

EVIDENCE FOR ENHANCED REACTIVITY IN THE PHOTOFRAGMENTATION OF THE BRIDGED DINUCLEAR SYSTEM



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Summary

Experimental evidence that the dinuclear complex $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)]_2$ shows enhanced reactivity over its mononuclear analog $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ in photofragmentation to produce bibenzyl and Fe—Fe bonded product is presented. Information from a series of competition and crossover experiments indicate that two factors are involved in the enhancement: (1) the ability to photochemically produce a 16-electron unsaturated benzyl unit in close proximity to a saturated partner, and (2) the inability of the Fe—Fe bonded species to quench free benzyl radicals in solution. Chemical reaction of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)]_2$ with Me_3NO produces bibenzyl and establishes that loss of CO is the initial step in the fragmentation reaction. In addition, trapping experiments with 9,10-dihydroanthracene show that bibenzyl is formed from free benzyl radicals; Based on these results an overall mechanism is proposed.

Introduction

The photochemically induced replacement of CO in transition metal complexes by phosphine ligands is well documented [1]; however, in the absence of ligand, irradiation of some mononuclear alkylmetal and metal-hydride carbonyl complexes is observed to eventually result in homolytic cleavage of the metal—alkyl or metal—hydride bond and formation of metal—metal bonded species [2]. One complex that is known to exhibit such behavior is the saturated alkyliron system $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ (1), (FpBz). Irradiation of FpBz in the presence of triphenylphosphine produces $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ [3] whereas irradiation in the absence of ligand gives $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2(\text{Fp}_2)$ and bibenzyl as products [4].

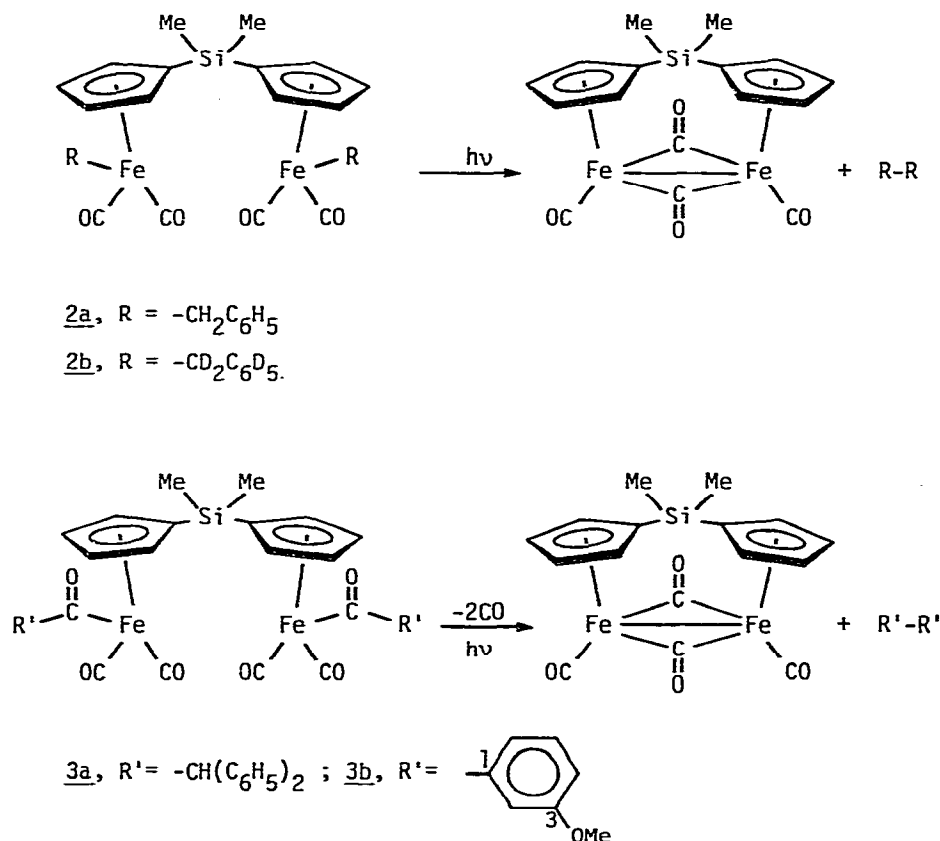
The present paper reports the preparation, characterization, and photolysis of a series of dinuclear complexes, $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-R})]_2$ (R =

$\text{CH}_2\text{C}_6\text{H}_5$ and $\text{CD}_2\text{C}_6\text{D}_5$) (**2a** and **2b**, respectively), which show an enhanced degree of reactivity toward the photolytic coupling process. The source of the reactivity enhancement is discussed on the basis of the results obtained from a series of crossover and competition experiments performed with both the mononuclear and dinuclear systems. Finally, based on these results and earlier work in a related system, an overall mechanism is suggested.

Results and discussion

With the initial goal of forming bis-bridged dialkyl complexes, the readily available di- η^1 -benzyl complex **2a** was photolyzed in the presence of bis(1,2-diphenylphosphino)ethane (dppe). This reaction results in the isolation of the dinuclear Fe—Fe bonded species $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})]_2\text{dppe}$ [**5**] and an organic product that is identified as bibenzyl. By NMR it can be observed that a major pathway to the dinuclear complex is the photochemical substitution of dppe on the bridged dimer $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})]_2$ (**4**); thus indicating that the photochemical coupling reaction is competitive with the substitution of dppe for the CO's on **2a**. Irradiation of compounds **2** and **3a** in benzene- d_6 (0.04 M) in the absence of ligand consistently gives as products the Fe—Fe bonded dimer **4** (85%) and the bibenzyl derivatives (90%) (Scheme 1).

SCHEME 1



Solutions of the mononuclear FpBz (0.08 M) and the dinuclear analogue 2a (0.04 M) in benzene- d_6 are irradiated separately and the rates of product appearance are measured by NMR techniques. The photochemical coupling reaction in the mononuclear FpBz system shows a distinct leveling off of product formation at ca. 50% completion whereas the dinuclear complex 2a maintains a relatively constant rate of product formation throughout the course of the reaction (Fig. 1).

These data indicate that linking the two metal sites is altering the reactivity significantly relative to the mononuclear system. To explore this point and also to obtain more information concerning the coupling reaction in the benzyliron system, the following competition and cross-over experiments are conducted.

(i) A benzene- d_6 solution containing $[\eta^5\text{-C}_5\text{H}_4\text{CH}_3\text{Fe}(\text{CO})_2]_2(\text{MeFp}_2)$ (0.02 M) and FpBz (0.04 M) is irradiated for 2 h; the ^1H NMR shows a ca. 50/50 mixture of $\eta^5\text{-C}_5\text{H}_4\text{CH}_3\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)(\text{MeFpBz})$ and FpBz with only minor conversion ($\approx 5\%$) to bibenzyl [6]. The Fe-Fe bonded species found in the reaction mixture are $\text{Fp}_2/[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2][\eta^5\text{-C}_5\text{H}_4\text{CH}_3\text{Fe}(\text{CO})_2](\text{FpMeFp})/\text{MeFp}_2$ in a ratio of 1/2/1, respectively. It is well known that Fe-Fe bonded dimers of the type MeFp_2 fragment to radicals under photolytic conditions [7]. These experimental results and the knowledge that benzyl radicals are being formed (see below) suggest reactions 1-6. Step 4 is shown for completeness and will be discussed later in the paper.

(ii) A benzene- d_6 solution containing 4 (0.02 M) and FpBz (0.04 M) is irradiated for 2 h; the ^1H NMR shows a 35% conversion of FpBz to bibenzyl and Fp_2 with essentially no change in complex 4. The fact that 4 is not converted into 2a is a most intriguing feature. This result suggests that the bridged species

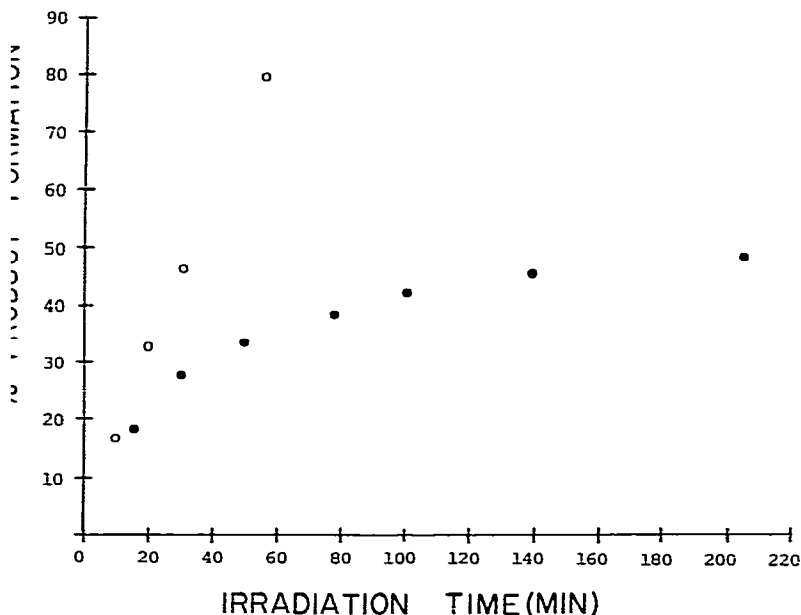
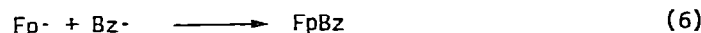
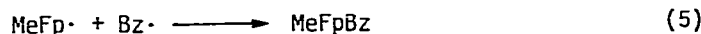
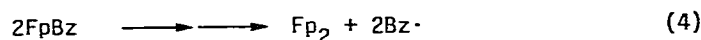
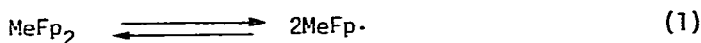
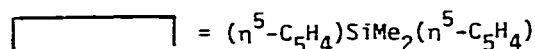
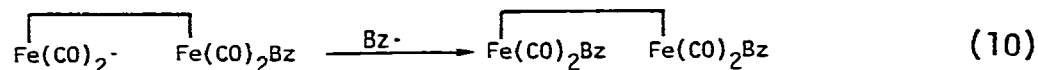
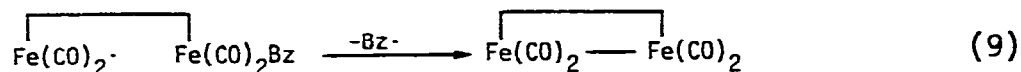
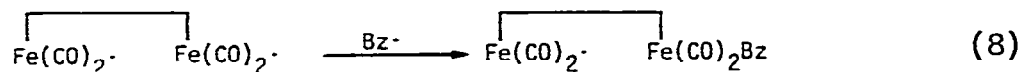
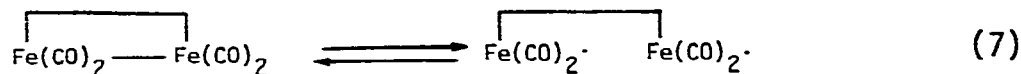


fig. 1. Plot of product formation (%) vs. time (min) for the coupling reaction: (●) mononuclear system, $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$; (○) dinuclear system, $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)]_2$.



4 has reaction 7 favored far to the left or alternatively step 9 is rapid relative to 10. One might also note that the rate of bibenzyl formation is not retarded by



the presence of the Fe—Fe bonded species 4 in contrast to the results from experiment (i). Since the UV-Vis spectra of 4 and Fp_2 are very similar in nature [8], the absorption of light by these complexes does not appear to significantly change the rate of the coupling reaction.

(iii) Two further crossover experiments are carried out to test for the possibility of an intramolecular transfer of the benzyl groups. A benzene- d_6 solution containing approximately equimolar amounts of $\text{Fp}(\eta^1\text{-CD}_2\text{C}_6\text{D}_5)$ and FpBz is irradiated until the reaction is nearly complete (ca. 60%). Analysis of the bibenzyl products by proton NMR shows the expected statistical ratio of ca. 1/2 for $(\text{C}_6\text{H}_5\text{CH}_2)_2/\text{C}_6\text{D}_5\text{CD}_2\text{CH}_2\text{C}_6\text{H}_5$, respectively*. Similar treatment of dilute solutions of 2a and $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CD}_2\text{C}_6\text{D}_5)]_2$ (2b) gives analogous product ratios. These results show that in both the mononuclear and the linked binuclear cases that the bibenzyl product arises by a statistical combination of benzyl- d_0 and - d_7 units. This observation is consistent with the pro-

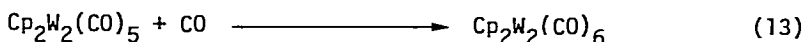
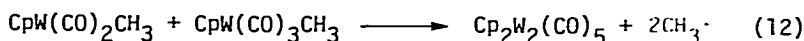
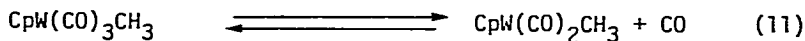
* The 250 MHz ^1H NMR spectrum of the crossover product exhibits two resonances at δ 2.737 and 2.727 ppm, corresponding to $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CD}_2\text{C}_6\text{D}_5$, respectively. The integral values for each resonance are used to calculate the ratio of the two benzyl derivatives. We are assuming that the amount of $\text{C}_6\text{D}_5\text{CD}_2\text{CD}_2\text{C}_6\text{D}_5$ formed is approximately the same as $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$.

posed coupling of free benzyl radicals to give the bibenzyl type products. These results, however, do not preclude the possibility of an intramolecular reaction in the binuclear case to produce the benzyl radicals.

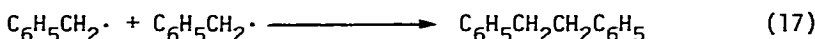
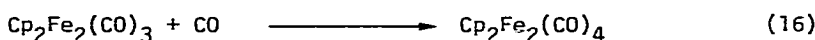
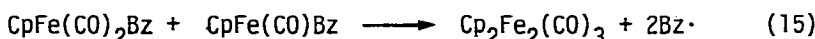
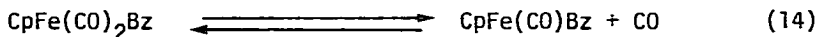
The above experiments suggest that the decrease in rate of product formation in the mononuclear system is not related to an entropy effect, but to a secondary reaction which takes place as the amount of Fp_2 builds up. That is reaction of Fp radical with a benzyl radical begins to compete successfully with the coupling of two benzyl radicals. This does not take place in the dinuclear system perhaps because the reverse of reaction 7 of the forward step in reaction 9 is very fast.

Support for the formation of benzyl radicals can be found in the photolysis of **1** and **2a** in the presence of a hydrogen atom donor, 9,10-dihydroanthracene. In both the mononuclear and dinuclear cases where a 20-fold excess of 9,10-dihydroanthracene is employed, we find that toluene (ca. 80%) is formed at the expense of bibenzyl. Further support is found in the photocoupling reaction times which are directly dependent upon the stability of the resultant radical. For example, irradiation for 2 h of $Me_2Si\{\eta^5-C_5H_4Fe(CO)_2[\eta^1-CO(3-MeOC_6H_4)]\}_2$ gives the expected decarbonylated product $Me_2Si\{\eta^5-C_5H_4Fe(CO)_2[\eta^1-(3-MeOC_6H_4)]\}_2$ with only minor amounts of coupled biphenyl type products. However, photolysis of **3a** under similar conditions gives tetraphenylethane and **4** in 30 min (Table 1). These relative rates of coupling are consistent with the stability of the radicals being formed.

Recently, Tyler investigated the photochemically induced fragmentation of $\eta^5-C_5H_5W(CO)_3CH_3$ and suggested the mechanism shown in steps 11–13 [9].



An entirely analogous mechanism, which is supported by all the data obtained thus far, can be proposed for the mononuclear coupling reaction in the benzyliron system (steps 14–17). The facile substitution of CO by PPh_3 in **1** is consistent with CO loss as a primary photoprocess. In addition, complex **2a**



also reacts with PPh_3 (5 fold excess) to form substitution products. Infrared spectroscopic monitoring of the reaction clearly shows the disappearance of bands for **2a** (1950 and 2000 cm^{-1}) with concomitant appearance of the bis- PPh_3 substituted product absorption band at 1905 cm^{-1} *. Further evidence for

* The bis-substituted product can be isolated in pure form. Anal. found: C, 72.40; H, 5.64. $C_{64}H_{58}Fe_2O_2P_2Si$ calcd.: C, 72.46; H, 5.51%.

TABLE I
RESULTS FOR THE PHOTOLYSIS OF COMPLEXES 2a, 3a, AND 3b^a

Complex	Irradiation time (min)	Organic product (%)	Fe—Fe bonded product (%)
2a	150	bibenzyl (90)	4 (85)
3a	30	tetraphenyl-ethane (70) ^b	4 (95)
3b	150	biphenyl (\approx 5) ^c	4 (\approx 5)

^a All samples are irradiated as ≈ 0.04 M benzene-*d*₆ solutions and yields are based on ¹H NMR integration.

^b Isolated yield. ^c The assumed product is 3,3'-dimethoxybiphenyl, however, is not isolated.

CO loss as a primary photoprocess has been obtained by examining the reaction of 1 and 2a with trimethylamine-*N*-oxide (Me₃NO), a known CO ligand abstractor of transition metal complexes [10]. The Me₃NO induced decomposition of both 1 and 2a in benzene solutions leads to the isolation of bibenzyl as a major organic product. This observation reveals that cleavage of the iron—benzyl bond and the subsequent carbon—carbon bond formation can be accomplished by initial CO loss.

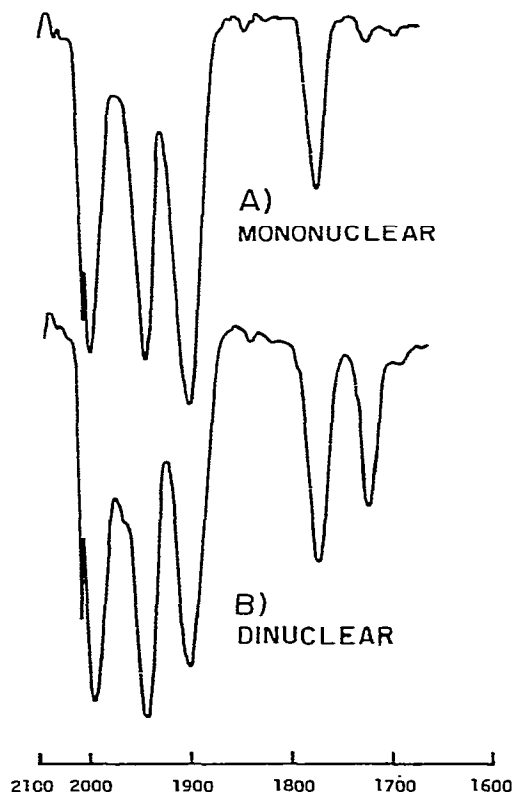
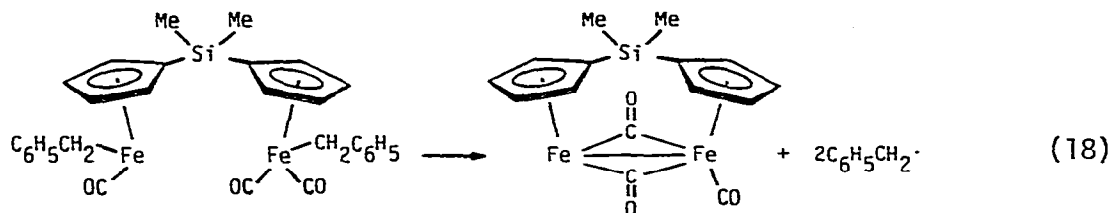
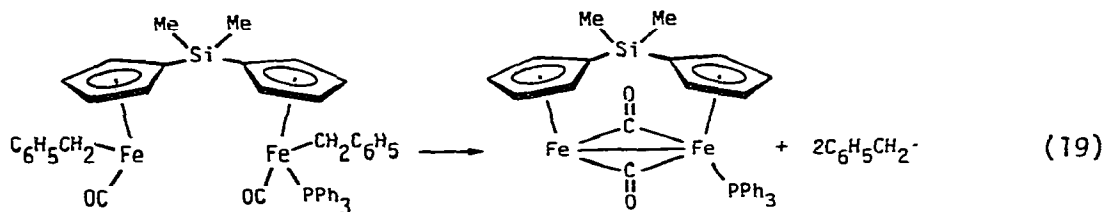


Fig. 2. Infrared spectra of the products after 15 min irradiation of a benzene solution containing (A) FpBz (≈ 0.0014 M) and PPh₃ (≈ 0.0014 M) and (B) 2a (≈ 0.0007 M) and PPh₃ (≈ 0.0014 M). The spectra are recorded in ClCH₂CH₂Cl.

Although, as pointed out above, excess PPh_3 inhibits the photocoupling reaction for both **1** and **2a**, further insight into the details of the reaction are obtained by comparison of the results from irradiation of dilute solutions of **1** and **2a** in the presence of one equivalent of PPh_3 . Irradiation of a benzene solution containing **1** ($\approx 0.0014 M$) and PPh_3 ($\approx 0.0014 M$) produces after 15 min infrared bands corresponding to Fp_2 (1776, 1954, and 1995 cm^{-1}), $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ (1905 cm^{-1}), and FpBz (1950 and 2000 cm^{-1}). Continued irradiation for an additional 15 min gives a relatively constant ratio between Fp_2 and $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ with a decrease in the ratio of FpBz relative to the former two complexes. In addition, a very weak band at 1732 cm^{-1} appears which can be assigned to the mono-substituted Fe—Fe bonded dimer, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{PPh}_3)$. The irradiation of a benzene solution of **2a** ($\approx 0.0007 M$) and PPh_3 ($\approx 0.0014 M$) for 15 min gives infrared bands attributable to **4** (1776, 1954, and 1995 cm^{-1}), $\text{Me}_2\text{Si}[(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_{4-n}(\text{PPh}_3)_n(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)_2]$ ($n = 1$, 1905 , 1950 , and 2000 cm^{-1} ; $n = 2$, 1905 cm^{-1}), and $\text{Me}_2\text{Si}[(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_3(\text{PPh}_3)]$ (1734 and 1952 cm^{-1}) [11]. The infrared spectra for the two solutions are shown in Fig. 2. From comparison of these spectra it is apparent that **2a** gives a higher ratio of coupling/substitution than does FpBz . The ability of **2a** to undergo the coupling reaction in dilute solutions is likely due to the inherent property of the bridge keeping the two metal centers in close proximity (eq. 18). A related feature that is noteworthy is the fact that a substantial amount of $\text{Me}_2\text{Si}[(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_3(\text{PPh}_3)]$ is formed in the dinuclear case after 15 min whereas only trace amounts of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{PPh}_3)$ appear in the mononuclear case at this



point. We feel that this is again indirect evidence for an intramolecular type of reaction as depicted in eq. 19 that does not take place in the mononuclear system*.



* It should be noted that the PPh_3 substituted benzyl complexes do undergo the coupling reaction, however, at a much slower rate.

Conclusion

The above results indicate that there are two features of the linked dinuclear system that causes it to have enhanced reactivity in the photochemical coupling reaction. They are: (1) the capability to photochemically produce a 16-electron unsaturated benzyliron unit in close proximity to a coordinatively saturated partner with which it can react as is in eq. 18 and (2) the inability of the bridged Fe—Fe bonded complex, 4, to quench the benzyl radicals as defined for the mononuclear system in eqs. 5 and 6.

In addition this work established that bibenzyl arises by the coupling of free benzyl radicals generated when the benzyliron species are photolyzed in benzene solutions. Furthermore, we have demonstrated that the coupling reaction is induced by CO loss from the benzyliron complexes. These observations are compatible with results obtained with the $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ system and have led to the proposed mechanism shown in steps 14–17.

This study lends further support to the idea that mechanically linked transition metal complexes can show enhanced reactivity in dinuclear reactions over their mononuclear analogs.

Experimental

General. All reactions and subsequent manipulations are carried out using standard Schlenk techniques under a purified nitrogen atmosphere. Solvents are routinely dried by Standard procedures and stored under nitrogen [12]. The NMR solvents are predried over 3A sieves, subjected to three consecutive freeze-pump-thaw cycles, and then stored in a Schlenk flask under a nitrogen atmosphere. In addition, NMR samples are routinely passed thru a short column of celite to remove finely divided decomposition particles.

Spectroscopic measurements utilize the following instrumentation: ^1H NMR, Varian EM360, Bruker 250FT (at 250 MHz); ^{13}C NMR, Bruker 250FT (at 62.9 MHz); IR, Perkin—Elmer 281B or a PE 398; UV, Perkin—Elmer 552; NMR chemical shifts are reported in δ versus Me_4Si assigning the CDCl_3 resonance in ^{13}C spectra to be 77.00 ppm. Carbon-13 spectra are run with ^1H -decoupling and resonances may be assumed to be singlets unless multiplicity is specified. The $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ [13], $(\text{C}_6\text{H}_5)_2\text{CHCOCl}$ [14], 3-methoxybenzoyl chloride [14], and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)$ are prepared by literature methods. The complex $\text{Me}_2\text{Si}[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2)]_2$ is prepared by modification of a literature method and is reported herein [15]. Deuterated solvents for use in the NMR experiments and for the preparation of $\text{C}_6\text{D}_5\text{CD}_2\text{Cl}$ are obtained from Aldrich. The sodium hydride (99%) is obtained from Alfa and used as received.

The photochemical reactions are performed by irradiating the sample in a standard 5 mm pyrex NMR tube ca. 7 cm from the light source (450 watt med. pressure Hg lamp inside a Hanovia quartz finger employing a pyrex filter). The photolysis samples are prepared by first transferring the appropriate compounds into a dry and degassed vial (2 dram), then dissolving these in benzene- d_6 (ca. 0.5 ml), and finally filtering (celite in a disposable pipet) into the NMR tube under a positive nitrogen flow. After irradiation, each of the samples

are centrifuged to obtain better resolution in the NMR spectra.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ (4). To a mixture of THF (100 ml) and NaH (99%, 6 g, 250 mmol) is added a THF (25 ml) solution containing cyclopentadiene (25 ml, 303 mmol) dropwise over a period of ca. 2 h. The resulting burgundy colored solution is then slowly (over a 30 min period) cannulated onto a chilled (0°C) THF (20 ml) solution containing Me_2SiCl_2 (15 ml, 124 mmol). As the addition proceeds agitation by manual methods (swirling the flask in the ice bath is quite effective) is required due to copious amounts of NaCl being formed and the exothermicity of the reaction. After the addition is complete, xylene (250 ml) is added and the resulting mixture is vacuum filtered, using a Fritted-glass funnel, into a flask containing xylene (200 ml). The precipitate is then washed on the filter with an additional 100 ml of xylene. To the clear yellow filtrate is added $\text{Fe}(\text{CO})_5$ (33 ml, 245 mmol), and this mixture is refluxed for 12 h under nitrogen. The deep purple reaction mixture is allowed to cool, filtered to remove decomposition material, and then the solvent removed under vacuum (Caution! Excess $\text{Fe}(\text{CO})_5$ should be collected by an efficient low temperature trap). The crude mixture (usually a mixture of crystals and oils) is treated with hexane (150 ml) and placed at -25°C for 12 h. The precipitated crystals of 4 are collected by filtration and washed with hexane until the washes appear near colorless, yields are usually 10–14 g (20–27%).

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-R})]_2$ ($R = \text{CH}_2\text{C}_6\text{H}_5$, 2a; $R = \text{CD}_2\text{C}_6\text{D}_5$, 2b) and $\text{C}_6\text{D}_5\text{CD}_2\text{Cl}$. A THF (50 ml) solution of 4 (0.50 g, 1.2 mmol) is stirred over sodium-amalgam (1% sodium, 30 g) for 30 min. The resulting THF solution is cannulated away from the Na/Hg into another flask and the benzyl chloride (0.60 g, 5 mmol) then added by syringe. The mixture is stirred for 30 min to insure completion of the reaction. The solvent is removed in vacuo, the residue is then extracted with benzene (3 ml) and placed on a column (alumina(III), 2 × 20 cm). Elution with hexane gives an initial yellow band and a red-brown band which remains near the top portion of the column. The yellow band is collected, and after solvent removal can be identified as 2a contaminated with benzyl chloride (^1H NMR). Further elution with a hexane/benzene (4/1, v/v) mixture results in appearance of a new fast moving yellow band from the slower moving red band. This yellow band is collected and identifies as pure 2a free of contamination by benzyl chloride. The red band can be characterized as complex 4 by spectroscopic means. Complex 2a; ^1H NMR spectrum (C_6D_6): δ 7.2 (m, 10, C_6H_5), 4.77 (m, 8, C_5H_4), 2.63 (s, 4, CH_2), 0.27 (s, 6, SiCH_3); IR spectrum ($\text{ClCH}_2\text{CH}_2\text{Cl}$): 1950 and 2000 cm^{-1} ; ^{13}C spectrum (CDCl_3): δ 216.91 (CO), 152.74 (methylene-bound phenyl carbon), 128.11, 127.41, and 123.22 (*ortho*-, *meta*-, and *para*-phenyl carbons, respectively), 93.14, 90.55 (C_5H_4), 85.94 (Si-bound, C_5H_4), 4.96 (CH_2), -1.49 (SiCH_3).

Anal. found: C, 60.85; H, 4.77. $\text{C}_{30}\text{H}_{28}\text{Fe}_2\text{O}_4\text{Si}$ calcd.: C, 60.83; H, 4.76%.

The $\text{C}_6\text{D}_5\text{CD}_2\text{Cl}$ is prepared by refluxing $\text{C}_6\text{D}_5\text{CD}_3$ in excess (5 fold) SO_2Cl_2 for 6 h. The product is collected by simple distillation as a colorless liquid boiling in the range of 160 to 180°C. By ^1H NMR the product's α -methylene has complete deuterium incorporation. The benzyl chloride- d_7 is used in the above preparation to afford complex 2b which is characterized similarly.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-COR})]_2$ ($R = \text{CH}(\text{C}_6\text{H}_5)_2$, 3a; $R =$

3-MeOC₆H₄), 3b). A THF (50 ml) solution of 4 (0.50 g, 1.2 mmol) is stirred over Na/Hg (30 g, 1% Na) for 30 min. The resulting solution is transferred away from the Na/Hg into another flask and is then cooled to 0°C. The 3-methoxybenzoyl chloride (0.5 g, 3 mmol) is added to the chilled solution which is stirred for an additional 10 min. The solvent is removed and the residue extracted with benzene (3 ml) and placed on a column (alumina(III), 2 × 20 cm). Elution with a hexane/benzene (1/1, v/v) gives three bands, an initial yellow band, a middle red band, and a slow moving yellow band. The bands are collected and characterized by ¹H NMR and IR spectroscopy to contain, Me₂Si{η⁵-C₅H₄Fe(CO)₂[η¹-(3-MeOC₆H₄)]₂, complex 4, and as the major product Me₂Si{η⁵-C₅H₄Fe(CO)₂[η¹-CO(3-MeOC₆H₄)]₂, respectively. The former complex gives ¹H NMR resonances at δ 7.1 (m, 8, phenyl), 4.35 (s, 8, C₅H₄), 3.50 (s, 6, OCH₃), 0.23 (s, 6, SiCH₃) and the latter, 3b, gives ¹H NMR signals at δ 7.1 (m, 8, phenyl), 4.48 (m, 8, C₅H₄), 3.31 (s, 6, OCH₃), 0.44 (s, 6, SiCH₃). Carbon-13 spectrum (CDCl₃) for 3b: δ 253.32 (CO, acyl), 213.92 (CO, terminal carbonyl), 159.23, 152.04, 128.93, 119.30, 116.21, 110.13 (phenyl carbons 3, 1, 5, 6, 4, and 2, respectively, as labeled in Scheme 1) 93.92, 89.79 (C₅H₄), 87.17 (Si-bound, C₅H₄), 55.32 (OCH₃), -1.71 (SiCH₃). IR spectrum of 3b in ClCH₂CH₂Cl gives bands at 1962, 2019 cm⁻¹.

Anal. found: C, 56.39; H, 4.10. C₃₂H₂₈Fe₂O₈Si calcd.: C, 56.49; H, 4.15%.

Complex 3a is prepared in a similar manner and displays the following spectroscopic data: ¹H NMR (C₆D₆): δ 7.2 (m, 20, phenyl), 5.80 (s, 2, CH(C₆H₅)), 4.40 (s, 8, C₅H₄), 0.30 (s, 6, SiCH₃); IR (ClCH₂CH₂Cl) ν(CO): 1964, 2020 cm⁻¹; ¹³C NMR (CDCl₃): 257.58 (CO, acyl), 214.04 (CO), 138.53 (methine-bound phenyl carbons), 128.93, 128.47, 126.85 (*ortho*-, *meta*-, and *para*-phenyl carbons, respectively), 93.72, 89.98 (C₅H₄), 87.36 (Si-bound, C₅H₄), 86.42 (CH(C₆H₅)₂) -1.85 (SiCH₃).

Photolysis of FpBz and [(η⁵-C₅H₄CH₃)Fe(CO)₂]₂(MeFp₂), Experiment (i). A benzene-*d*₆ (0.5 ml) solution of FpBz (20 mg, 0.7 mol) and MeFp₂ (12 mg, 0.3 mmol) is irradiated for 120 min. The proton NMR shows the appearance of resonances at δ 4.23 and 1.63 ppm corresponding to [(η⁵-C₅H₅Fe(CO)₂][(η⁵-C₅H₄CH₃)Fe(CO)₂](MeFpFp) and a resonance at δ 1.25 ppm which can be assigned to MeFpBz. Also a signal at 4.20 appears that is easily assigned to Fp₂. By use of integral values and approximations based on peak height and width characteristics, a ratio of 1/2/1 for Fp₂/MeFpFp/MeFp₂, respectively, is determined. Furthermore, a small peak at δ 2.73 ppm appears for bibenzyl, however, is not sufficiently resolved for integration and assigned a ca. value of 5% of the FpBz methylene resonance.

Photolysis of FpBz and Me₂Si[η⁵-C₅H₅Fe(CO)₂]₂ (4), Experiment (ii). A benzene-*d*₆ (0.5 ml) solution of FpBz (20 g, 0.7 mmol) and 4 (11 mg, 0.3 mmol) is irradiated for 120 min. The proton NMR shows new signals for Fp₂ (δ 4.20 ppm) and bibenzyl (δ 2.73 ppm). The resonances for complex 4 remain unchanged with respect to both the relative peak integrals and positions. Conversion of FpBz to Fp₂ and bibenzyl is calculated by integration and is 35%.

Irradiation of Me₂Si[η⁵-C₅H₄Fe(CO)₂(η¹-CH₂C₆H₅)]₂ (2a) and Me₂Si[η⁵-C₅H₄Fe(CO)₂(η¹-CD₂C₆D₅)]₂ (2b); and FpBz and η⁵-C₅H₅Fe(CO)₂(η¹-CD₂C₆D₅), Experiment (iii). A stock solvent system for the cross-over experiments is prepared using benzene-*d*₆ (9.32 g, 10.7 ml) and hexamethylbenzene

(C₆Me₆) (25.6 mg, 1.6 mmol). This solution (1.5×10^{-2} M in hexamethylbenzene) is used to calculate the concentrations of the benzyliron species. A second benzyliron stock solution is prepared by dissolving ≈ 200 mg of **2a** and **2b** in the C₆Me₆-benzene-*d*₆ solution (≈ 3 ml). Approximately 0.4 ml of the benzyliron stock solution is transferred into each of the 4 NMR tubes and then diluted with varying amounts of C₆Me₆/C₆D₆ solution. By comparison of peak integrations of **2a** and **2b** to that of C₆Me₆ a total benzyliron concentration range of 0.02 to 0.07 M is calculated for the samples. All the samples are photolyzed for 90 min, centrifuged, and then a 250 MHz ¹H NMR spectrum obtained. In all four samples two resonances at δ 2.737 and 2.727 ppm are observed for the bibenzyl products. The resonance at δ 2.737 is identified as bibenzyl-*d*₀ by addition of an authentic sample of bibenzyl and concomitant increase of intensity. The two resonances have ca. equal integral values thus corresponding to a molar ratio of 1/2 for bibenzyl-*d*₀/bibenzyl-*d*₇.

In a similar manner a dilute, equimolar benzene-*d*₆ solution (0.02 M) containing FpBz and η^5 -C₅H₅Fe(CO)₂(η^1 -CD₂C₆D₅) is irradiated for 4 h and the resulting mixture analyzed by proton NMR. Two resonances at δ 2.737 and 2.727 ppm were present having a peak integral ratio of ca 1/2.

*Reaction of Me₂Si[(η^5 -C₅H₄)Fe(CO)₂(η^1 -CH₂C₆H₅)]₂ (**2a**) with Me₃NO.* A benzene solution (10 ml) of **2a** (40 mg, 0.07 mmol) and Me₃NO (100 mg, 1.3 mmol) is treated at 65°C for 1 h. The solvent is removed under vacuum and the brown residue that remains is extracted with benzene (2 ml) and is placed on a column (alumina(III), 1 × 8 cm). Elution with hexane gives a single yellow band that is collected. After solvent removal, the band is found to contain bibenzyl by comparison of its ¹H NMR spectrum to that of an authentic sample.

In a similar manner **2a** is treated with Me₃NO at ambient temperature and allowed to react for 24 h. The reaction mixture is then worked-up as above and one finds it to contain bibenzyl and small amounts of unreacted **2a** by ¹H NMR spectroscopy.

*Irradiation of dilute benzene solutions of FpBz and Me₂Si[(η^5 -C₅H₄)Fe(CO)₂(η^1 -CH₂C₆H₅)]₂ (**2a**) each containing one equivalent of PPh₃.* A benzene (100 ml) solution containing **2a** (40 mg, 0.07 mmol) and PPh₃ (37 mg, 0.14 mmol) is irradiated for 15 min. A sample (2 ml) is withdrawn from the reaction mixture, the solvent removed under vacuum, and the IR spectrum is obtained (Fig. 2). New IR(ClCH₂CH₂Cl) ν (CO) bands appear at 1734, 1776, and 1905 cm⁻¹ corresponding to Me₂Si[(η^5 -C₅H₄)₂Fe₂(CO)₃(PPh₃)], **4**, and a phosphine substituted benzyliron species, respectively. The former two complexes also possess IR ν (CO) bands at 2000 and 1954 cm⁻¹ which coincide with those of complex **2a**. The benzene solution is irradiated for an additional fifteen min and a sample withdrawn and treated as before. The IR spectrum (ClCH₂CH₂Cl) shows an increase of the 1776 and 1734 cm⁻¹ bands relative to the 1905 cm⁻¹ absorption.

A benzene (100 ml) solution of FpBz (38 mg, 0.14 mmol) and PPh₃ (37 mg, 0.14 mmol) is irradiated for 15 min. The IR spectrum for the ν (CO) bands is shown in Fig. 2. The benzene solution is photolyzed for an additional 15 min, a sample withdrawn, the benzene removed, and the IR spectrum is recorded (see results and discussion for details).

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