# 107. Dimeric Metal Complexes as Mediators for Radical C–C Bond-Forming Reactions

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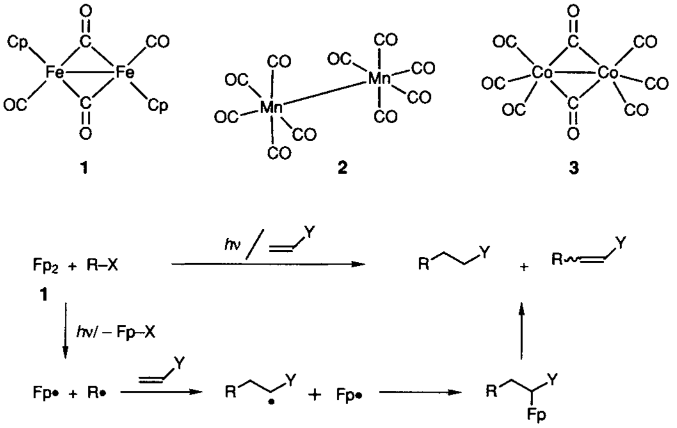
Irradiation of dicarbonyl($\eta^5$-cyclopentadienyl)iron dimer **1** or decacarbonyldimanganese (**2**) in the presence of alkyl halides leads to C-centered radicals which can be trapped by alkenes and yields saturated and/or unsaturated addition products. Carbon radicals are generated *via* halogen abstraction by the initially formed metal-centered radicals resulting from homolysis of the metal–metal bond of dimeric mediators **1** and **2**. No reaction occurs using octacarbonyldicobalt (**3**).

**1. Introduction.** – Irradiation of dimeric metal complexes in the presence of alkyl halides can lead to metal halogen complexes [1] *via* halogen abstraction by the initially formed 17-electron metal-centered radicals [2]. In the case of dicarbonyl($\eta^5$-cyclopentadienyl)iron dimer **1** (*Scheme 1*), we have recently shown that I-abstraction from alkyl iodides generates free alkyl radicals which can be used in organic synthesis [3]. In the presence of alkenes, these radicals are trapped and form adduct radicals; subsequent recombination with Fe-centered radicals leads to adduct complexes. Solvolysis of the adduct complexes competes with $\beta$-elimination, resulting in saturated and/or unsaturated addition products.

*Scheme 1*

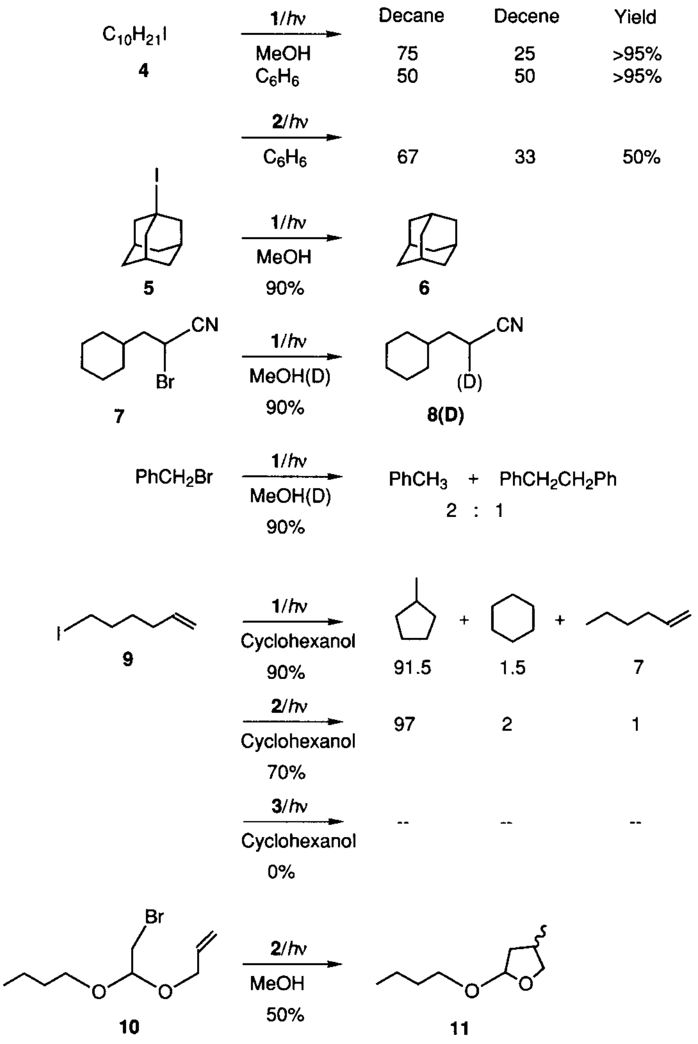


Fp = Fe(CO)$_2$Cp

Here, we present more detailed experimental data for this new 'iron method', as well as experiments using decacarbonyldimanganese (**2**) and octacarbonyldicobalt (**3**) as mediators.

**2. Results and Discussion.** – Alkyl iodides or activated bromides can be reduced upon irradiation of the iron complex **1**. Decyl iodide (**4**) produces decane and decene isomers almost quantitatively (*Scheme 2*). In $CH_3OD$, decane is found to be 70% monodeuterated. 1-Adamantyl iodide (**5**) yields adamantane (**6**). The degree of deuteration in $CH_3OD$ is 80%. Activated bromonitrile **7** is reduced to produce **8** which is quantitatively monodeuterated,

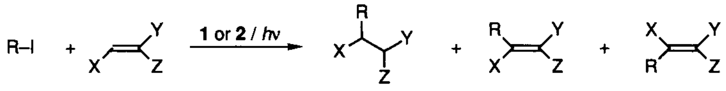
*Scheme 2*



if the reaction is carried out in $CH_3OD$. Photolysis of the iron complex **1** in the presence of $PhCH_2Br$ leads to toluene and bibenzyl in a 2:1 ratio. Irradiation of hex-5-enyl iodide (**9**) results in the formation of methylcyclopentane, cyclohexane, and hex-1-ene. Five- and six-membered rings are produced in a 98:2 ratio, which is typical for cyclization of hex-5-enyl radicals [4]. Similar results are obtained using pentacarbonyldimanganese (**2**) as mediator. With **2**, cyclization of bromo acetal **10** forms cyclized product **11**. Iron complex **1** does not react with bromide **10**. Thus, the Mn-centered radical generated from complex **2** is more reactive than the Fe radical. Octacarbonyldicobalt (**3**) is completely unreactive, even towards activated halides.

Intermolecular C–C bond-forming reactions are also possible using the 'iron method'. Thus, photolysis of cyclohexyl iodide (**12**) and various electron-poor alkenes **13** in the presence of dimeric iron complex **1** leads to saturated addition products **14** and unsaturated substitution products **15** and **16** (*Scheme 3*).

*Scheme 3*



**12** **13** **14** **15** **16**

R = Cyclohexyl

The data in *Table 1* show that protic solvents and electron-withdrawing groups at the alkene give saturated compounds **14**, whereas less electron-withdrawing substituents and

Table 1. *Photolysis of Metal Complexes* **1** *or* **2** *in the Presence of Cyclohexyl Iodide* (**12**) *and Alkenes* **13** (see *Scheme 3*)

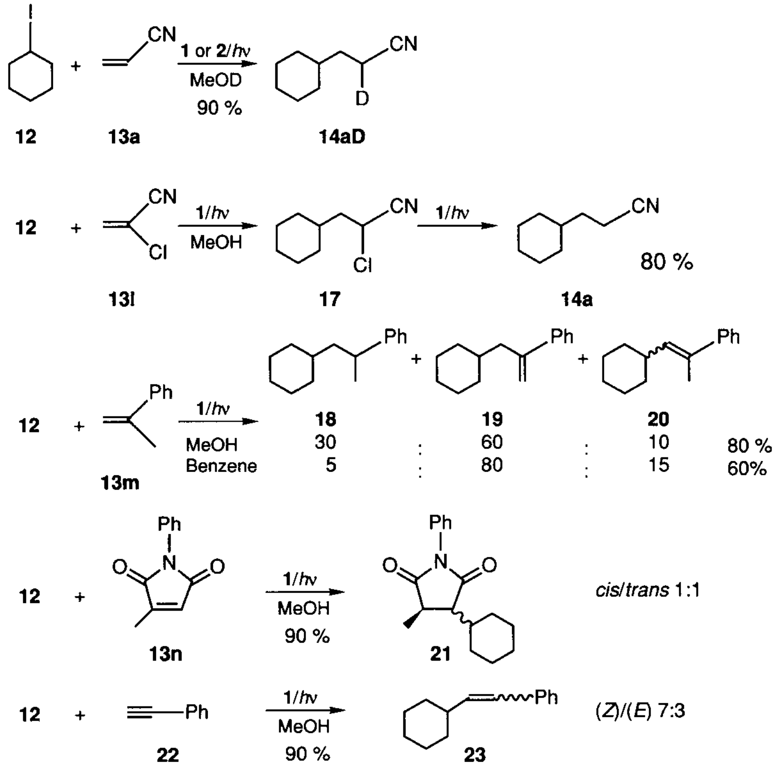
| Alkene 13 | | | | Metal complex | Solvent | 14 | 15 | 16 | Yield [%] |
|---|---|---|---|---|---|---|---|---|---|
| | X | Y | Z | | | | | | |
| **a** | H | CN | H | 1 | MeOH | 100 | – | – | 90 |
| | | | | | $CH_2Cl_2$ | 55 | 18 | 27 | 80 |
| | | | | | $C_6H_6$ | 50 | 20 | 30 | 75 |
| | | | | 2 | MeOH | 94 | 3 | 3 | 45 |
| | | | | | $CH_2Cl_2$ | 93 | 3 | 4 | 60 |
| | | | | | $C_6H_6$ | 93 | 2 | 5 | 30 |
| **b** | H | $CO_2Me$ | H | 1 | MeOH | 100 | – | – | 55 |
| **c** | H | CN | OEt | 1 | AcOH | 88 | | 12 | 55 |
| | | | | | MeOH | 88 | | 12 | 80 |
| | | | | | $C_6H_6$ | | 50 | 50 | 65 |
| **d** | H | Ph | H | 1 | MeOH | 40 | 26 | 34 | 50 |
| | | | | | $C_6H_6$ | 5 | 37 | 58 | 45 |
| **e** | H | Ph | Ph | 1 | MeOH | 67 | | 33 | 60 |
| | | | | | $C_6H_6$ | | 10 | 90 | 55 |
| **f** | Me | CN | H | 1 | MeOH | 100 | – | – | 50 |
| **g** | H | $CO_2Et$ | $CO_2Et$ | 1 | MeOH | 100 | – | – | 75 |
| **h** | Me | $CO_2Et$ | $CO_2Et$ | 1 | MeOH | 100 | – | – | 55 |
| **i** | i-Pr | $CO_2Me$ | $CO_2Me$ | 1 | MeOH | 100 | – | – | 15 |
| **k** | *t*-Bu | $CO_2Me$ | $CO_2Me$ | 1 | MeOH | – | – | – | – |

aprotic solvents favor the unsaturated products **15** and **16**. Alkyl groups X at the reactive C-center (*cf.* **13f**, **13h–k**) lead to lower yields as their bulkiness increases. *t*-Bu-substituted methylidenemalonate **13k** gives no addition products. C–C Bond formation can also not be achieved with electron-rich alkenes such as methyl vinyl ether.

The reaction of cyclohexyl iodide (**12**) with acrylonitrile (**13a**) using the complex **2** as mediator yields saturated product **14a** and unsaturated products **15a** and **16a**. However, no solvent dependence of the product ratio was observed. Even in protic solvents, such as $CH_3OH$, small amounts of unsaturated compounds **15a** and **16a** are produced. In $CH_2Cl_2$ or benzene, the ratio remains unchanged, but the yields are lower than those obtained using the iron complex **1**. Probably, the adduct radicals formed *via* alkyl-radical addition to the alkene are trapped less efficiently using the Mn than the Fe complex. The Fe–Fe bond of **1** is weaker (96 kJ/mol [5]) than the Mn–Mn bond of **2** (150 kJ/mol [6]). Therefore, the concentration of Mn radicals should be lower than that of Fe radicals, leading to less effective trapping of adduct radicals by the Mn radicals.

The reaction of **12** with **13a** in $CH_3OD$ leads quantitatively to deuterated addition product **14aD** using either mediators **1** or **2** (*Scheme 4*). Irradiation of **1** in the presence of cyclohexyl iodide (**12**) and $\alpha$-chloroacrylonitrile (**13l**) yields nitrile **14a** which is presumably formed *via* reduction of the initially produced chloronitrile **17**. Reaction of $\alpha$-methylstyrene (**13m**) leads to unsaturated compounds **19** and **20** as the main products, with

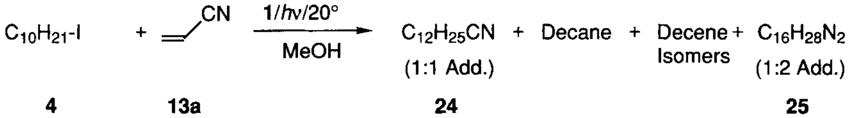
*Scheme 4*



the terminal alkene **19** as the favored regioisomer. Cyclic alkene **13n** gives addition product **21** in a 1:1 *cis/trans* ratio and phenylacetylene (**22**) yields styrene derivatives **23** in a 7:3 (*Z*)/(*E*) ratio.

The influence of the alkene concentration on the product ratio and the yield was studied by irradiation of decyl iodide (**4**) and acrylonitrile (**13a**) with the iron complex **1**, yielding nitrile **24**, decane, and small amounts of decene isomers (*Scheme 5*). The best yields of addition product **24** are obtained using 10 to 20 equiv. of the alkene. Lower alkene concentrations lead to increasing amounts of decane, whereas higher alkene concentrations result in the formation of 1:2 addition product **25** which can be detected by GC/MS.

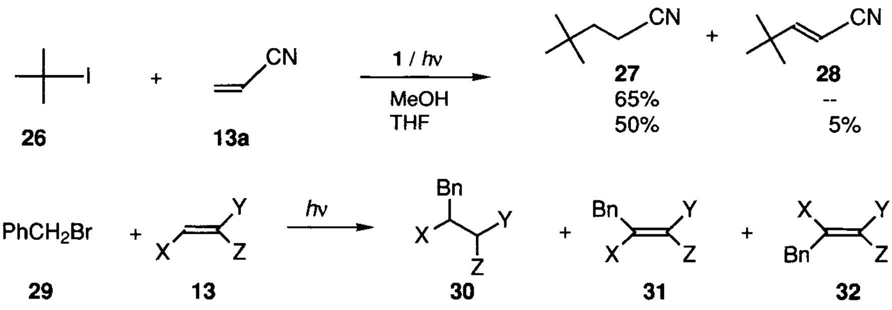
*Scheme 5*



| **13a / 4** | **24** [%] | Decane [%] | Decene Isomers [%] | **25** [%] |
|---|---|---|---|---|
| 1 | 47 | 50 | 3 | - |
| 2 | 63 | 35 | 2 | - |
| 5 | 78 | 21 | 1 | - |
| 10 | 83 | 16 | 1 | - |
| 20 | 85 | 12 | - | 1 |
| 50 | 85 | 5 | - | 5 |

The reaction of *t*-BuI (**26**) with **13a** in MeOH using the iron complex **1** as mediator leads exclusively to saturated product **27** (*Scheme 6*). Even in THF, only a small amount of unsaturated compound **28** is formed. Photolysis of the iron complex **1** in the presence of $PhCH_2Br$ (**29**) and electron-poor alkenes yields saturated products **30** and/or unsaturated addition products **31** and **32** depending on the solvent and the substituents on the alkene (*Table 2*).

*Scheme 6*



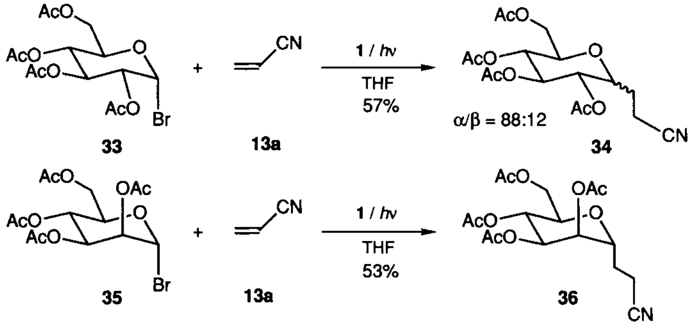
Bn = $PhCH_2$

Table 2. *Photolysis of the Iron Complex* **1** *in the Presence of Benzyl Bromide* (**29**) *and Alkenes* **13** (see *Scheme 7*)

| Alkene 13 | | | | Solvent | 30 | 31 | 32 | Yield [%] |
|---|---|---|---|---|---|---|---|---|
| | X | Y | Z | | | | | |
| **a** | H | CN | H | MeOH | 100 | – | – | 65 |
| | | | | $C_6H_6$ | 55 | 25 | 20 | 60 |
| **b** | H | $CO_2Me$ | H | MeOH | 98 | – | 2 | 55 |
| **e** | H | Ph | Ph | $C_6H_6$ | | 2 | 98 | 50 |
| **f** | Me | CN | H | $C_6H_6$ | 100 | – | – | 50 |
| **o** | Me | $CO_2Et$ | H | $C_6H_6$ | 100 | – | – | 40 |
| **p** | CN | CN | H | THF | 100 | – | – | 50 |

Glycosyl bromides **33** and **35** can also be used for radical C–C bond formation. In the presence of **13a**, bromide **33** leads to *C*-glycoside **34** with an *α*/*β* ratio of 88:12, whereas **35** gives exclusively the *α*-isomer **36** (*Scheme 7*). The *α*/*β* ratios of **34** and **36** are identical to those obtained using $Bu_3SnH$ as mediator [7].

*Scheme 7*



**3. Conclusion.** – Dimeric metal complexes are useful mediators in inter- and intramolecular radical addition reactions to C–C *π*-bonds. Various halides can be used as radical precursors. Both saturated and unsaturated addition products are formed using the iron complex **1**, depending on the choice of solvent and substituents at the alkene. The Mn radical generated from the dimeric manganese complex **2** is more reactive towards alkyl halides, but the yields of the addition products are lower than those with the iron complex **1**.

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## Experimental Part

*General.* The irradiation experiments were carried out with an *Osram Power Star HQI T 250/D* sunlamp in *Pyrex* vessels that were cooled with $H_2O$. The reaction mixtures were irradiated through *Pyrex* and $H_2O$. 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: *Varian Gemini 300* (TMS as internal standard). MS: *VG 70-250* or a *Varian MAT 212*.

*Reduction Reactions.* A soln. of the halide (1.0 mmol) and metal complex **1** or **2** (1-2 mmol) in degassed solvent (20 ml) was irradiated at 15–20° for 2–3 h. The solvent was removed *in vacuo* and the residue extracted with $Et_2O$ (20 ml). Chromatography on aluminium oxide with pentane/$Et_2O$ (starting with pentane, then pentane/$Et_2O$ 20:1–5:1) gives the products. Adamantane (**6**) was eluted with pure pentane. Decane and decene isomers were analyzed by GC/MS. Solvents and yields are given in *Scheme 2*. The degrees of deuteration were determined by $^1$H-NMR and/or MS. Using **1** as mediator, ferrocene, dicarbonyl($\eta^5$-cyclopentadienyl)iodo- and -bromoiron were isolated in addition to the products of C–C bond formation. All products are known compounds.

*Intramolecular C–C Bond-Forming Reactions. Reaction with Hex-5-enyl Iodide* (**9**). A soln. of **9** (210 mg, 1.0 mmol) and metal complex **1**, **2**, or **3** (1–2 mmol) in degassed cyclohexanol (20 ml) was irradiated at 15° for 12 h. The cyclized products were analyzed by comparison of their GC/MS with authentic samples. In the case of octacarbonyldicobalt, starting material **9** was not consumed even at 60°.

*Reaction with Bromoacetaldehyde Allyl Butyl Acetal* (**10**) [8]. A soln. of **10** (240 mg, 1.0 mmol) and **2** (400 mg, 2.0 mmol) in degassed MeOH (20 ml) was irradiated at 15° for 2 h. The solvent was removed *in vacuo* and the residue extracted with $Et_2O$ (20 ml). Chromatography on aluminium oxide with pentane/$Et_2O$ (starting with pentane, then pentane/$Et_2O$ 20:1–5:1) gives 79 mg of product **11** in 50% yield which was characterized by comparison with an authentic sample [8].

*Intermolecular C–C Bond-Forming Reactions.* A soln. of halide (1.0 mmol), alkene (10–20 mmol), and metal complex **1**, **2**, or **3** (1–2 mmol) in degassed solvent (20 ml) was irradiated at 15–20° for 2–3 h. The solvent was removed *in vacuo* and the residue extracted with $Et_2O$ (20 ml). Chromatography on aluminium oxide with pentane/$Et_2O$ (starting with pentane, then pentane/$Et_2O$ 20:1–5:1) yields the products. Solvents and yields are given in *Schemes 3–7* and *Tables 1* and *2*. The degree of deuteration was determined by $^1$H-NMR. The *C*-glycosides **34** and **36** were purified by flash chromatography on silica gel with pentane/$Et_2O$ 1:1.

*3-Methyl-4-phenylbutanenitrile* (**30f**): IR (film): 2240. $^1$H-NMR (300 MHz, $CDCl_3$): 1.13 (*d*, $J = 6.6$, $CH_3$); 2.15–2.32 (*m*, 2 H–C(2), H–C(3)); 2.67 (*d*, $J = 7.1$, 2 H–C(4)); 7.15–7.35 (*m*, Ph). $^{13}$C-NMR (75 MHz, $CDCl_3$): 19.3 ($CH_3$); 23.4 (C(2)); 32.4 (C(3)); 41.9 (C(4)); 118.8 (CN); 126.7 (C(4')); 128.8 (C(3'), C(5')); 129.2 (C(2'), C(6')); 139.2 (C(1')). MS ($C_{11}H_{13}N_5$): calc.: 159.1047; found: 159.1048.

*Ethyl 3-Methyl-4-phenylbutanoate* (**30o**): IR (film): 1740. $^1$H-NMR (300 MHz, $CDCl_3$): 0.95 (*d*, $J = 5.8$, $CH_3$); 2.15 (*m*, H–C(3)); 2.30 (*m*, 2 H–C(2)); 2.51 (*dd*, $J = 13.0$, 7.4, 1 H–C(4)); 2.62 (*dd*, $J = 13.0$, 7.4, 1 H–C(4)); 3.65 (*s*, $CH_3O$); 7.15–7.31 (*m*, Ph). $^{13}$C-NMR (75 MHz, $CDCl_3$): 19.4 ($CH_3$); 32.1 (C(2)); 40.7 (C(3)); 42.9 (C(4)); 126.2 (C(4')); 128.4 (C(3'), C(5')); 129.4 (C(2'), C(6')); 140.4 (C(1')); 173.8 (C(1)). MS ($C_{12}H_{16}O_2$): calc.: 192.1164; found: 192.1150.

*2-Benzylbutanedinitrile* (**30p**): IR (film): 2220. $^1$H-NMR (300 MHz, $CDCl_3$): 2.64 (*m*, 2 H–C(3)); 3.02 (*m*, H–C(2), $PhCH_2$); 7.24–7.42 (*m*, Ph). $^{13}$C-NMR (75 MHz, $CDCl_3$): 20.0 (C(3)); 30.0 (C(2)); 36.9 (Ph$CH_2$); 115.5 (C(1)); 118.5 (C(4)); 128.0 (C(4')); 129.0 (C(3'), C(5')); 129.1 (C(2'), C(6')); 134.4 (C(1')). EI-MS: 170 ($M^+$), 91. Anal. calc. for $C_{11}H_{10}N_2$ (170.22): C 77.62, H 5.92, N 16.46; found: C 77.35, H 6.02, N 16.19.

All other products are known compounds.

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