=C(Ph)C(O)C(Ph)=C(Ph)]$ and $[Fe_2(CO)_6{C(Me)=C(Ph)C(O)C(Ph)=C(Me)}]$ (3) the same colour (yellow) as $[Fe_2(CO)_6 \{C(Me)=C(Me)C(O)C(Me)=$ C(Me)] (1). This obviously indicates that the R and R^{'''} substituents deeply influence the energy gap of the σ - σ * transition. In more quantitative terms, the wavenumbers (\tilde{v}_{max}) of the visible bands, which represent the transition energies, depend on the field effect of the C^1 substituents. As a matter of fact, a good linear correlation (r = 0.990) is obtained by plotting the \tilde{v}_{max} values against the sum of the Taft σ^* values of



Figure 4. Plot of \tilde{v}_{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 mol dm⁻³ NBuⁿ₄ClO₄.¹² The least-squares slope is $-7 \, 115 \, \text{cm}^{-1} \, \text{V}^{-1}$ and the correlation coefficient 0.998

the C¹ substituents only. The best correlation (r = 0.998) is observed using, as abscissa parameter, the optimized function σ_x obtained from equation (1). This relationship (Figure 3)

$$\sigma_{\mathbf{x}} = 0.9 \; (\sigma_{\mathbf{R}}^* + \sigma_{\mathbf{R}''}^*) \; + \; 0.1 \; (\sigma_{\mathbf{R}'}^* + \sigma_{\mathbf{R}''}^*) \tag{1}$$

unambiguously indicates that the transmission of the electronic effect from the substituents to the metallic frame is mainly brought about through the Fe–C¹ σ bonds, in agreement with the previous theoretical¹⁰ and electrochemical¹² studies.

A second free-energy linear correlation can be found when the \tilde{v}_{max} values are plotted against the formal electrode potential $E^{0'}$ for the monoreduction process (0/1-) of the flyover complexes ¹² (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 [Fe₂-(CO)₆{(RC₂R)₂CO}]^{•-}. Electron-withdrawing substituents decrease the h.o.m.o.-l.u.m.o. gap (then lower the \tilde{v}_{max} values) and make the reduction easier (in other words at less negative potentials).

Photolysis of (6) in the Presence of PPh₃ and Ph₂PCH₂CH₂PPh₂.—Irradiation at $\lambda \ge 400$ nm of a toluene solution of [Fe₂(CO)₆{(PhC₂Ph)₂CO}] (6) and PPh₃ (1:3 mol ratio) with light of intensity 10⁻⁷ einstein min⁻¹ leads to a fast reaction affording the monosubstituted derivative [Fe₂(CO)₅-(PPh₃){(PhC₂Ph)₂CO}] (7) (Table 2).



Figure 5. I.r. spectral changes during irradiation of complex (6) in the presence of excess of 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) $(\lambda_{max}, 502 \text{ nm})$ to (7) $(\lambda_{max}, 510 \text{ nm}; \varepsilon 1 150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$. There is precedent in the electronic spectra of $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]^{20}$ dimers where phosphine substitution leads to a decrease in energy for the σ - σ * transition and then to a red shift.

Preparative photolysis (λ 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, [Fe₂(CO)₅(PPh₃){(PhC₂Ph)₂CO}] (7) is quite light and heat sensitive: prolonged irradiation or heating at $T \ge 80$ °C causes its irreversible fragmentation to [Fe(CO)₃{(PhC₂Ph)₂CO}] and [Fe(CO)₂(PPh₃){(PhC₂Ph)₂-CO}] (mol ratio *ca.* 1:1, total yield 40%), identified by i.r., ¹³C, and ³¹P n.m.r. spectroscopy, and by t.l.c. comparison with authentic samples.²¹

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 ¹³C n.m.r. study has been carried out on samples of the parent complex [Fe₂(CO)₆{(PhC₂Ph)₂CO}] (6) at different degrees of ¹³CO enrichment. A solution of (6) (15% ¹³CO-enrichment) in CDCl₃ at -30 °C exhibits three signals of integrated intensity 1:1:1 at 209.7, 206.9, and 206.2 p.p.m. as previously reported.^{5.8} At this level of enrichment no ¹³C-¹³C couplings are detectable. When a higher ¹³COenriched sample (*ca.* 40%) is employed, the two high-field resonances become apparent triplets, where the sidebands are



Figure 6. ¹³C N.m.r. spectrum (67.9 MHz) of $[Fe_2(CO)_5(PPh_3)-{(PhC_2Ph)_2CO}]$ (7) in CDCl₃ at -30 °C for (*a*) 15% ¹³CO enrichment and (*b*) 40% ¹³CO enrichment

due to ${}^{13}C{-}^{13}C$ coupling (${}^{2}J_{CC}$ ca. 10 Hz), which is in the range observed for carbonyls in a cis arrangement.²² 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).⁵ Then the two samples of (**6**) are directly transformed to (**7**) by light-assisted reaction with PPh₃. The spectrum of the 15%-enriched sample in CDCl₃ at -30 °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 Fe(CO)₃ moiety, and two partially overlapping doublets, centred at 211.4 and 211.2 p.p.m. (${}^{2}J_{CP}$ ca. 16 and 10 Hz respectively) attributed to the Fe(CO)₂(PPh₃) 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 ${}^{2}J_{CC}$ coupling constant, the downfield signal becomes an entangled multiplet due to the ${}^{31}P{-}^{13}C$ and ${}^{13}C{-}^{13}C$ splittings, but, importantly, the peak at 210.4 p.p.m., is affected neither by ³¹P nor by ¹³C 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,²³ phosphorus,²⁴ sulphur,²⁵ and cumulene²⁶ bridged di-iron complexes where the Fe₂(CO)₆ moiety has approximately the same sawhorse geometry. Also in [Ru₂(CO)₅(AsPh₃)- ${C(Ph)=C(Me)C(O)C(Me)=C(Ph)]}$ a similar solution structure has been suggested.¹¹ 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 PPh₃, affords $[Fe_2(CO)_5(dppe-P){(PhC_2Ph)_2CO}]$ (8), in which the second

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phosphorus donor atom is 'dangling' as unambiguously shown by the ${}^{31}P$ spectrum: two doublets at 46.7 (region of transitionmetal co-ordinated PPh₂) and -12.8 p.p.m. (region of free PPh₂; Table 2). The i.r. and ${}^{13}C$ n.m.r. spectra indicate that the solution structure of (8) is identical to that of (7), *i.e.* dppe-*P* coordinated *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 (λ 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 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 π -co-ordination of the olefin,



Reaction time (h)	Transformation (%)	cis-trans Ratio (in pent-2-ene produced)	Activation condition
1	15	0.24	
2	22	0.23	Hg lamp,
34	28	0.25	7. 500 nm
1	7	0.17	1
2	14	0.19	Sunlight
5	22	0.21	
1	2	0.28	1
2	4	0.30	\rightarrow Thermal, +68 °C
2	4	0.29	
1	3	0.31	1
2	6	0.28	\rightarrow Thermal, +80 °C
3	8	0.29	
50	4	0.30	Sunlight

^{*a*} At this time the catalyst is totally decomposed. ^{*b*} $[Fe_2(CO)_6\{(EtC_2Et)_2-CO\}]$ (2) is employed in place of $[Fe_2(CO)_6\{(PhC_2Ph)_2CO\}]$ (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 λ 500 nm (light intensity of 10⁷ einstein 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 crowded²⁷ 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 $[Fe_2(CO)_6-{(EtC_2Et)_2CO}]$ (2) $(\lambda_{max}$. 453 nm) is employed in lieu of $[Fe_2(CO)_6{(PhC_2Ph)_2CO}]$ 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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