Synthesis of Novel Polynuclear Iron Carbonyl Complexes Using the Reactions of Methylidenecarbenes with $Fe_3(CO)_{12}$

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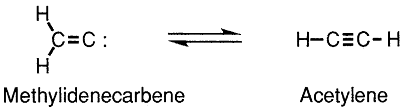
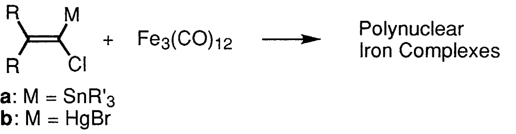
The reaction of 1-chloro-1-tributylstannylethylenes with $Fe_3(CO)_{12}$ produces the dinuclear and trinuclear ferraindene complexes with the methylenediferracyclopropane derivatives. The structures of the ferraindene complexes were determined by X-ray analysis.

Acetylenes consisting of *sp*-hybridized carbons are known to form a variety of polynuclear complexes by using their perpendicularly arranged π-orbitals.[1] We have been interested in the reactivity of methylidenecarbenes with transition metals, because methylidenecarbene is one of the most important C_2H_2-isomers of acetylene (eq. 1), and because methylidenecarbene can react very easily with transition metal complexes.



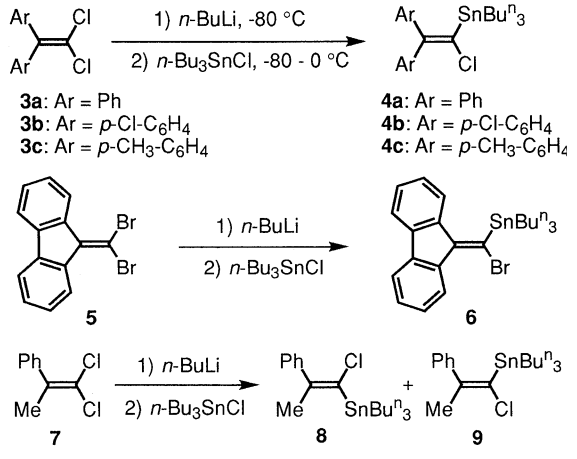
(1)

Although methylidenecarbenes (**1**) are known to exist only as a transient species,[2] methylidenecarbenoids (**2**) such as tin-carbenoids (**2a**) and mercury-carbenoids (**2b**) are stable enough for isolation and characterization.[3] We, therefore, investigated the reactions of tin-carbenoids (**2a**) with $Fe_3(CO)_{12}$ (eq. 2).



(2)

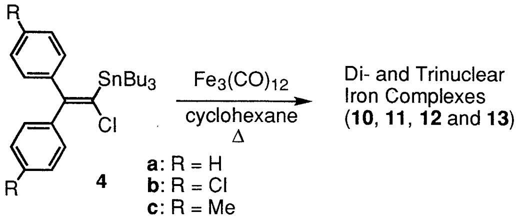
The synthesis of tin-carbenoids was carried out starting from 1,1-dihalogenoethylenes (Scheme 1). The reaction of **3a** with *n*-butyllithium (1.1 equiv.) at -80 °C in THF, followed by treatment with tri-*n*-butyltin chloride (1.2 equiv.) at -80 - 0 °C produced the tin-carbenoid (**4a**) in 87% yield.[4]



Scheme 1.

In a similar manner, the successive treatments of **3b**, **3c** and **5** with *n*-butyllithium and tri-*n*-butyltin chloride afforded **4b**, **4c** and **6** in 81, 77 and 53% yields, respectively. A similar reaction of **7** with *n*-butyllithium at -85 - -90 °C, followed by treatment with tri-*n*-butyltin chloride at -90 °C - room temperature gave **8** and **9** in 42 and 21% yields, respectively.

The tin-carbenoids (**4a-c**) are stable at room temperature but react slowly at elevated temperatures. Thus, the reaction of **4a** with $Fe_3(CO)_{12}$ (1.5 equiv.) at 80 °C in cyclohexane produced four products (**10-13**) (eq. 3). Similar reactions of **4b** and **4c** with $Fe_3(CO)_{12}$ gave the corresponding di- and trinuclear iron complexes. The results are summarized in Table 1.



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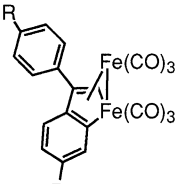

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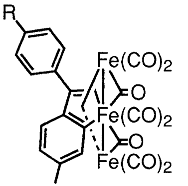

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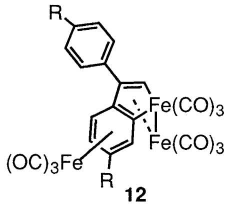

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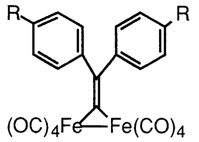

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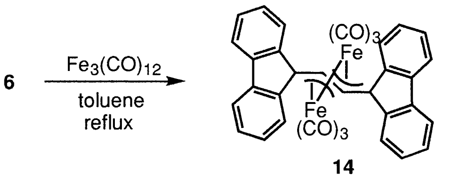
Table 1. The reaction of **4a-c** with $Fe_3(CO)_{12}$[a]

	Reaction conditions		Products/%[b]			
	Temp/°C	Time/h	**10**	**11**	**12**	**13**
4a[c]	reflux	24	10	11	10	7
4b[d]	80	29	19	13	-	4
4c[e]	80	24	11	12	12	-

[a] The mixture of **4** and $Fe_3(CO)_{12}$ (1.5 equiv.) in cyclohexane was heated under N_2. The products were separated by column chromatography on silica gel. The yields of the products are based on the consumed **4**. [b] Isolated yields. [c] The recovered **4a** (46%). [d] The recovered **4b** (39%). [e] The recovered **4c** (43%).

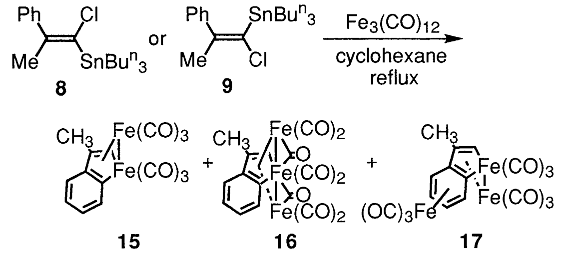
As shown in Table 1, the reaction of **4a** with $Fe_3(CO)_{12}$ gave **10a**-**13a** in 7-11% yields. In the case of **4b**, no trinuclear complex (**12b**) was obtained, presumably due to the low reactivity of the chlorine-substituted benzene ring. On the other hand, the reaction of **4c** with Fe$_3$(CO)$_{12}$ produced no methylenediferracyclopropane (**13c**). Since **13a**[5] and **13b** are not stable to the atmospheric oxygen, **13c** may decompose during the work-up procedure. For the reaction of **4** with Fe$_3$(CO)$_{12}$, toluene can be used as the solvent. However, the reaction in toluene afforded **10** and **11** together with small amounts of indanone derivatives which may be the decomposition products of **10**.

In contrast to the reaction of **3a-c**, the treatment of **6** with Fe$_3$(CO)$_{12}$ (1 equiv.) in refluxing toluene for 7 h produced the butatriene complex **14** in 40% yield (eq. 4). Although the reaction of **5** with Fe$_3$(CO)$_{12}$ was reported to give **14** in a low yield,[6] the corresponding reaction of **6** proceeded smoothly to produce **14** in a moderate yield.



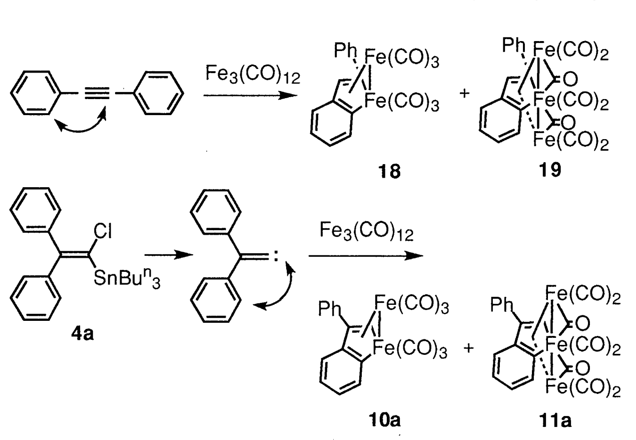
(4)

In order to obtain further information on the reaction mechanism, the reactions of *(E)*- and *(Z)*-1-chloro-2-phenyl-1-tributylstannylpropenes (**8** and **9**) with Fe$_3$(CO)$_{12}$ were carried out (eq. 5). Treatment of **8** with Fe$_3$(CO)$_{12}$ (1.5 equiv.) in refluxing cyclohexane for 24 h produced the corresponding iron complexes **15** (18%), **16** (10%) and **17** (4%). The reaction of **9** with Fe$_3$(CO)$_{12}$ afforded the same products (**15-17**) in similar yields. Therefore, the reactions of the tin-carbenoids (**8** and **9**) produce the same intermediate which leads to the iron complexes (**15-17**).



(5)

Di- and trinuclear ferraindene complexes were obtained from the reactions of acetylenes with Fe$_3$(CO)$_{12}$ and the structures of some derivatives were determined by X-ray analysis (Scheme 2).[1] Thus, diphenylacetylene reacts with Fe$_3$(CO)$_{12}$ to give the di- and trinuclear complexes (**18** and **19**).[7] In contrast, the tin-carbenoid (**3a**) reacts with Fe$_3$(CO)$_{12}$ to produce the isomeric di- and trinuclear complexes (**10a** and **11a**). Therefore, the reaction of acetylene and methylidenecarbene proceeds without a skeletal rearrangement to form the ferraindene structure.



Scheme 2.

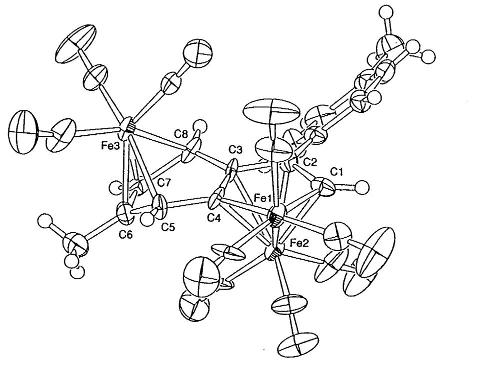


Figure 1. Molecular structure of **12c**. The selected distances (Å): Fel-Cl 1.961(2); C1-C2 1.418(3); C2-C3 1.427(3); C3-C4 1.417 (3); Fel-C4 1.959(2); Fel-Fe2 2.5129(4); Fe3-C6 2.085(2); Fe3-C7 2.046(2).

The structures of **10**, **11** and **12** were confirmed by X-ray analysis.[8] Figure 1 shows the ORTEP drawing of **12c**.[9] The structure of **12c** contains a ferraindene framework. The tolyl substituent in **12c** is located at the β-position of the ferraindene ring. Interestingly, the coordination of the Fe(CO)$_3$ moiety forces the benzene ring to take a boat form with the puckered angle of 34°.

References and Notes

1 J. L. Davidson, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1982), Vol. 4, Chap. 31.5, p. 615.

2 For a review, see: P. J. Stang, *Acc. Chem. Res.*, **15**, 348 (1982).

3 For mercury-carbenoids, see: D. Seyferth and D. Dagani, *J. Organomet. Chem.*, **104**, 145 (1976).

4 All new compounds described here gave IR, ^{1}H- and ^{13}C-NMR, and mass spectroscopic data consistent with the assigned structure. **10a**: red cryst., mp 75-76 °C, MS (*m/z*) 458 (M$^+$), ^{1}H NMR (CDCl$_3$) δ 7.84 (d, J = 8.6 Hz, 1H), 7.66-7.62 (m, 3H), 7.52-7.45 (m, 3H), 7.33 (m, 1H), 7.01 (m, 1H), 6.76 (s, 1H). **11a**: black cryst., mp 124.5-125 °C, MS (*m/z*) 570 (M$^+$), ^{1}H NMR (CDCl$_3$) δ 8.64 (d, J = 9.0, 1H), 8.20 (d, J = 7.1, 2H), 7.68-7.58 (m, 3H), 7.31-7.26 (m, 1H), 6.63-6.55 (m, 2H), 2.78 (s, 1H). **12a**: orange cryst., mp 121.5-122 °C, MS (*m/z*) 570 (M$^+$-28), ^{1}H NMR (CDCl$_3$) δ 7.41-7.37 (m, 5H), 6.84 (s, 1H), 6.72 (m, 1H), 6.46 (m, 1H), 3.83 (m, 1H), 3.45 (m, 1H). **13a**: orange cryst., mp 112-113 °C (decomp.), MS (*m/z*) 514 (M$^+$), ^{1}H NMR (CDCl$_3$) δ 7.35-7.32 (m, 4H), 7.28-7.22 (m, 6H). **10b**: red cryst. mp 119.5-120.5 °C. **11b**: black cryst., mp 158-159 °C. **13b**: dark red solid. **10c**: red cryst., mp 92.5-93 °C. **11c**: black cryst., mp 168-169.5 °C. **12c**: orange cryst., mp 154.5-155 °C. **15**: red cryst., mp 104.5-105.5 °C. **16**: black cryst., 164.5-165.5 °C. **17**: orange cryst., mp 154.5-155 °C.

5 Only the X-ray analysis of **13a** together with short comments on the properties were reported: O. S. Mills and A. D. Redhouse, *J. Chem. Soc. (A)*, **1968**, 1282.

6 K. K. Joshi, *J. Chem. Soc. (A)*, **1966**, 594.

7 W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); P. Y. Degrève, J. Meunier-Piret, M. Van Meerssche, and P. Piret, *Acta Cryst.*, **23**, 119 (1967).

8 X-ray analysis of **10b** and **11b**: Y. Kuwatani, M. Yoshida, T. Yada, and M. Iyoda, to be published.

9 Crystal data for **12c**: C$_{25}$H$_{14}$O$_9$Fe$_3$, FW = 625.92, triclinic, space group P$\bar{1}$; a = 10.929(3) Å, b = 11.742(7) Å, c = 10.441(3) Å, α = 95.00(3)°, β = 106.61(2)°, γ = 101.13(4)°, V = 1245.3(9) Å^3, Z = 2, D$_c$ = 1.669 gcm^{-3}, the finial *R* = 0.025 (*R*$_w$ = 0.025).