108. C–C Bond Formation *via* Carbon-Centered Radicals Generated from Dicarbonyl(η^5-cyclopentadienyl)organoiron Complexes

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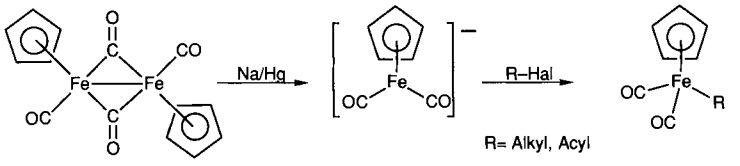
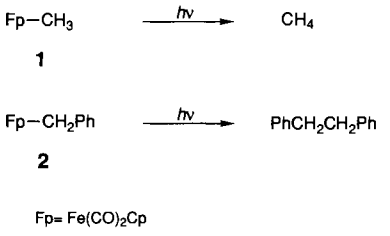
Irradiation of benzyldicarbonyl(η^5-cyclopentadienyl)iron complex (**2**) leads to homolytic cleavage of the Fe–C bond. In the presence of activated alkenes, radical addition occurs, and both saturated and unsaturated addition products **7–9** are formed. Photolysis of alkyliron complexes **2**, **3**, and **20** in the presence of acrylonitrile leads to the same products as the irradiation of the respective acyliron complexes **28–30**. This indicates that, under photolytical conditions, alkyl and acyl complexes are in equilibrium with each other.

1. Introduction. – Homolysis of metal–C bonds upon thermal or photochemical activation is a typical reaction of organometallic compounds. In many cases, the unstable intermediates can be detected both spectroscopically and chemically by the use of trapping reagents [1]. Homolysis of C–Co bonds is probably the most intensively investigated case so far. In cobalamines, C–Co bond cleavage can be induced both electrochemically and *via* one-electron reduction by metals [2][3]. Photolysis of cobaloximes leads to free radicals [4] which can be used in various C–C bond-forming reactions [5]. Acyl radicals are generated from acylcobalt complexes [6].

In contrast to C–Co bonds in cobalamines and cobaloximes, the homolytic cleavage of the C–Fe bond of dicarbonyl(η^5-cyclopentadienyl)iron complexes has been less thoroughly investigated. These complexes are readily available from dicarbonyl(cyclopentadienyl)iron dimer *via* sodium-amalgam reduction followed by treatment with alkyl or acyl halides (*Scheme 1*) [7]. Irradiation of methyl complex **1** leads to methane formation [8]. However, the intermediacy of methyl radicals is not certain [8][9]. Photolysis of benzyl complex **2** yields bibenzyl, indicating the formation of benzyl radicals [10]. ESR studies also support the intermediacy of benzyl radicals in this reaction [9].

Scheme 1

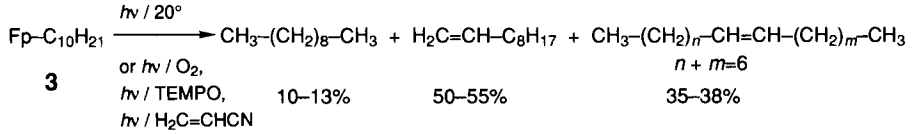


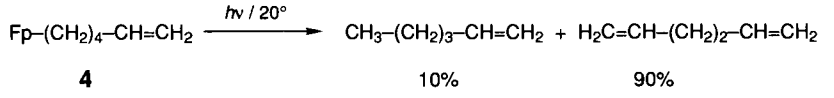


We have been interested in generating synthetically useful radicals from dicarbonyl(η^5-cyclopentadienyl)iron complexes *via* homolytic bond cleavage, and therefore, carried out a series of photolysis experiments in the presence of a variety of radical traps.

2. Results and Discussion. – Photolysis of decyl complex **3** leads quantitatively to the formation of decane, dec-1-ene, and four decene isomers [11][1]) (*Scheme 2*). Irradiation of **3** in the presence of radical traps such as O_2, 2,2,5,5-tetramethylpiperidine *N*-oxide (TEMPO), or acrylonitrile gives an identical product mixture within experimental error. Photolysis of hexenyl complex **4** also results in reduction and β-elimination; cyclization products indicative of hex-5-enyl radical intermediates[2]) are not detected.

Scheme 2





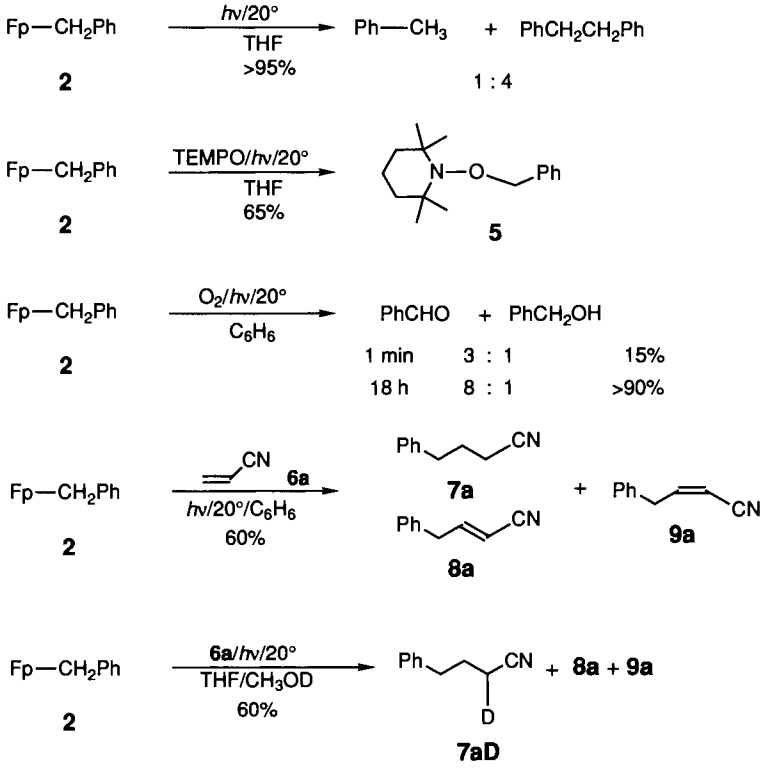
[1]) The formation of decane can be explained by the reaction of alkyl iron complex **3** with dicarbonyl(cyclopentadienyl)hydridoiron which is produced during the β-elimination [12].

[2]) For cyclization of hexenyl radicals, see [13].

We, therefore, conclude that irradiation of alkyl dicarbonyl(η^5-cyclopentadienyl)iron complexes **3** and **4** does not lead to homolytic cleavage of the C–Fe bond, as alkyl radicals could not be trapped either inter- or intramolecularly. Apparently, β-elimination occurs faster than homolysis. To make homolysis more probable, β-elimination should be inhibited. We, therefore, examined substrates containing no β-H-atoms.

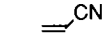
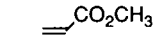
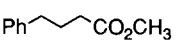
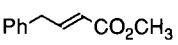
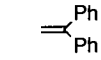
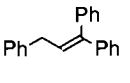
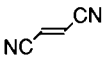
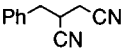
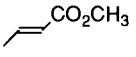
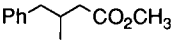
Photolysis of benzyl complex **2** in THF yields a 1:4 mixture of toluene and bibenzyl, quantitatively (*Scheme 3*). In the dark, **2** is stable even in the presence of excess TEMPO, O_2, or acrylonitrile. Photolysis in the presence of TEMPO leads to the combination product **5**. Upon irradiation with O_2, PhCHO and $PhCH_2OH$ are formed. The amount of aldehyde increases as the reaction proceeds. A control experiment shows that $PhCH_2OH$ is partially oxidized by O_2 under the irradiation conditions. The formation of O-containing products occurs presumably *via* oxygen insertion into the C–Fe bond. Decomposition of the peroxy intermediate could give aldehyde and alcohol. Irradiation of **2** in the presence of acrylonitrile (**6a**) and benzene as solvent yields products **7a–9a**.

Scheme 3



C–C Bond formation can also be effected in the presence of other electron-poor alkenes **6** (*Table 1*). Photolysis of **2** in benzene leads to saturated addition products **7** and unsaturated products **8** and **9**. In the presence of electron-rich alkenes, such as methyl vinyl ether and vinyl acetate, only toluene and bibenzyl are formed.

Table 1. *C–C Bond-Forming Reactions of Benzyl Complex* **2** (1.00 mmol) *with Alkenes* **6** (10–20 mmol) *in Benzene* (10 ml) *at 20° under Irradiation*

Alkene **6**	**7**	**8/9**	Yield [%]
a 			60
	3 : 1		
b 			40
	1 : 5		
c 	–		50
d 		–	60
e 		–	50
f 		–	50

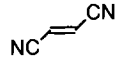
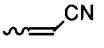
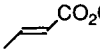
The C–C bond-forming step proceeds *via* free benzyl radicals, as demonstrated by competition kinetic experiments[3]). Benzyl radicals are generated in the presence of at least a tenfold excess of alkene pairs using the Sn method [15]. The product ratios of these pseudo-first-order reactions lead to relative rates of addition of free benzyl radicals to alkenes. Photolysis of iron complex **2** in the presence of the same alkene pairs gives identical relative rates within experimental error (*Table 2*). Therefore, we conclude that irradiation leads to homolytic cleavage of the C–Fe bond in **2** and generates free benzyl radicals, which are trapped by the alkenes.

In contrast to the radical C–C bond formation, the new C–H bond is formed *via* an ionic mechanism. Photolysis of **2** in the presence of acrylonitrile (**6a**) and MeOD leads to monodeuterated nitrile **7aD**. In perdeuterated THF, **7aD** cannot be detected. Therefore, we propose a mechanism (*Scheme 4*) that is similar to that where cobaloximes are used as radical precursors [4], or where dicarbonyl(cyclopentadienyl)iron dimer reacts with alkyl halides [16].

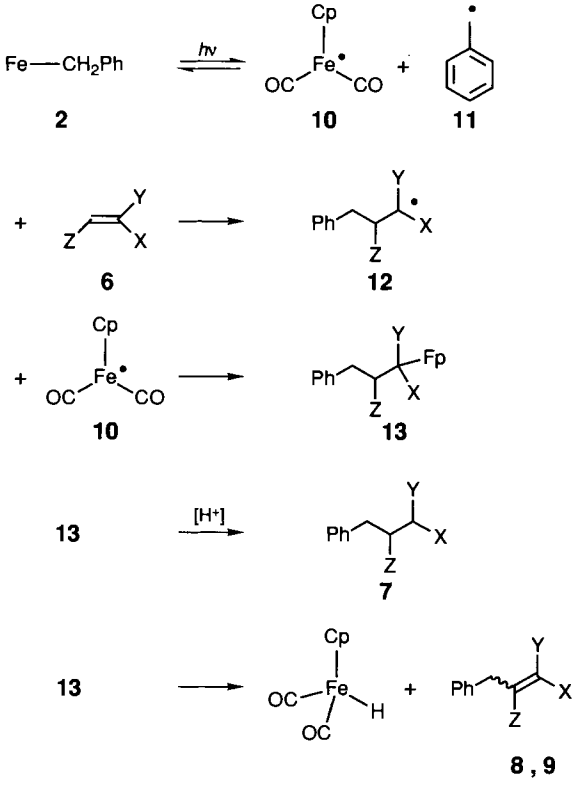
Irradiation of **2** leads to homolysis of the C–Fe bond and generates benzyl radical (**11**) which is trapped by alkene **6**. Recombination of adduct radical **12** with the Fe-centered radical **10** yields iron complex **13**. The final products are formed either *via* protolysis or by β-elimination of **13**. The data in *Table 1* show that a CN group in **6a** favors the formation of addition product **7a**, whereas the ester group in **6b** leads to larger amounts of unsaturated

[3]) For the kinetic method, see [14].

Table 2. *Relative Rates of Addition of Benzyl Radical* (**11**) *to Alkenes* **6**

Alkene **6**	$PhCH_2Br/Bu_3SnH/AIBN/Benzene/80°$	$Cp(CO)_2FeCH_2Ph$ (**2**) Benzene/*hν*/80°
d 	4.2	4.1
c 	1.5	1.3
a 	≡1.0	≡1.0
b 	0.27	0.24
e 	0.047	0.049
f 	0.026	0.022

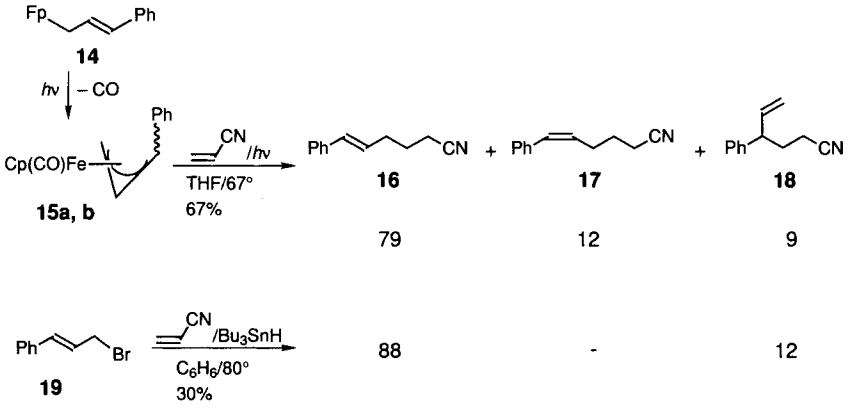
Scheme 4



product **8b**. The diphenyl-substituted olefin **6c** gives unsaturated product **8c** exclusively. Thus, electron-withdrawing groups polarize the C–Fe bond of adduct complex **13** and favor protolysis, while less electron-withdrawing substituents slow down the protolysis and lead to a larger amount of β-elimination products. 1,2-Disubstituted alkenes such as crotonyl derivatives **6e** and **6f** or dinitrile **6d** yield exclusively saturated products.

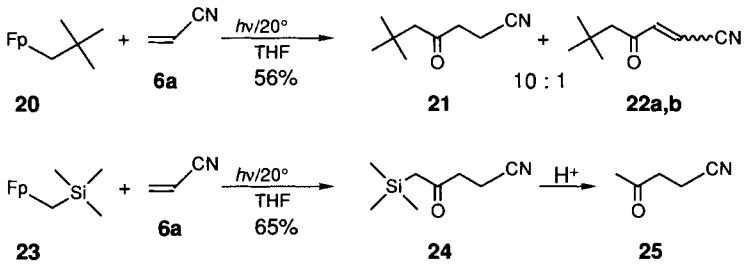
Photolysis of σ-allyl complex **14** in the presence of acrylonitrile (**6a**) gives C–C bond-formation products **16–18** (*Scheme 5*). Reaction occurs presumably *via* η^3-allyl complex **15** which is formed upon irradiation of **14**. At least two isomers of complex **15** are produced. Such σ–π rearrangements of similar η^1-allyl complexes have been previously described by *Rosenblum* and coworkers [17]. Treatment with acrylonitrile (**6a**) after the photolytic rearrangement of σ-allyl complex **14** into π-allyl complex **15** leads to the same product mixture as experiments where **6a** is added before irradiation of **14**. It is interesting to note that the π-complex **15** reacts with **6a** with similar regioselectivity as the 3-phenylallyl radical generated from 3-phenylallyl bromide (**19**) *via* the Sn method. However, during this radical reaction under thermal conditions with Bu_3SnH as the H-donor, the (*Z*)-isomer **17** could not be detected.

Scheme 5



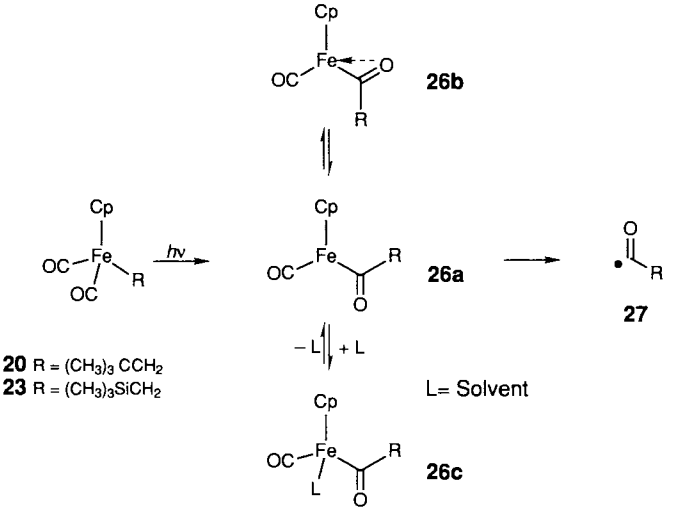
Interestingly, irradiation of either neopentyl complex **20** or (trimethylsilyl)methyl complex **23** in the presence of acrylonitrile (**6a**) leads to acylation products **21**+**22a,b** and **24**, respectively (*Scheme 6*). The Me_3Si group in **24** is lost during workup, yielding product **25**.

Scheme 6



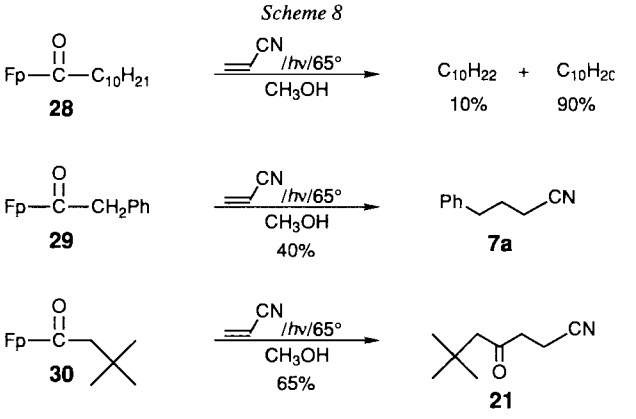
Thus, in contrast to benzyl- or allyliron complexes, acyl products are formed instead of the expected alkyl products. In these cases, carbonyl insertion into the C–Fe bond competes successfully with the generation of alkyl radicals. A possible mechanism is shown in *Scheme 7*. The 16-electron species **26a** could be stabilized *via* either η^2-coordination of the acyl ligand (→**26b**) [18] or by coordination of a solvent molecule (→**26c**). Homolysis of the C–Fe bond leads to acyl radicals **27** which are trapped by acrylonitrile (**6a**).

Scheme 7



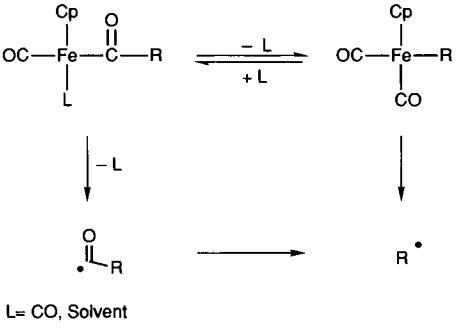
To gain further insight into the behavior of acyliron complexes, we synthesized acyl complexes **28–30** (for the synthesis, see *Scheme 1*) and photolyzed them in the presence of excess acrylonitrile (*Scheme 8*). The observed product mixtures are very similar to those obtained using the respective alkyliron complexes **3**, **2**, and **20**.

Scheme 8



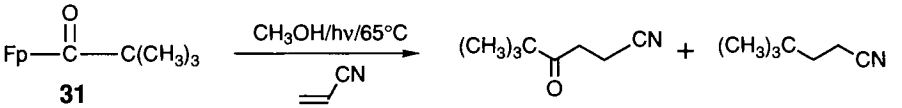
The undecanoyl complex **28** yields only decane and decene isomers, whereas the benzylcarbonyl complex **29** gives benzylated compound **7a**, and the carbonylneopentyl complex **30** leads to the formation of acylated product **21**. A possible explanation is that acyl- and alkyliron complexes are in rapid equilibrium with each other (*Scheme 9*).

Scheme 9



Thus, photolysis of acyl complexes yields alkyl complexes and alkyl radicals. Hovever, the formation of alkyl radicals can also occur *via* decarbonylation of acyl radicals. To examine this, acyl complex **31** was synthesized (*Scheme 10*). Homolysis of the C–Fe bond leads to (*tert*-butyl)carbonyl radical which decomposes less rapidly than benzylcarbonyl radical [19]. Photolysis in the presence of acrylonitrile gives acylated and alkylated addition products **32** and **33**, respectively. The product ratio depends on the concentration of acrylonitrile.

Scheme 10



0.07 mmol	0.14 mmol	36	:	64
	0.70 mmol	50	:	50
	7.00 mmol	90	:	10

The increase of the amount of the acylated product **32** with increasing acrylonitrile concentration and the increase of the amount of alkylated compound **33** with decreasing acrylonitrile concentration shows that acyl radicals are formed, which decompose and generate alkyl radicals.

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Experimental Part

General. THF was freshly distilled from potassium benzophenone. Benzene was distilled from CaH_2 and stored over molecular sieves. All reactions and manipulations of organometallic reagents were carried out under Ar. M.p.: uncorrected. The irradiation experiments were carried out with an *Osram Power Star HQI T 250/D* sunlamp. Chromatography utilized silica gel: *C 560KV* 35–70 μm (*Chemische Fabrik Uetikon*) or aluminium oxide: *507C* neutral (*Fluka*, activity III according to *Brockmann*). GC: *Carlo Erba 6000* with flame-ionization detector coupled to a *Shimadzu C-R4A* integrator (conditions: 25 m *OV-1701* or 25 m *SE-30*, 50° to 260° at 10°/min). GC/MS: *Hewlett-Packard 5790A* gas chromatograph coupled to a *Hewlett-Packard 5970A* mass-selective detector (conditions; 25 m *SE-30*, 50° to 260° at 10°/min). IR: *Perkin Elmer 781* spectrophotometer. ^{1}H- and ^{13}C-NMR: either a *Varian Gemini 300* or a *Varian VXR 400* (TMS as internal standard). MS: *VG 70-250* or a *Varian MAT 212*.

Preparation of Benzyl-, η¹-Allyl- and Alkyldicarbonyl(η⁵-cyclopentadienyl)iron Complexes. General Procedure. A mixture of dicarbonyl(η^5-cyclopentadienyl)iron dimer (1.60 g, 4.50 mmol) and Na/Hg (31 g, 1%, 13.5 mmol Na) in THF (20 ml) was stirred under Ar for 2 h at r.t. The color of the soln. changed from red-brown to orange-brown. The soln. was separated from the amalgam by a syringe and transferred into a second reaction vessel. To the soln. was added dropwise 9.00 mmol of $PhCH_2Cl$, 3-phenylallyl chloride, or alkyl bromide in THF (15 ml) at 20°. After 2 h, the solvent was removed. The brown residue was diluted with pentane (100 ml), filtered, and purified by chromatography on aluminium oxide (pentane). The yellow band was collected. Removal of the solvent gave the pure iron complex.

Benzyldicarbonyl(η⁵-cyclopentadienyl)iron (**2**). 74%. Yellow crystals. M.p. 55–56°. IR (KBr): 2018, 2007, 1954. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.70 (*s*, PhCH_2); 4.65 (*s*, C_5H_5); 6.92–7.27 (*m*, Ph). ^{13}C-NMR (101 MHz, $CDCl_3$): 4.7 (PhCH_2); 86.0 (C_5H_5); 123.1 (C(4)); 127.5 (C(3), C(5)); 128.2 (C(2), C(6)); 153.5 (C(1)); 217.5 (2 CO). FD-MS : 268 (M^+). Anal. calc. for $C_{14}H_{12}FeO_2$ (268.09): C 62.70, H 4.50; found: C 62.58, H 4.43.

Dicarbonyl(η⁵-cyclopentadienyl)(decyl)iron (**3**). 79%. Amber oil that crystallized at 10°. IR (film): 2020, 2012, 1952. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, *J* = 6.6, CH_3); 1.26 (br. *s*, $-(CH_2)_8-$); 1.45 (br. *s*, Fe–CH_2); 4.72 (*s*, C_5H_5). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.5 (Fe–CH_2); 13.9 (CH_3); 22.5, 29.2, 29.3, 29.5, 29.6, 31.8, 34.8, 38.3 ($-(CH_2)_8-$); 85.3 (C_5H_5); 218.2 (2 CO). FD-MS: 318 (M^+), 177. Anal. calc. for $C_{17}H_{26}FeO_2$ (318.24): C 64.16, H 8.24; found: C 64.21, H 8.49.

Dicarbonyl(η⁵-cyclopentadienyl)(hex-5-enyl)iron (**4**). 82%. Amber oil. IR (film): 2019, 2012, 1952. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.45 (br. *s*, Fe–$CH_2CH_2CH_2$); 2.06 (br. *s*, CH_2=CH–CH_2); 4.71 (*s*, C_5H_5); 4.94 (*m*, CH_2=CH); 5.81 (*m*, CH_2=CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.1 (Fe–CH_2); 33.4 (Fe–CH_2CH_2); 33.8 ($CH_2CH_2CH_2$–CH=); 37.6 (CH_2CH_2CH=); 114.1 (CH_2=CH); 139.7 (CH_2=CH–CH_2); 218.3 (2 CO). FI-MS: 260 (M^+), 232, 177. Anal. calc. for $C_{13}H_{16}FeO_2$ (260.12): C 60.03, H 6.20; found: C 60.31, H 6.14.

Dicarbonyl(η⁵-cyclopentadienyl)(3-phenylprop-2-enyl)iron (**14**). 34%. Yellow crystals. M.p. 84–85°. IR (KBr): 2013, 1994, 1950. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.31 (*d*, *J* = 7.8, Fe–CH_2); 4.72 (*s*, C_5H_5); 6.24 (*m*, PhCH=C*H*); 6.54 (*m*, PhC*H*=CH); 7.05–7.35 (*m*, Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 4.3 (Fe–CH_2); 85.8 (C_5H_5); 122.2 (PhCH=C*H*); 125.5 (C(2), C(6)); 125.9 (C(4)); 128.7 (C(3), C(5)); 139.2 (C(1)); 142.0 (Ph*C*H=CH); 217.3 (2 CO). FI-MS: 294 (M^+). Anal. calc. for $C_{16}H_{14}FeO_2$ (294.13): C 65.34, H 4.80; found: C 65.13, H 4.80.

Dicarbonyl(η⁵-cyclopentadienyl)(2,2-dimethylpropyl)iron (**20**). 53%. Amber oil that crystallized at 10°. IR (film): 2007, 1995, 1937. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.94 (*s*, *t*-Bu); 1.74 (*s*, Fe–CH_2); 4.74 (*s*, C_5H_5). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.9 (Fe–CH_2); 32.9 ((CH_3)$_3$C); 33.0 ((CH_3)$_3$*C*); 85.7 (C_5H_5); 219.1 (2 CO). FI-MS: 248 (M^+). Anal. calc. for $C_{12}H_{16}FeO_2$ (248.10): C 58.09, H 6.50; found: C 58.16, H 6.49.

Dicarbonyl(η⁵-cyclopentadienyl)[(trimethysilyl)methyl]iron (**23**). 84%. Amber oil that crystallized at 10°. IR (film): 2012, 2001, 1952. ^{1}H-NMR (300 MHz, $CDCl_3$): –0.34 (*s* , $FeCH_2$); 0.02 (*s*, (CH_3)$_3$Si); 4.78 (*s*, C_5H_5). ^{13}C-NMR (75 MHz, $CDCl_3$): –23.8 (CH_2); 1.8 ((CH_3)$_3$Si); 84.9 (C_5H_5); 218.1 (2 CO). FI-MS: 264 (M^+). Anal. calc. for $C_{11}H_{16}FeO_2$ (264.15): C 50.00, H 6.10; found: C 50.22, H 6.34.

Preparation of Acyldicarbonyl(η⁵-cyclopentadienyl)iron Complexes. General Procedure. A mixture of dicarbonyl(η^5-cyclopentadienyl)iron dimer (3.00 g, 8.45 mmol) and Na/Hg (58 g, 1%, 25.2 mmol of Na) in THF (20 ml) was stirred under Ar for 2 h at r.t. The color of the soln. changed from red-brown to orange-brown. The soln. was separated from the amalgam by a syringe and transferred into a second reaction vessel. To this were added dropwise 16.9 mmol acyl chloride in THF (30 ml) at –78°. After 15 h stirring at 20°, the solvent was removed, the brown residue diluted with pentane/Et_2O 1:1 (100 ml), filtered, and purified by chromatography on aluminium oxide (pentane/Et_2O 9:1). The yellow band was collected. Removal of the solvent and recrystallization (pentane/Et_2O 1:1, –78°) gave the pure iron complex.

Dicarbonyl(η⁵-cyclopentadienyl)(decanoyl)iron (**28**). 43%. Amber oil that crystallized at 10°. IR (KBr): 2010, 1950, 1650. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.85 (*t*, *J* = 7.0, CH_3); 1.21 (br. *s*, $-(CH_2)_7-$); 1.43 (*q*, *J* = 7.0, Fe–$COCH_2$); 4.82 (*s*, C_5H_5). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.7 (CH_3); 22.3, 24.9, 28.7, 28.9, 29.0, 29.1, 29.3, 31.6 ($-(CH_2)_8-$); 66.6 (Fe–$COCH_2$); 86.3 (C_5H_5); 215.1 (2 CO); 257.6 (Fe–CO). FAB-MS: 347 ([*M* + 1]$^+$), 318, 205. Anal. calc. for $C_{18}H_{26}FeO_3$ (346.25): C 62.44, H 7.58; found: C 62.68, H 7.88.

(Benzylcarbonyl)dicarbonyl(η⁵-cyclopentadienyl)iron (**29**). 38%. Yellow crystals. M.p. 78–79°. IR (KBr): 2020, 1960, 1645. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.10 (*s*, Fe–$COCH_2$); 4.75 (*s*, C_5H_5); 7.10–7.40 (*m*, Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 71.5 (Fe–$COCH_2$); 86.2 (C_5H_5); 126.7 (C(4)); 128.6 (C(3), C(5)); 129.8 (C(2), C(6)); 135.0 (C(1)); 214.9 (2 CO); 254.5 (Fe–CO). FAB-MS: 297 ([*M* + 1]$^+$), 205. Anal. calc. for $C_{15}H_{12}FeO_3$ (262.09): C 60.85, H 4.09; found: C 60.88, H 4.38.

Dicarbonyl(η⁵-cyclopentadienyl)[(2,2-dimethylpropyl)carbonyl]iron (**30**). 53%. Yellow crystals. M.p. 61–62°. IR (KBr): 2015, 1940, 1645. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86 (*s*, *t*-Bu); 2.82 (*s*, Fe–$COCH_2$); 4.74 (*s*, C_5H_5). ^{13}C-NMR (75 MHz, $CDCl_3$): 29.1 ((CH_3)$_3$C); 32.4 ((CH_3)$_3C$); 79.2 (Fe–$COCH_2$); 86.4 (C_5H_5); 215.2 (2 CO); 256.9 (Fe–CO). FAB-MS: 277 ([*M* + 1]$^+$), 276 (*M*$^+$), 248, 205. Anal. calc. for $C_{13}H_{16}FeO_3$ (276.16): C 56.55, H 5.84; found: C 56.72, H 5.98.

*[(*tert*-Butyl)carbonyl]dicarbo*nyl(*η⁵-cyclopentadienyl)iron* (**31**). 42%. Yellow crystals. M.p. 69–70°. IR (KBr): 2000, 1935, 1620. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*s*, *t*-Bu); 4.96 (*s*, C_5H_5). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.7 ((CH_3)$_3$C); 57.8 (Fe–*C*OC); 86.3 (C_5H_5); 216.1 (2 CO); 263.9 (Fe–CO). FAB-MS: 263 ([*M* + 1]$^+$), 234, 205. Anal. calc. for $C_{12}H_{14}FeO_3$ (262.09): C 54.99, H 5.38; found: C 54.93, H 5.17.

Photolysis of **3** *in the Absence and in the Presence of Radical Traps, such as 2,2,5,5-Tetramethylpiperidine* N-*Oxide (TEMPO), Acrylonitrile* (**6a**), *and* O_2. A soln. of **3** (50 mg, 0.16 mmol) in THF (10 ml) was irradiated at 20° for 2 h. The mixture was analyzed by GC/MS. Decane and decene isomers were formed almost quantitatively. Decane and dec-1-ene were identified by comparison by GC/MS with commercially available samples, the olefin isomers by MS. In the presence of excess (10 equiv.) TEMPO, acrylonitrile, or O_2, identical product mixtures were formed.

Photolysis of Dicarbonyl(η⁵-cyclopentadienyl)(hex-5-enyl)iron (**4**). A soln. of **4** (50 mg, 0.19 mmol) in 2,3,4,5-tetrahydro-2,3,4,5-tetramethylfuran (10 ml) was irradiated at 20° for 2 h. The mixture was analyzed by GC/MS. Hex-1-ene and hexa-1,5-diene were formed almost quantitatively in a 1:9 ratio. The products were identified by comparison by GC/MS with authentical samples.

Photolysis of Benzyldicarbonyl(η⁵-cyclopentadienyl)iron (**2**). A soln. of **2** (100 mg, 0.37 mmol) in THF (10 ml) was irradiated for 20 h at 20°. The mixture was analyzed by GC/MS. Toluene and bibenzyl were formed almost quantitatively in a 1:4 ratio. The products were identified by comparison by GC/MS with authentical samples.

Photolysis of Benzyldicarbonyl(η⁵-cyclopentadienyl)iron (**2**) *in the Presence of TEMPO.* N-*(Benzyloxy)-2,2,6,6-tetramethylpiperidine* (**5**). A soln. of **2** (134 mg, 0.50 mmol) and TEMPO (345 mg, 2.50 mmol) in THF (10 ml) was irradiated at 20°. After 2 h, the solvent was removed and the residue purified by chromatography on aluminium oxide with pentane/Et_2O 10:1 to yield 75 mg (61%) of colorless oil **5**. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*s*, 2 CH_3); 1.25 (*s*, 2 CH_3); 1.30–1.50 (*m*, $CH_2CH_2CH_2$); 4.82 (*s*, PhCH_2); 7.30–7.50 (*m*, Ph). MS (GC/MS): 247 (*M*$^+$), 232, 156, 91.

Photolysis of Benzyldicarbonyl(η⁵-cyclopentadienyl)iron (**2**) *in the Presence of Alkenes* **6**. *General Procedure.* A soln. of **2** (268 mg, 1.00 mmol) and alkene **6** (10.0 mmol) in 10 ml of solvent was irradiated at 20°. After 3 h, the solvent was removed and the residue purified by chromatography on aluminium oxide with pentane/Et_2O 10:1. In the cases of *acrylonitrile* (**6a**) and *methyl acrylate* (**6b**), the products were isolated as a mixture of colorless oils. The product ratios were determined by GC before workup. In the other cases, only one product was formed. Solvents, product ratios, and yields are given in *Table 1*. All products are known compounds.

Photolysis of Benzyldicarbonyl(η⁵-cyclopentadienyl)iron (**2**) *in the Presence of* O_2. Dry O_2 was bubbled through a soln. of **2** (50 mg, 0.16 mmol) in benzene (10 ml), while the soln. was irradiated at 20°. The mixture was analyzed by GC. Benzaldehyde and benzyl alcohol were identified by comparison by GC/MS with authentical samples. The yields are given in *Scheme 3*.

Photolysis of Benzyl Alcohol in the Presence of O_2. Dry O_2 was bubbled through a soln. of $PhCH_2OH$ (20 mg, 0.19 mmol) in benzene (10 ml), while the soln. was irradiated at 20°. The mixture was analyzed by GC. After 20 h, 25% of the benzyl alcohol had been oxidized to form benzaldehyde.

Photolysis of Dicarbonyl(η⁵-cyclopentadienyl)(3-phenylprop-2-enyl)iron (**14**). *Carbonyl(η⁵-cyclopentadienyl)(phenyl-η³-allyl)iron* (**15**). A soln. of **14** (15.0 mg, 0.05 mmol) in C_6D_6 (0.7 ml) was irradiated at 20°. After 20, 80, and 200 s, the irradiation was interrupted, and ^{1}H-NMR spectra were recorded. The signals of **14** decreased, while the signals of two new compounds **15a** and **15b** appeared in a 7:5 ratio.

15a: ^{1}H-NMR (300 MHz, C_6D_6): 1.37 (*d*, *J* = 11, 1 H); 2.31 (*d*, *J* = 10, 1 H); 2.85 (*m*, 1 H); 4.09 (*s*, C_5H_5); 4.50 (*m*, 1 H).

15b: ^{1}H-NMR (300 MHz, C_6D_6): 0.78 (*d*, *J* = 10, 1 H); 2.68 (*d*, *J* = 5, 1 H); 2.90 (*m*, 1 H); 3.86 (*s*, C_5H_5); 4.95 (*m*, 1 H).

The upfield shift of the allylic proton signals of **15a** and **15b** compared to the olefinic signals of **14** is typical for η^3-allyl complexes [17].

Photolysis of **14** *in the Presence of* **6a**. *(E)-6-Phenylhex-5-enenitrile* (**16**), *(Z)-6-Phenylhex-5-enenitrile* (**17**), *and 4-Phenylhex-5-enenitrile* (**18**). A soln. of **14** (150 mg, 0.51 mmol) and **6a** (270 mg, 5.10 mmol) in THF (10 ml) was irradiated at 67°. After 3 h, the solvent was removed, and chromatography on aluminium oxide (pentane/Et_2O 10:1) yielded 50 mg (57%) of a colorless oil **16** that was identified by comparison by GC/MS and ^{1}H-NMR with an authentic sample (see addition of *3-phenylallylbromide* (**19**) to **6a**). The mixture was analyzed by GC/MS before workup. Compounds **17** and **18** were identified by comparison by GC/MS with authentic samples. The product ratio **16/17/18** was determined by GC before workup to be 79:12:9.

Addition of PhCH$_2$Br to 1,1-Diphenylethene (**6c**). *1,1,3-Triphenylpropane* (**7c**). To a soln. of **8c** (1.80 g, 10.0 mmol) and $PhCH_2Br$ (6.84 g, 40.0 mmol) in benzene (20 ml) at 80° were added within 4 h *via* a syringe pump Bu_3SnH (14.7 g, 50.0 mmol) and azobisisobutyronitrile (AIBN; 0.82 g, 5.00 mmol) in benzene (20 ml). After another 2 h, the mixture was cooled to 20°. I_2 was added in small portions, until the soln. remained red. The solvent was removed and the residue dissolved in Et_2O (100 ml). To this soln. were added H_2O (3 ml) and KF (6.00g, 100 mmol). The mixture was stirred for 12 h. Filtration over $MgSO_4$, removal of the solvent, and flash chromatography on a silica-gel column (pentane/Et_2O 10:1) yielded 1.90 g (70%) of the colorless oil **7c**. IR (film): 3080, 3060, 3020, 2930, 2860, 1600, 1490, 1450. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.37 (*m*, 2 H–C(2)); 2.56 (*m*, 2 H–C(3)); 3.91 (*t*, *J* = 7.7, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 33.9 (C(2)); 37.2 (C(3)); 50.6 (C(1)); 126.0–128.7 (15 arom C); 142.3, 145.1 (2 arom. C). EI-MS: 272 (M^+), 167. Anal. calc. for $C_{21}H_{20}$ (272.37): C 92.60, H 7.40; found: C 92.86, H 7.55.

Addition of **19** *to* **6a**. *Compounds* **16** *and* **18**. To a soln. of **6a** (8.06 g, 152 mmol) and **19** (3.00 g, 15.2 mmol) in benzene (25 ml) at 80° were added within 4 h *via* a syringe pump Bu_3SnH (6.68 g, 22.8 mmol) and AIBN (0.20 g, 1.20 mmol) in benzene (20 ml). The workup as described above gave 0.78 g (30%) of a colorless oil consisting of a mixture **16/18**. The product ratio before workup was 88:12.

16: IR (film): 2250. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.86 (*quint.*, *J* = 7.1, 2 H–C(3)); 2.38–2.45 (*m*, 2 H–C(2), 2 H–C(4)); 6.15 (*dt*, *J* = 15.8, 7.1, H–C(5)); 6.49 (*d*, *J* = 15.8, H–C(6)); 7.23–7.45 (*m*, Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 16.1 (C(2)); 24.7 (C(3)); 31.4 (C(4)); 119.6 (CN); 126.2 (C(3), C(5)); 127.5 (C(4) or C(5)); 127.7 (C(4) or C(5)); 128.7 (C(2), C(6)); 132.1 (C(6)); 137.2 (C(1)). EI-MS: 171 (M^+), 130, 129, 117, 115, 91.

18: IR (film): 2240.^{1}H-NMR (300 MHz, $CDCl_3$): 2.08 (*m*, 2 H–C(3)); 2.29 (*m*, 2 H–C(2)); 3.43 (*q*, *J* = 7.7, H–C(4)); 5.15 (br. *d*, *J* = 10.0, (*E*)-H–C(6)); 5.17 (br. *d*, *J* = 17.4, (*Z*)-H–C(6)); 5.95 (*ddd*, *J* = 17.4, 10.0, 7.7, H–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.1 (C(2)); 30.5 (C(3)); 48.3 (Ph); 115.9 (C(6)); 119.3 (CN); 127.1 (C(4)); 127.6 (C(3), C(5)); 129.0 (C(2), C(6)); 140.1 (C(5)); 142.0 (C(1)). EI-MS: 171 (M^+), 130, 129, 117, 115, 91.

Competition Kinetic Experiments. Bu$_3$SnH as Mediator. A soln. of Bu_3SnH (50 mg, 17 mmol) and AIBN (5 mg) in benzene (5 ml) was added within 15 min to a soln. of $PhCH_2Br$ (50 mg, 0.29 mmol), acrylonitrile, and the competing alkene at 80°. The olefins were used in large excess (at least 20 equiv. compared to the Bu_3SnH). The relative rate constants were determined for three different alkene ratios. The product ratios were determined by GC.

Compound **2** *as Radical Source*. A soln. of **2** (20 mg, 0.075 mmol), acrylonitrile, and the competing alkene in benzene (5 ml) was irradiated at 80° for 1 h. The olefins were used in large excess (at least 20 equiv. compared to **2**). The relative rate constants were determined for three different alkene ratios. The product ratios were determined by GC. The selective rate ratios were determined according to pseudo-first-order kinetics [14].

Photolysis of Alkyliron Complexes **20** *and* **23** *in the Presence of* **6a**. *6,6-Dimethyl-4-oxoheptanenitrile* (**21**), *(E)-6,6-Dimethyl-4-oxohept-2-enenitrile* (**22a**), *and (Z)-6,6-Dimethyl-4-oxohept-2-enenitrile* (**22b**). A soln. of **20** (200 mg, 0.81 mmol) and **6a** (430 mg, 8.10 mmol) in THF (10 ml) was irradiated at 20°. After 2 h, the solvent was removed and the residue purified by chromatography on aluminium oxide (pentane/Et_2O 5:1). This gave 70 mg (56%) of a colorless oil consisting of **21**, **22a**, and **22b**. The ratio of the products before the workup was 90:3:7.

21: IR (film): 2245, 1720. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.03 (*s*, 3 CH_3); 2.35 (*s*, 2 H–C(5)); 2.56 (*t*, *J* = 7.1, 2 H–C(3)); 2.78 (*t*, *J* = 7.1, 2 H–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 29.5 (3 CH_3); 11.0 (C(2)); 31.1 (C(6)); 39.8 (C(3)); 54.5 (C(5)); 119.2, (CN); 206.3 (C(4)). EI-MS: 153 (M^+), 138, 82, 57.

2,4-Dinitrophenylhydrazone of **21**: M.p. 144–145°. MS: calc. for $C_{15}H_{19}N_5O_4$: 333.1438; found: 333.1442.

22a: ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*s*, 3 CH_3); 2.50 (*s*, 2 H–C(5)); 6.30 (*d*, *J* = 16.2, H–C(2)); 6.95 (*d*, *J* = 16.2, H–C(3)). EI-MS: 150 ([*M* – 1]$^+$), 136, 96, 80, 57.

22b: ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*s*, 3 CH_3); 2.05 (*s*, 2 H–C(5)); 5.72 (*d*, *J* = 9.7, H–C(2)); 6.80 (*d*, *J* = 9.7, H–C(3)). EI-MS: 150 ([*M* – 1]$^+$), 136, 96, 80, 57.

4-Oxo-5-(trimethylsilyl)pentanenitrile (**24**) *and 4-Oxopentanenitrile* (**25**). A soln. of **23** (500 mg, 1.89 mmol) and **5a** (1000 mg, 18.9 mmol) in THF (20 ml) was irradiated at 20°. After 2 h, the solvent was removed and the residue purified by chromatography on aluminium oxide (pentane/Et_2O 5:1). This yielded 120 mg (65%) of **25** as a colorless oil. IR (film): 2250 1720. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.20 (*s*, CH_3); 2.55 (*t*, *J* = 6.9, 2 H–C(3)); 2.82 (*t*, *J* = 6.9, 2 H–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.0 (C(2)); 29.3 (C(5)); 38.4 (C(3)); 119.1 (C(1)); 204.2 (C(4)). EI-MS: 97 (*M*$^+$), 82, 54, 43.

2,4-Dinitrophenylhydrazone of **25**: M.p. 140–141°. MS: calc. for $C_{11}H_{11}N_5O_4$: 277.0811, found: 277.0823.

Before chromatography, **24** was characterized as the main product by GC/MS: 169 (*M*$^+$), 154, 98, 73.

Photolysis of Acyliron Complexes **28**–**31** *in the Presence of* **6a**. *General Procedure*. A soln. of **28**, **29**, **30**, and **31** (1.0 mmol) and **6a** (1.06 g, 20.0 mmol) in MeOH (20 ml) was irradiated at 65°. After 2 h, the solvent was removed and the residue purified by chromatography on aluminium oxide to yield the products as colorless oils. The known products were characterized by comparison by GC/MS and/or ^{1}H-NMR with authentic samples. The yields are given in *Scheme 8*.

5,5-Dimethyl-4-oxohexanenitrile (**32**). 57%. IR (film): 2250, 1715. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*s*, 3 CH_3); 2.55 (*t*, *J* = 7.1, 2 H–C(3)); 2.88 (*t*, *J* = 7.1, 2 H–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.5 (C(2)); 26.1 (3 CH_3); 32.2 (C(3)); 43.7 (C(5)); 119.4 (C(1)); 212.0 (C(4)). EI-MS: 124 ([*M* – 15]$^+$), 111, 82, 57, 41. MS (CI$^+$): 157 ([*M* + NH_4]$^+$), 111. Anal. calc. for $C_8H_{13}NO$ (139.20): C 69.03, H 9.41, N 10.06; found: C 69.50, H 9.63, N 10.30.

Dependence of the Reaction of (tert-*Butyl*)*carbonyliron Complex* **31** *on the Concentration of* **6a**. A soln. of **31** (19 mg, 0.07 mmol) and 0.14, 0.7, or 7.00 mmol of **6a** in MeOH (3 ml) was irradiated at 65° for 2 h. The mixtures were analyzed by GC. The ratios are given in *Scheme 10*. Products **32** and **33** were characterized by comparison by GC/MS with authentic samples.

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