Journal of Organometallic Chemistry, 438 (1992) C9–C12
Elsevier Sequoia S.A., Lausanne
JOM 22841PC

Preliminary communication

Activation of carbon–carbon bond in the Mn-mediated cycloaddition reaction between disilacyclobutene and cyclohepta-1,3-diene

Hui-Jean Chiang and Chao-Shiuan Liu
Department of Chemistry, National Tsing Hua University, Hsinchu (Taiwan, ROC)

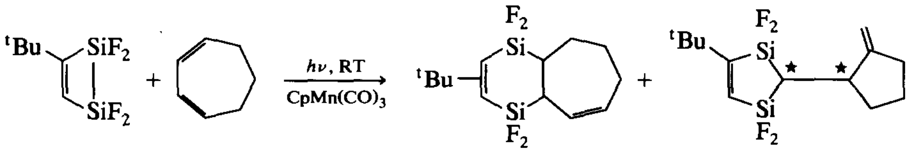
(Received February 28, 1992)

Abstract

The cycloaddition reaction between 1,1,2,2-tetrafluoro-1,2-disilacyclobutene and cyclohepta-1,3-diene mediated by $CpMn(CO)_3$ under photochemical conditions generates the product $SiF_2(^tBu)C{=}CHSiF_2CH{-}CHCH_2CH_2CH_2C{=}CH_2$ resulted from a C–C cleavage of the cycloheptadiene, a process involving the conversion of a σ-bonded Mn-cyclobutane derivative to a Mn-carbene intermediate.

We have demonstrated that under the mediation of metal carbonyl derivatives, tetrafluorodisilacyclobutene and conjugate dienes undergo a variety of reaction pathways which can be controlled by the electronic and steric properties of the metal and the dienes [1]. The fine-tuning scheme of this reaction system can be illustrated as shown in Scheme 1.

For cyclic conjugate dienes, the reactions proceed almost exclusively *via* the 1,2-addition pathway [2]. However, when the reaction between **1** and cyclohepta-1,3-diene was mediated by $CpMn(CO)_3$, in addition to the expected products of 1,2-addition (**7**), products (**8a/8b**, a pair of diastereoisomers) [3*] formed *via* the cleavage of a C–C bond of the cycloheptadiene were obtained.



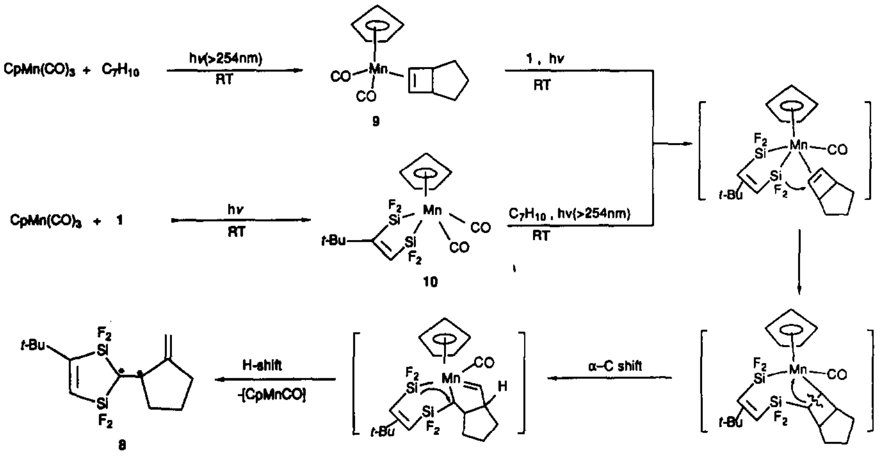
(1) 7 (8a/8b)

When the reaction of $CpMn(CO)_3$ and cyclohepta-1,3-diene in a benzene solution was carried out under photochemical conditions in a quartz tube at room

---

Correspondence to: Dr. C.-S. Liu.

* Reference number with asterisk indicates a note in the list of references.



Scheme 1.

temperature, compound **9** was obtained in 80% yield. Compound **9** was identified by elemental analysis, mass spectrum and ^{1}H and ^{13}C NMR spectroscopies [4*] in the solution and X-ray diffraction in the solid state (Fig. 1). It appears that under the irradiation, cyclohepta-1,3-diene rearranges to [3,2,0]bicyclohept-6-ene [5] before forming the olefin complex **9** with Mn.

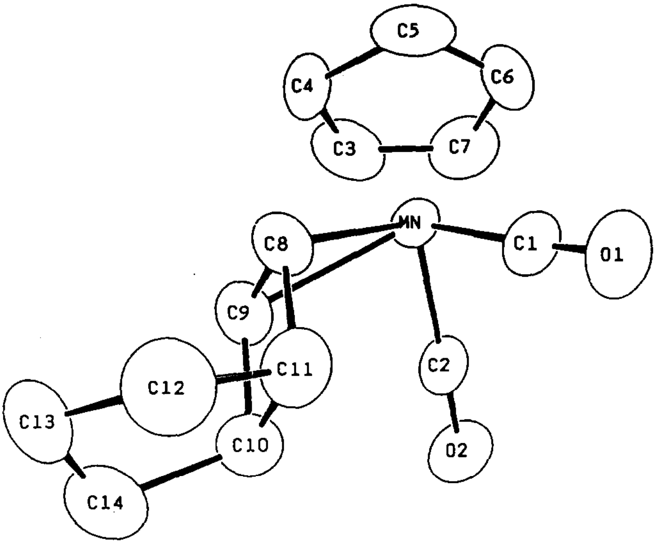
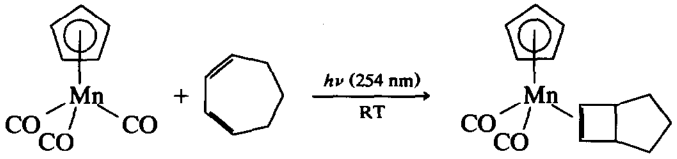
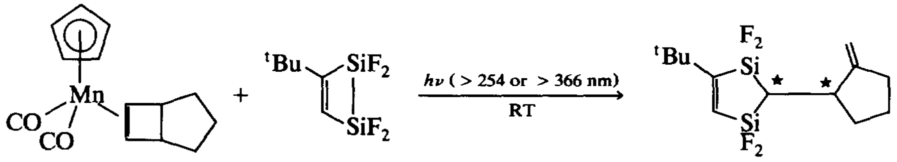


Fig. 1. Crystal structure of compound **9**. Selected bond distances (Å) and bond angles (°): Mn–C(8) 2.174(8), Mn–C(9) 2.164(8), C(8)–C(9) 1.377(12), C(8)–C(11) 1.500(12), C(9)–C(10) 1.530(12), C(10)–C(11) 1.572(14); C(1)–Mn–C(8) 81.8(4), C(1)–Mn–C(9) 108.5(4), C(2)–Mn–C(8) 108.1(4), C(2)–Mn–C(9) 82.1(4), C(8)–Mn–C(9) 37.0(3), C(9)–C(8)–C(11) 94.7(7), C(8)–C(9)–C(10) 92.7(7), C(9)–C(10)–C(11) 86.1(6).



(9)

Irradiating **9** with **1** in a quartz tube or a Pyrex tube generates compound **8a/8b** as the only reaction product with 70% yield based on **9**.



(9) **(1)** **8a/8b**

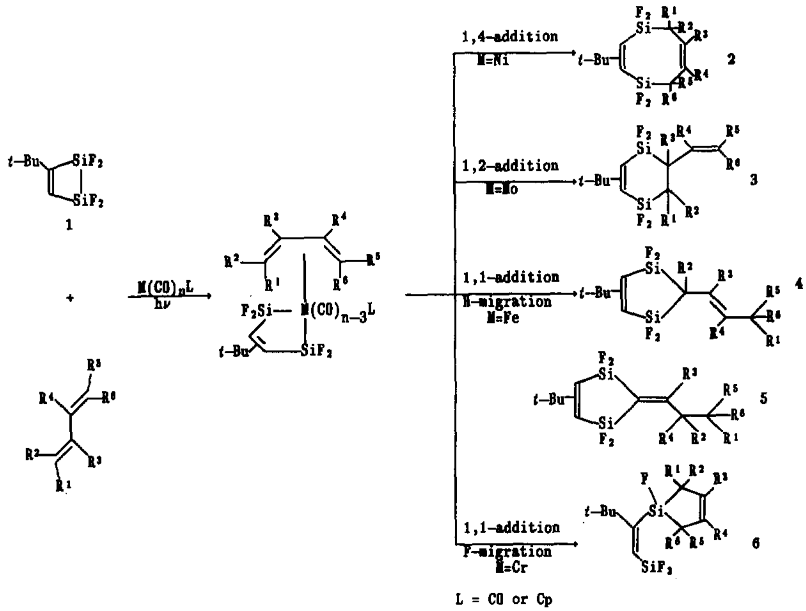
Alternatively, compound **8a/8b** could be obtained (with 55% yield based on **10**) by first reacting CpMn(CO)$_3$ with **1** to form the disilametallacycle intermediate **10** [1c], then irradiating **10** with C_7H_{10} in a quartz tube.

$$\mathrm{CpMn(CO)_3} + \mathbf{1} \xrightarrow[\mathrm{RT}]{h\nu\ (>254 \text{ or } >366\ \mathrm{nm})} \mathrm{Cp(CO)_2}\overline{\mathrm{Mn{-}SiF_2CH{=}C(^tBu)SiF_2}}$$

(10)

$$\mathbf{10} + \mathrm{C_7H_{10}} \xrightarrow[\mathrm{RT}]{h\nu\ (>254\ \mathrm{nm})} \mathbf{8a/8b}$$

These observations strongly suggest a reaction mechanism for the formation of compound **8a/8b** as illustrated in Scheme 2. The conversion of the σ-bonded



Scheme 2.

metal-cyclobutane derivative to a metal-carbene intermediate has recently been demonstrated by a number of workers [6].

Details of the crystal data, lists of bond distances, bond angles and atomic parameters are available from the authors.

References and notes

1 (a) C.H. Lin, C.Y. Lee, and C.S. Liu, Organometallics, 6 (1987) 1861; (b) *idem, ibid.*, 6 (1987) 1869; (c) *idem, ibid.*, 6 (1987) 1878; (d) *idem, ibid.*, 6 (1987) 1882; (e) T.T. Tzang, C.Y. Lee and C.S. Liu, *ibid.*, 7 (1988) 1265; (f) T.T. Tzang and C.S. Liu, *ibid.*, 7 (1988) 1271.

2 C.H. Lin, C.Y. Lee, T.T. Jzang, C.C. Lin and C.S. Liu, J. Organomet. Chem., 356 (1988) 325.

3 Compound **8a/8b**, a colourless liquid, a pair of diastereoisomers (ratio 3:2). MS: m/z 308 (M^+, $C_{13}H_{20}Si_2F_4^+$), 293 ($C_{12}H_{17}Si_2F_4^+$), 280 ($C_{11}H_{16}Si_2F_4^+$), 265 ($C_{10}H_{13}Si_2F_4^+$), 251 ($C_9H_{11}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). ^{19}F NMR (**8a** or **8b**): δ (C_6D_6) 128.8 (ddd); 132.9 (dd); 135.1 (ddd); 139.6 (dd); (**8b** or **8a**): 129.7 (ddd); 134.1 (dd); 134.6 (ddd); 138.2 (dd). ^{1}H NMR: δ 1.1 (s, 9H, ^{t}Bu); 4.96 (s); 5.08 (s, 2H, CH_2=); 2.18 (m, 2H, $=\mathrm{C}-\mathrm{C}H_2-\mathrm{CH_2}$); 1.43 (m, 2H, $-CH_2-CH_2-\mathrm{CH_2}-$); 2.14 (m, 1H, $-\mathrm{CH}-CH_2-\mathrm{CH_2}$); 2.73 (m, 1H, $-\overset{|}{\mathrm{C}}\mathrm{H}-\overset{|}{\mathrm{C}}H-\mathrm{C}=$); 0.84 (m, 1H, $-(\mathrm{SiF_2})_2-\overset{|}{\mathrm{C}}H-\overset{|}{\mathrm{C}}\mathrm{H}-$); 6.54 (tt, 1H, $H\overset{\|}{\mathrm{C}}-\mathrm{SiF_2}-$). ^{13}C NMR: δ 29.46 (s(q), $(C\mathrm{H_3})_3\mathrm{C}-$); 37.42 (s(s), $(\mathrm{CH_3})_3C-$); 181.80 (tt(tt), $(^t\mathrm{Bu})-\overset{\|}{C}-$); 141.11 (tt(dtt), $-\mathrm{SiF_2}-\overset{\|}{C}\mathrm{H}$); 12.01 (m(dm), $(-\mathrm{SiF_2})_2-C\mathrm{H}-$); 38.24 (s(d), $-\overset{\|}{\mathrm{C}}-\overset{|}{C}\mathrm{H}-\mathrm{CH_2}-$); 35.22 (s(t), $-\overset{|}{\mathrm{C}}\mathrm{H}-C\mathrm{H_2}-\mathrm{CH_2}-$); 23.66 (s(t), $-\mathrm{CH_2}-C\mathrm{H_2}-\mathrm{CH_2}-$); 31.97 (s(t), $-\mathrm{CH_2}-C\mathrm{H_2}-\overset{\|}{\mathrm{C}}-$); 156.57 (s(s), $\mathrm{CH_2}=\overset{|}{C}-$); 105.61 (s(t), $C\mathrm{H_2}=\overset{|}{\mathrm{C}}-$).

4 Compound **9**, a yellow solid, decomposes at 98–99°C. MS: m/z 270 (M^+, $C_{14}H_{15}MnO_2^+$); 242 ($C_{13}H_{15}MnO^+$); 214 ($C_{12}H_{15}Mn^+$); 148 ($C_6H_5MnO^+$); 120 ($C_5H_5Mn^+$); 94 ($C_7H_{10}^+$). ^{1}H NMR: δ (C_6D_6) 1.83 (m, 2H, $-\mathrm{CH_2}-CH_2-\mathrm{CH_2}-$); 1.46 (m, 4H, $-\mathrm{CH}-CH_2-\mathrm{CH_2}-$); 2.49 (d, 2H, $=\mathrm{CH}-CH-\mathrm{CH_2}-$); 3.35 (s, 2H, $-CH=CH-$); 3.90 (s, 5H, C_5H_5). ^{13}C NMR: δ 24.41 (s(t), $-\mathrm{CH_2}-C\mathrm{H_2}-\mathrm{CH_2}-$); 30.84 (s(t), $-\mathrm{CH}-C\mathrm{H_2}-$); 48.67 (s(d), $=\mathrm{CH}-C\mathrm{H}-\mathrm{CH_2}-$); 61.14 (s(d), $-C\mathrm{H}=C\mathrm{H}-$); 84.43 (s(d), C_5H_5); 234.8 (s(s), CO). Crystal data: $MnC_{14}H_{15}O_2$, $M = 270.1$, orthorhombic, space group $Pna2_1$, $a = 17.903(3)$, $b = 6.1993(10)$, $c = 11.0401(18)$ Å; $U = 1225.3(3)$ Å^3; $Z = 4$; $D_c = 1.465$ mg m^{-3}; $\lambda(\mathrm{Mo}\text{-}K_\alpha) = 0.7107$ Å, crystal size $0.05 \times 0.40 \times 0.40$ mm^3, $F(000) = 551.92$, $2 \leq 2\theta \leq 50°$. 1134 reflections were collected; $R = 0.036$.

5 (a) W.G. Dauben and R.L. Cargil, Tetrahedron, 12 (1961) 186; (b) O.L. Chapman, D.J. Pasto, G.W. Borden and A.A. Griswold, J. Am. Chem. Soc., 84 (1962) 1220.

6 (a) D.J. Crowther, S. Tivakornpannarai and W.M. Jones, Organometallics, 9 (1990) 739; (b) Y. Stenstrom and W.M. Jones, *ibid.*, 5 (1986) 178; (c) Y. Stenstrom, G. Klanck, A. Koziol, G.J. Palenik and W.M. Jones, *ibid.*, 5 (1986) 2155; (d) J.R. Lisko and W.M. Jones, *ibid.*, 4 (1985) 944; (e) Y. Stenstrom, A.E. Koziol, G.J. Palenik and W.M. Jones, *ibid.*, 6 (1987) 2079.