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Activation of the carbon–carbon bond in the Mn-mediated cycloaddition reaction between disilacyclobutene and cyclic conjugated dienes

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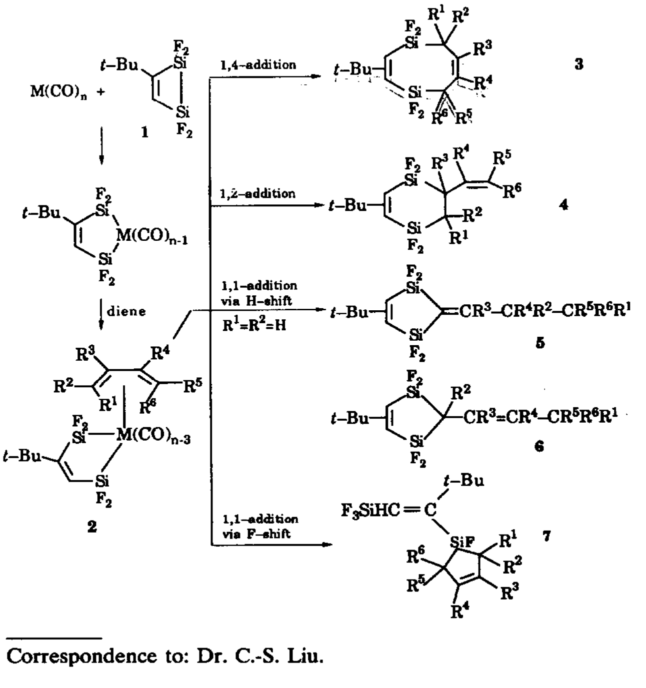
Abstract

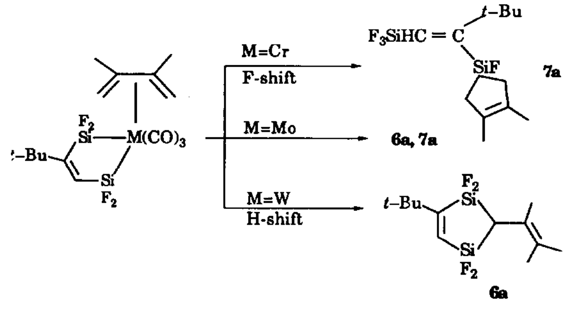
Cycloaddition reactions between 1,1,2,2-tetrafluoro-1,2-disilacyclobutene and cyclic conjugate dienes mediated by $CpMn(CO)_3$ under photochemical conditions generate the products resulting from a C–C cleavage of the cyclic conjugate dienes.

1. Introduction

We have demonstrated that in the metal-mediated cycloaddition reaction between disilacyclobutene **1** and conjugate dienes an intermediate species in the form of η^4-diene disilametallacycle **2** can be used as a model for fine-tuning the reaction pathways [1–6].



The cycloaddition reactions involving H-shift as opposed to F-shift are interpreted in terms of the "hardness" of the central metal [3] as follows:



(hardness of M : Cr > Mo > W)

We are particularly interested in the mediation effect of the "harder" metals. One reason is that "harder" transition metals seem to be better able to activate C–C bonds (such metals as Sc, V, Ti, Zr, Ta, etc. [7–9]) whereas the "softer" transition metals are more often involved in the activation of C–H bonds (such metals as Fe, Ru, Pd, Pt etc. [10–12]). If one considers C–C bond as a "harder base" than C–H, appropriate choice of a harder metal in our system may also reveal the tendency towards activation of C–C bonds.

No product involving C–C bond activation was observed in our system of reactions with various conjugated dienes mediated by the hard metals such as Cr [3,13]. In this study we chose $CpMn(CO)_3$ because Mn is relatively "hard" and the formal charge of +1 is believed further to enhance the hardness of Mn [3].

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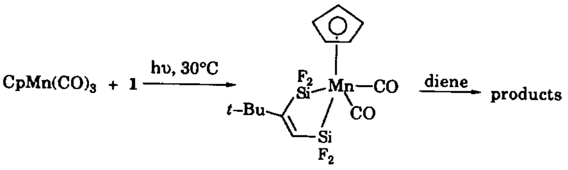
In order to avoid the other major competitive reaction pathway (namely, 1,2 H-shift or β-hydride *syn*-elimination) so that C–C bond activation may become prevalent, cyclic conjugated dienes were used in this study [2,14].

2. Results and discussion

The reactions were carried out either by reacting **1**, the diene and $CpMn(CO)_3$ all together or by forming **8** first, followed by the reaction with several dienes [3]. In practice the latter method was more convenient.



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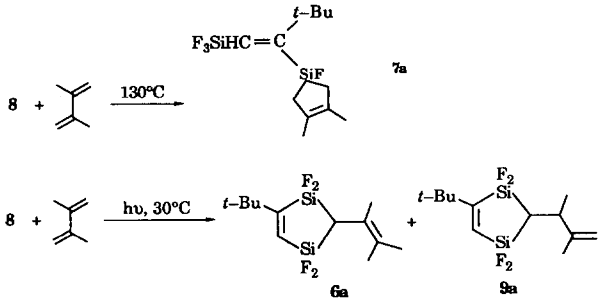
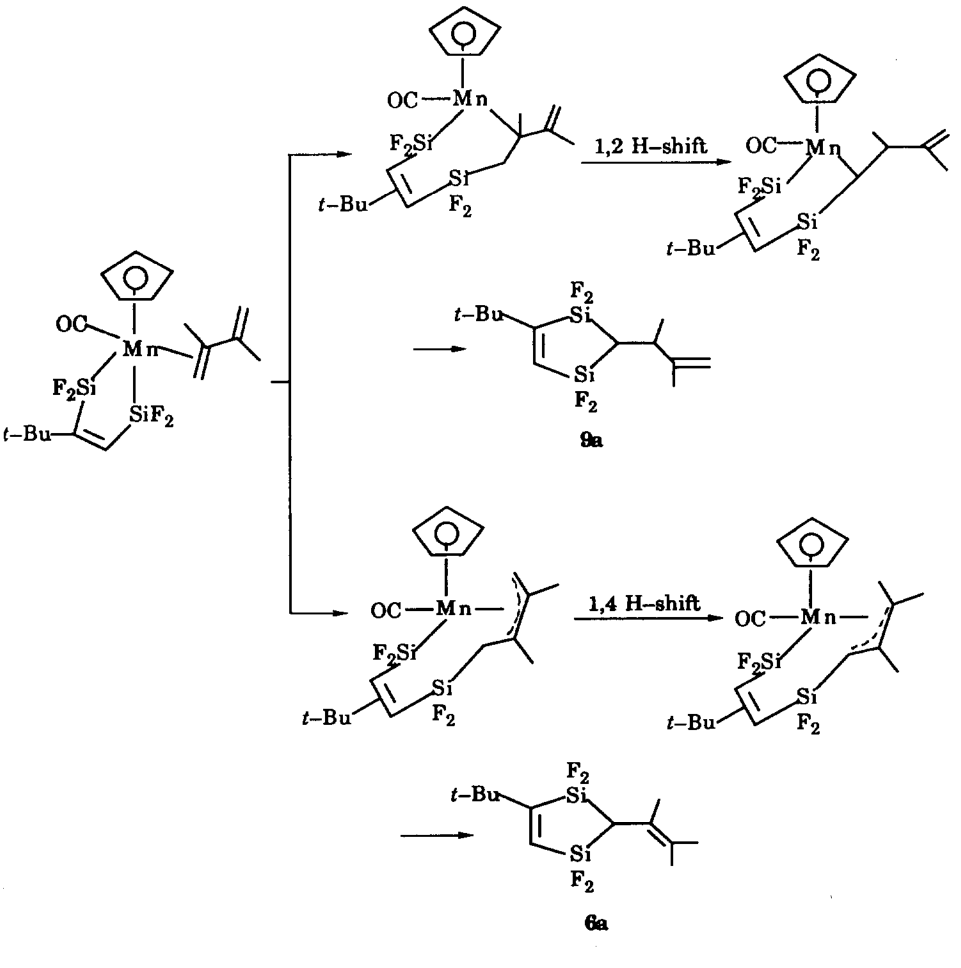
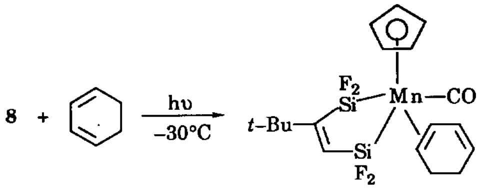
It is interesting to note that reaction conditions reflect the reaction pathways: thermal reactions at 130°C lead to products of F-shift, but photochemical reactions at 30°C result exclusively in products of H-shift. Example are shown below:



The appearance of **6a** and **9a** is believed to be the consequence of the competition between 1,4 H-shift and 1,2 H-shift in a 1,1-addition reaction involving an η^2-diene complex as the intermediate. The pathway of the 1,4 H-shift generates **6a** and the 1,2 H-shift gives **9a**.



In the reaction between **8** and cyclohexa-1,3-diene the η^2-diene intermediate **10** could be isolated at low temperature.



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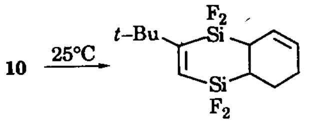
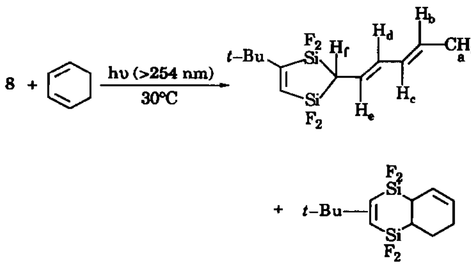
The observation of an η^2-diene complex of the $CpMn(CO)_3$ derivative is in agreement with many previously reported cases where $CpMn(CO)_3$ derivatives tend to form η^2-diene instead of η^4-diene complexes [15–17].

On warming **10** to room temperature it decomposed in a regiospecific manner to form the 1,2-addition product **4a** [18].



4a (47%)

It is interesting to note that, when the reaction between **8** and cyclohexa-1,3-diene was carried out photochemically in a quartz tube at 30°C, in addition to trace amounts of the 1,2-addition products (**4a** and **4b**) [18], the major product **11a** was obtained from the 1,1-addition with opening of the six-membered ring.



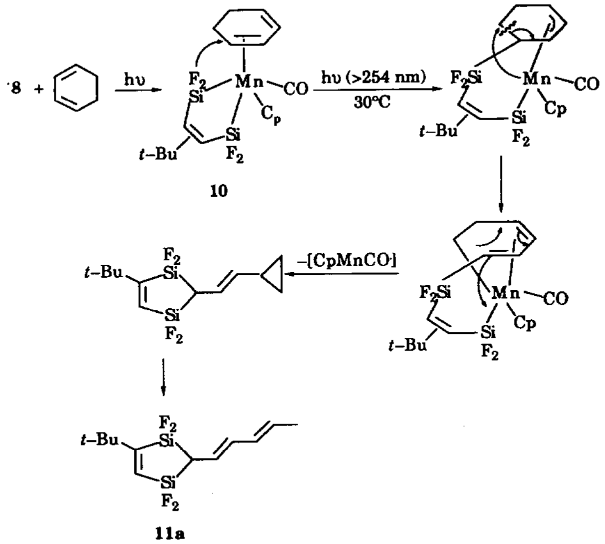
11a (60%)

(trace)

4a/4b

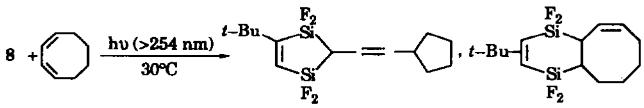
The structure of **11a** was supported by the coupling constants J_{ab}, J_{bc}, J_{cd}, J_{de} and J_{ef} being 7.1, 10.8, 11.0, 14.9 and 10.2 Hz respectively, together with the chemical shift of the methyl group (H_a) (δ 1.62, doublet). All chemical shifts of H_b–H_f are reasonably assigned. The ^{13}C–^{1}H correlation spectrum helps determination of the ^{13}C chemical shifts of the four sp^2 carbons in the conjugate diene chain. The *trans, trans* configuration is determined by the magnitude of the coupling constants of J_{bc} (10.8 Hz) and J_{de} (14.9 Hz).

It is obvious that the formation of **11a** involves a C–C cleavage in the cyclohexa-1,3-diene. A plausible reaction mechanism is proposed in Scheme 1.



Scheme 1.

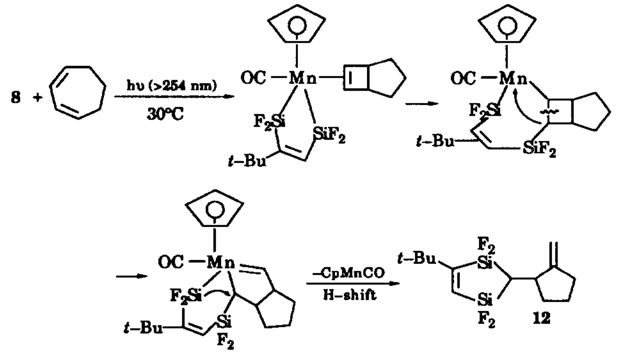
The 1,1-addition in our system, involving a C–C activation of the cyclic conjugate diene, is a new type of reaction pathway. The proposed mechanism is supported by the observation of compound **11b** in the reaction between **8** and cycloocta-1,3-diene under similar reaction conditions. However, the products of 1,2-addition (**4e**/**4f**) are more abundant in this case.



11b (25%)

4e,4f (23%,23%)

The photochemical reaction between **8** and cyclohepta-1,3-diene yielded compound **12**, the product resulting from a different type of C–C cleavage pathway which involved the rearrangement of cyclohepta-1,3-diene prior to the silyl attack. This reaction mechanism has been reported previously [19].



3. Experimental section

3.1. Syntheses

3.1.1. Preparation of 3-tert-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1)

Compound **1** was prepared by the cocondensation reaction between 3,3-dimethylbut-1-yne and difluorosilylene. The preparation procedures were as reported previously [20].

3.1.2. Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2\overline{MnSiF_2C(t\text{-}Bu)=CHSiF_2}$ (8)

Compound **8** was prepared by reacting **1** and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ under UV irradiation. The procedures and spectral data were reported previously [3].

3.1.3. Preparation of $(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_6H_8)(CO)\overline{MnSiF_2C(t\text{-}Bu)=CHSiF_2}$ (10)

Compound **8** (0.5 g, 1.3 mmol) and 0.5 g (6.2 mmol) of cyclohexa-1,3-diene were added to 10 ml of dried and degassed toluene in a Pyrex tube under vacuum. The reaction mixture was irradiated at −30°C for 24 h and **8** was completely converted to compound **10**. Compound **10**, a colourless crystal, was not stable at room temperature, decomposing slowly to give 180 mg (0.61 mmol) of compound **4a**, in 47% yield based on the quantity of **10** used. MS of **10**: m/e 414 ($M^+ - CO$, $C_{17}H_{23}Si_2F_4Mn^+$), 294 ($C_{12}H_{18}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 120 ($C_5H_5Mn^+$), 80 ($C_6H_8^+$), 65 ($C_5H_5^+$). $^{19}F\{^1H\}$ NMR of **10**: 95.22 (d), 99.58 (d), $=CHSiF_2$, 105.27 (d), 116.29 (d) $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR of **10**: δ 21.04 (s(t), CH_2CH_2), 30.28 (s(q), $C(CH_3)_3$), 37.78 (s(s), $C(CH_3)_3$), 74.45 and 84.58 (s(d), coordinated $C=C$), 82.12 (s(d), C_5H_5), 125.62 and 129.26 (s(d), free $C=C$), 143.85 (t(dt), $=CHSiF_2$), 183.12 (t(t), $=C(t\text{-}Bu)SiF_2$), 191.0 (s(s), CO). ^1H NMR of **10**: δ 1.1 (s, 9H, t-Bu), 2.1–2.4, (4H, $-CH_2-$), 3.2 and 4.5, (2H, coordinated $-HC{=}CH-$), 4.8 (s, 5H, C_5H_5), 5.7–5.8 (2H, free $-HC{=}CH-$), 6.7 (tt, 1H, $=CH(SiF_2)-$).

3.1.4. Preparation of 11a

Compound **8** (0.4 g, 1.0 mmol) and 0.4 g (5.0 mmol) of cyclohexa-1,3-diene were added to 10 ml of toluene in a quartz tube under vacuum. The reaction mixture was irradiated at 30°C for 48 h. After removal of solvent, vacuum distillation at 90–110°C generated an orange-red liquid. About 200 mg of PPh_3 and 2 ml of hexane were added to the liquid and the mixture was heated at 110°C for 2 h. Vacuum distillation at 60 ~ 70°C yielded 190 mg of colourless liquid products which contained 90% of **11a** and 10% of **4a/4b**. The yield based on the quantity of **8** was 65%. Anal. Calcd for **11a**: C, 48.98; H, 6.12; F, 25.85. Found: C, 49.17; H, 5.97; F, 25.61%. MS of **11a**: m/z 294 (M^+, $C_{12}H_{18}Si_2F_4^+$), 279 ($C_{11}H_{15}Si_2F_4^+$), 237 ($C_8H_9Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$). ^1H NMR of **11a**: δ 1.10 (s, 9H, t-Bu), 1.62 (d, 3H, CH_3), 1.69 (m, 1H, $CH(SiF_2)_2$), 5.34 (m, 1H, $=CH-CH_3$), 5.57 (dd, 1H, $(SiF_2)_2CH-CH=$), 5.97 (dd, 1H, $-CH=CHCH_3$), 6.35 (dd, 1H, $(SiF_2)_2CH-CH=CH$), 6.46 (m, 1H, $=CHSiF_2$). $^{19}F\{^1H\}$ NMR of **11a**: 133.46 and 140.71 (ddd and dd respectively, $=C(t\text{-}Bu)SiF_2$, $^2J(FF) = 34.2$ Hz), 138.80 and 135.53 (ddd and dd respectively, $=CHSiF_2$, $^2J(FF) = 35.4$ Hz, $^4J(FF) = 4.9$ Hz). ^{13}C NMR of **11a**: δ 13.22 (s(q), $=C-CH_3$), 14.09 (m(dm), $(SiF_2)_2CH$), 28.81 (s(q), $C(CH_3)_3$), 38.32 (s(s), $C(CH_3)_3$), 120.02 (s(d), $(SiF_2)_2CH-CH=$), 124.53 (s(d), $=CHCH_3$), 128.62 (s(d), $=CHCH{=}CHCH_3$), 129.37 (s(d), $-CH{=}CHCH_3$), 140.35 (tt(dtt), $=CHSiF_2$), 182.00 (tt(tt), $=C(t\text{-}Bu)SiF_2$).

3.1.5. Preparation of 11b and 4e/4f

Compound **8** (0.4 g, 1.0 mmol) and 0.54 g (5.0 mmol) of cycloocta-1,3-diene were added to 10 ml of dried and degassed toluene in a quartz tube under vacuum. The reaction mixture was irradiated at 30°C for 72 h. After removal of solvent, vacuum distillation at 100–120°C generated a yellow liquid. About 200 mg of PPh_3 and 2 ml of hexane were added to the liquid and the mixture was heated at 110°C for 3 h. Then, vacuum distillation at 60–70°C yielded 220 mg of colourless liquid products which contained 35% of **11b** and 65% of **4e/4f**. The yield based on the quantity of **8** was 70%. MS of **11b** and **4e/4f**: m/z 322 (M^+, $C_{14}H_{22}Si_2F_4^+$), 307 ($C_{13}H_{19}Si_2F_4^+$), 294 ($C_{12}H_{18}Si_2F_4^+$), 280 ($C_{11}H_{16}Si_2F_4^+$). The ^1H COSY, ^{13}C–^1H correlation and INADEQUATE experiments help to identify the proton, carbon signals of compounds **11b** and **4e/4f**.

3.2. Spectra

All mass spectra were obtained from a JEOL JMS-100 mass spectrometer operating at 12 eV. The NMR spectra were recorded on a JEOL JMX-100 spectrometer operating at 99.55, 93.65 and 25.0 MHz for ^1H, ^{19}F and ^{13}C spectra, respectively, and a Bruker AM 400 spectrometer operating at 400.0, 376.5 and 100.0 MHz for ^1H, ^{19}F and ^{13}C spectra, respectively. Chemical shifts of ^1H and ^{13}C were measured in δ values; ^{19}F chemical shifts were measured in parts per million upfield from internal standard CCl_3F (C_6D_6 was the solvent for all NMR data). For the ^{13}C data listed below, the spectral multiplicity following each chemical shift is due to the coupling with heteronuclei; the coupling patterns in $^{13}C\{^1H\}$ are included in parentheses.

^{1}H NMR of **4e** or **4f** δ 1.07 (s, 9H, t-Bu), 1.08 (m, 2H, $\mathrm{-CH{=}CH-CH_2C}H_2\mathrm{-}$), 1.20 (m, 1H, $\mathrm{{=}CH-CH(SiF_2)-C}H\mathrm{(SiF_2)-}$), 1.45 (m, 2H, $\mathrm{-CH{=}CH-CH_2CH_2C}H_2\mathrm{-}$), 1.60 (m, 2H, $\mathrm{{=}CH-CH(SiF_2)-CH(SiF_2)C}H_2$), 1.85 (m, 2H, $\mathrm{-CH{=}CH-C}H_2\mathrm{-CH_2-}$), 2.34 (m, 1H, $\mathrm{-C}H\mathrm{(SiF_2)-CH{=}CH-}$). 5.38 (m, 1H, $\mathrm{-(CH(SiF_2)-C}H\mathrm{{=}CH-}$), 5.81 (m, 1H, $\mathrm{(-CH(SiF_2)-CH{=}C}H\mathrm{-}$), 6.45 (tt, $\mathrm{{=}C}H\mathrm{SiF_2-}$). ^{19}F{^{1}H} NMR of **4e** or **4f** 134.75 (d) and 138.85 (d), $\mathrm{{=}CHSi}F_2\mathrm{-}$, ^2J(F,F)=17.7 Hz; 141.76 (d) and 145.54 (d), $\mathrm{{=}C(t{-}Bu)SiF_2-}$, ^2J(F,F) = 17.7 Hz; ^{19}F{^{1}H} NMR of **4f** or **4e** 136.48 (d) and 140.03 (d), $\mathrm{{=}CHSiF_2}$, ^2J(F,F) = 16.0 Hz; 141.38 (d) and 143.50 (d), $\mathrm{{=}C(t{-}Bu)SiF_2-}$, ^2J(F,F) = 16.0 Hz; 141.38 (d) and 143.50 (d), $\mathrm{{=}C(t{-}Bu)SiF_2-}$, ^2J(F,F) = 19.1 Hz. ^{13}C NMR of **4e** or **4f**: δ 21.56 (t(dt), $-C\mathrm{H(SiF_2)-CH{=}CH-}$), 24.6 (s(t), $\mathrm{-CH(SiF_2)-CH(SiF_2)-}C\mathrm{H_2-}$), 25.01 (s(d), $\mathrm{{=}CH-CH(SiF_2)-}C\mathrm{H(SiF_2)-}$), 26.31 (s(t), $\mathrm{-CH{=}CH-CH_2-CH_2-}C\mathrm{H_2-}$), 27.2 (s(t), $\mathrm{-CH{=}CH-}C\mathrm{H_2-}$), 29.75 (s(q), $\mathrm{C(}C\mathrm{H_3)_3}$), 29.78 (s(t), $\mathrm{-CH{=}CH-CH_2-}C\mathrm{H_2-}$), 39.44 (s(s), $C\mathrm{(CH_3)_3}$), 122.61 (s(d), $\mathrm{-CH(SiF_2)-}C\mathrm{H{=}CH-CH_2-}$), 134.64 (s(d), $\mathrm{-CH(SiF_2)-CH{=}}C\mathrm{H-CH_2-}$), 135.32 (tt(dtt), $\mathrm{{=}}C\mathrm{HSiF_2-}$), 174.43 (tt(tt), $\mathrm{{=}}C\mathrm{(t{-}Bu)SiF_2-}$).

^{1}H NMR of **11b** δ 1.07 (s, 9H, t-Bu), 1.37 (m, 2H, $\mathrm{-CH{=}CH-\overset{|}{C}HC}H_2\mathrm{CH_2-}$), 1.67 (m, 2H, $\mathrm{-CH{=}CH-\overset{|}{C}HCH_2C}H_2\mathrm{-}$), 2.01 (m, 1H, $\mathrm{-(SiF_2)_2\overset{|}{C}}H\mathrm{-)}$), 5.32 (m, 1H, $\mathrm{-(SiF_2)_2CH-C}H\mathrm{{=}CH-}$), 5.52 (m, 1H, $\mathrm{-(SiF_2)_2CH-CH{=}C}H\mathrm{-}$), 6.58 (tt, 1H, $\mathrm{{=}CHSiF_2-}$). ^{13}C NMR of **11b** δ 21.85 (m(dm), $\mathrm{-(SiF_2)_2}C\mathrm{H-}$), 25.61, 27.90, 28.85 ($\mathrm{-\overset{|}{C}HCH_2CH_2-}$), 29.10 (s(q), $\mathrm{C(}C\mathrm{H_3)}$), 38.45 (s(s), $C\mathrm{(CH_3)_3}$), 123.28 (s(d), $\mathrm{-(SiF_2)_2CH-}C\mathrm{H{=}CH-}$), 133.93 (s(d), $\mathrm{-(SiF_2)_2CH-CH{=}}C\mathrm{H-}$), 138.97 (tt(dtt), $\mathrm{{=}}C\mathrm{HSiF_2-}$), 173.10 (tt(tt), $\mathrm{{=}}C\mathrm{(t{-}Bu)SiF_2-}$).

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