Reduction of Ruthenium and Iron μ-Methylene Complexes with Hydrosilanes Producing Alkane: a Model System for Methanation *via* the Fischer–Tropsch Mechanism

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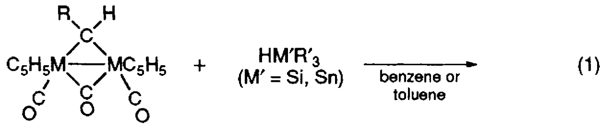
Reduction of the Ru and Fe μ-methylene complexes $[M_2(C_5H_5)_2(\mu\text{-CHR})(\mu\text{-CO})(CO)_2]$ (**2**: M = Ru, R = H; **3**: M = Fe, R = CH_2Ph) with hydrosilanes produces alkane (RMe) by way of dinuclear hydrido-methylene and methyl intermediates as confirmed by the reaction of $[Ru_2(C_5H_5)_2(\mu\text{-CHR})(\mu\text{-CO})(CO)(NCMe)]$ **9** with hydrosilanes; such a reaction sequence can be viewed as a model system for methanation *via* the Fischer–Tropsch mechanism.

Although a number of μ-methylene complexes have been prepared and studied as model compounds for surface-bound methylene species, they have proved to be not so reactive as expected presumably owing to the extraordinary stability of the dimetallacyclopropane skeleton.[1] We have been studying reduction of hydrocarbyl ligands using group 14 metal hydrides as an equivalent for dihydrogen,[2] and in a previous paper[2c] we reported a model system for production of ethylene *via* the Fischer–Tropsch mechanism, *i.e.* reduction of $[Ru_2(C_5H_5)_2(\mu\text{-CO})_2(CO)_2]$ **1** with di- and tri-hydrosilanes produces the μ-methylene complex $[Ru_2(C_5H_5)_2(\mu\text{-CH}_2)(\mu\text{-CO})(CO)_2]$ **2** and the di-μ-methylene complex $[Ru_2(C_5H_5)_2(\mu\text{-CH}_2)_2(CO)_2]$ successively, and the latter liberates ethylene upon thermolysis *via* coupling of the two methylene ligands. Herein we report



2; M = Ru, R = H
3; M = Fe, R = CH$_2$Ph

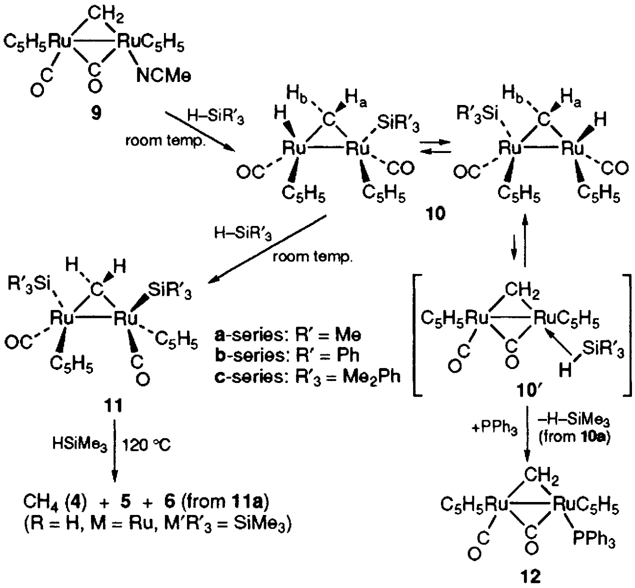
$$R\text{–}Me + R\text{–}CH_2M'R'_3 + M(C_5H_5)(H)(CO)(M'R'_3)_2 + M(C_5H_5)(CO)_2\text{–}M'R'_3$$

Complex	HM'R'$_3$	Conditions	4	5	6	7
2 (Ru)	HSiMe$_3$	170 °C, 14 d	42	18	9	22
3 (Fe)	HSiMe$_3$	120 °C, 14 h	33	25	0	Trace
	H$_2$SiEt$_2$	120 °C, 14 h	90	0	0	16
	HSnMe$_3$	120 °C, 14 h	70	0	Trace	90

reduction of $[M_2(C_5H_5)_2(\mu\text{-CHR})(\mu\text{-CO})(CO)_2]$ (**2**: M = Ru, R = H;[3] **3**: M = Fe, R = CH$_2$Ph[4]) with hydrosilanes giving alkane (RMe).

Thermolysis of a sealed [^{2}H$_8$]toluene solution of the diruthenium μ-methylene complex **2** in the presence of trimethylsilane afforded methane **4** as a major organic product together with tetramethylsilane **5** and the two mononuclear silyl complexes **6**† and **7** [eqn. (1)].[5] The reduction of the diiron complex **3** proceeded under milder conditions to give **4** and **5**. Although employment of dihydrosilane (H$_2$SiEt$_2$)‡ improved the yield of the alkane **4**, a complicated mixture of organometallic products containing **6**, **7** and a μ-silylene complex $[Fe_2(C_5H_5)_2(\mu\text{-SiEt}_2)(\mu\text{-CO})(CO)_2]$ **8** was obtained. Furthermore the reduction with trimethyltin produced **4** and the organometallic product **7** with good selectivity.

To find a clue to the reduction mechanism, the viability of an initial decarbonylation process was examined by using the labile diruthenium complex $[Ru_2(C_5H_5)_2(\mu\text{-CH}_2)(\mu\text{-CO})(CO)(NCMe)]$ **9**[6] as an equivalent for the coordinatively unsaturated species (Scheme 1). Addition of HSiR'$_3$ to a C$_6$D$_6$ suspension of **9** at ambient temperature resulted in immediate dissolution to give the hydrido-silyl-μ-methylene complex **10**† and MeCN quantitatively.[7] When a mixture containing an excess of HSiR'$_3$ was left for 3 h, **10** was converted gradually to the disilyl-μ-methylene complex **11**† in quantitative yields. Finally, heating **10** and **11** in the presence of an excess of HSiMe$_3$ at 120 °C produced methane **4** accompanied by **5** and **6**. Thus the methane formation, which is initiated by decarbonylation, results from the reduction of the silylated μ-methylene complexes **10** and/or **11**.



Scheme 1

The disilyl complexes **11** were characterized readily on the basis of their symmetrical spectral features, that is, all the two C$_5$H$_5$, CH_2, CO and SiR'$_3$ parts were observed equivalently and the η^1-coordination of CO was confirmed by IR and ^{13}C NMR spectroscopy. These data are consistent with the *trans*-configuration (C_2 symmetry) confirmed by X-ray crystallography.[8] On the other hand, because **10** was not stable enough to be isolated in a pure form, it was characterized spectroscopically in comparison with **11**. Complex **10a** was fluxional as revealed by the coalescence of the two C$_5$H$_5$ signals (^{1}H NMR) separately observed below −20 °C,§ while no change was observed for the hydride and CH$_2$ signals (AB quartet) in the temperature range −80–20 °C. These phenomena indicated that the H and SiR'$_3$ ligands exchanged *via* an intramolecular process (see below) and that, at a higher temperature, **10** possessed apparent C_s symmetry [*cis*-configuration with respect to the C$_5$H$_5$ (or CO) ligands] where H$_a$ and H$_b$ remained non-equivalent (Scheme 1).[9] Although the liberation of HSiMe$_3$ and the phosphine complex **12** from **10a** induced by addition of PPh$_3$ suggested the η^2-coordination of the H–Si bond (**10'**),[10] no spectroscopic data supporting **10'** [*e.g.* $^1J_{\text{H–}^{29}\text{Si}}$ for Ru–H or the presence of μ-CO] was

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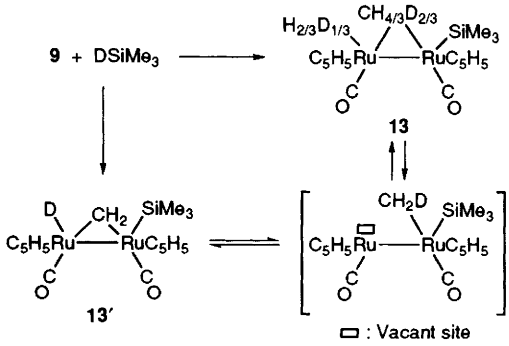
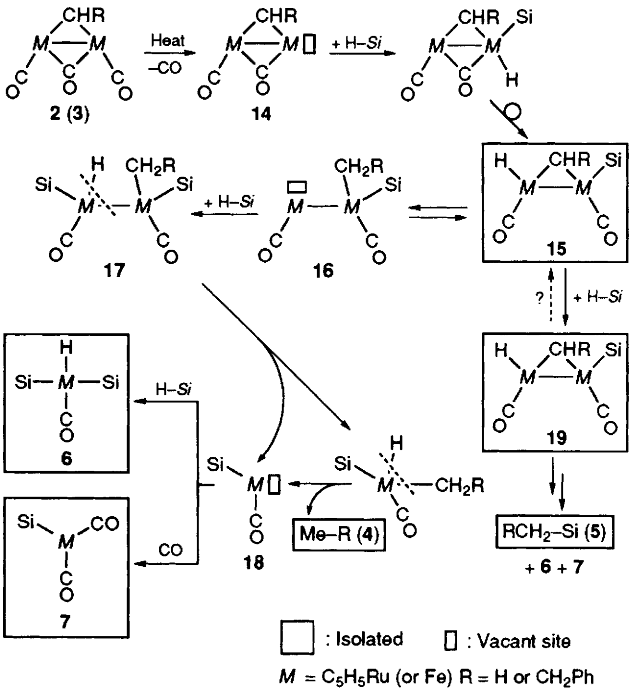
† *Spectral data* for **6** (M = Ru, M'R'$_3$ = SiMe$_3$): ^{1}H NMR (in C$_6$D$_6$ at 90 MHz) δ 4.56 (5H, s, C$_5$H$_5$), 0.51 (18H, s, 2SiMe$_3$), −10.80 (1H, s, Ru–H); ^{13}C NMR (in C$_6$D$_6$ at 67 MHz at 27 °C) δ 201.9 (s, CO), 88.1 (d, $^1J_{\text{C–H}}$ 177 Hz, C$_5$H$_5$), 10.3 (q, $^1J_{\text{C–H}}$ 119 Hz, SiMe$_3$); IR 1942 cm^{-1} (CH$_2$Cl$_2$). For **10a**: ^{1}H NMR (in CD$_2$Cl$_2$ at 90 MHz) at −60 °C δ 6.90, 6.80 (1H × 2, d × 2, $^2J_{\text{H–H}}$ 3.6 Hz, CH$_2$), 5.26, 5.21 [5H × 2, s × 2, (C$_5$H$_5$)$_2$], 0.37 (9H, s, SiMe$_3$), −10.09 (1H, s, Ru–H); at 20 °C δ 6.94, 6.87 (1H × 2, d × 2, $^2J_{\text{H–H}}$ 3.6 Hz), 5.21 [10H, s, (C$_5$H$_5$)$_2$], 0.37 (9H, s, SiMe$_3$), −10.08 (1H, s, Ru–H); ^{13}C NMR (in CDCl$_3$ at 67 MHz at 27 °C) δ 205.7, 203.3 (s × 2, 2CO), 110.0 (t, $^1J_{\text{C–H}}$ 144 Hz, CH$_2$), 90.1 (d, $^1J_{\text{C–H}}$ 178 Hz, C$_5$H$_5$), 88.6 (d, $^1J_{\text{C–H}}$ 177 Hz, C$_5$H$_5$), 6.9 (q, $^1J_{\text{C–H}}$ 119 Hz, SiMe$_3$); IR 1924 cm^{-1} (CH$_2$Cl$_2$). For **10b**: ^{1}H NMR (in CD$_2$Cl$_2$ at 90 MHz at 27 °C) δ 7.1–7.8 (m, SiPh$_3$ and CH$_2$), 4.80, 5.11 [5H × 2, s × 2, 2(C$_5$H$_5$)], −10.15 (1H, s, Ru–H); IR 1924 cm^{-1} (CH$_2$Cl$_2$). For **11a**: ^{1}H NMR (in CDCl$_3$ at 90 MHz) δ 6.13 (2H, s, CH$_2$), 5.14 [10H, s, 2(C$_5$H$_5$)], 0.32 (18H, s, 2SiMe$_3$); ^{13}C NMR (in CDCl$_3$) δ 206.7 (s, CO), 117.0 (t, $^1J_{\text{C–H}}$ 141 Hz, CH$_2$), 90.6 (d, $^1J_{\text{C–H}}$ 178 Hz, C$_5$H$_5$), 3.9 (q, $^1J_{\text{C–H}}$ 118 Hz, SiMe$_3$); IR 1904 cm^{-1} (CH$_2$Cl$_2$). For **11b**: ^{1}H NMR (in CDCl$_3$) δ 7.2–7.6 (m, 30H, 2SiPh$_3$), 7.15 (2H, s, CH$_2$), 4.53 [10H, s, 2(C$_5$H$_5$)]; ^{13}C NMR (in CDCl$_3$) δ 207.8 (s, CO), 136.4, 128.1, 127.2 (Ph, one of the signals could not be located), 128.3 (t, $^1J_{\text{C–H}}$ 143 Hz, CH$_2$), 91.8 (d, $^1J_{\text{C–H}}$ 180 Hz, C$_5$H$_5$); IR 1915 cm^{-1} (CH$_2$Cl$_2$). For **11c**: (in CDCl$_3$) δ 7.27–7.64 (m, 10H, 2SiPh), 6.41 (2H, s, CH$_2$), 4.78 [10H, s, 2(C$_5$H$_5$)], 0.57, 0.64 (6H × 2, s × 2, 2SiMe$_2$); ^{13}C NMR (in CDCl$_3$) δ 207.2 (s, CO), 146.9, 133.8, 127.9, 127.1 (Ph), 120.8 (t, $^1J_{\text{C–H}}$ 141 Hz, CH$_2$), 90.9 (d, $^1J_{\text{C–H}}$ 177 Hz, C$_5$H$_5$), 5.9 (q, $^1J_{\text{C–H}}$ 119 Hz, SiMe), 5.1 (q, $^1J_{\text{C–H}}$ 120 Hz, SiMe); IR 1909 cm^{-1} (CH$_2$Cl$_2$).

‡ Reduction of the Ru complex **2** with dihydrosilanes resulted in methylenation.[2c]

§ At room temp. **10a** was fluxional on the time-scale of ^{1}H NMR (90 MHz) but not fluxional on the time-scale of ^{13}C NMR (67 MHz). Complex **10b** was not fluxional even on the time-scale of ^{1}H NMR (90 MHz) at room temp., although the C$_5$H$_5$ signals were very broad.



Scheme 2

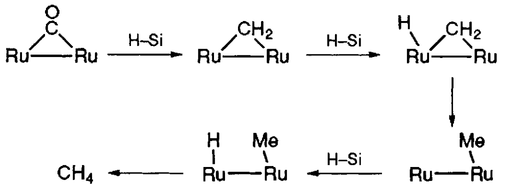


Scheme 3

obtained. In addition to the fluxional process, **10** and **11** showed complicated exchange reactions of the H, CH_2 and SiR'_3 parts. (*i*) Treatment of **9** with $DSiMe_3$ did not give **13′** but the completely scrambled product **13** (Scheme 2). This result can be explained in terms of a fast reductive elimination –oxidative addition equilibrium and suggests occurrence of a similar hydrido-methylene ⟷ methyl interconversion[11] on a heterogeneous catalyst surface. (*ii*) The H, CH_2 and SiR'_3 parts of **10** and **11** exchanged with an externally added hydrosilane.¶ For **10a** these processes were much slower than the above-mentioned intramolecular H ⟷ SiR'_3 exchange, because the fluxional behaviour was observed without incorporation of the externally added excess $DSiMe_3$.

On the basis of the results obtained, a plausible mechanism of the methane formation from **2** (**3**) is summarized in Scheme 3, while a couple of problems [*e.g.* backward reaction from **19** to **15** (or **11** ⟶ **10**)] have remained to be solved. Thermolysis of **2** (**3**) generates the coordinatively unsaturated species **14**, to which $HSiR'_3$ oxidatively adds to form the hydridosilyl intermediate **15** (**10**) after rearrangement. Complex **15** is in equilibrium with the coordinatively unsaturated alkyl species **16**, to which $HSiR'_3$ adds again to give the hydrido-alkyl intermediate **17**. Double reductive elimination from **17** produces alkane (**4**) and 2 equiv. of the coordinatively unsaturated mononuclear species **18**, which is trapped either by CO or by $HSiR'_3$ to give **6** or **7**, respectively.[2b] Reaction of **15** with an excess of $HSiR'_3$ affords the disilyl intermediate **19** (**11**), which follows the reaction sequence similar to the alkane formation to produce the silane (**5**) and **18**.

In combination with the previously reported methylenenation of **1** with di- or tri-hydrosilane leading to **2**,[2c] the present system serves as a model system for methanation *via* the Fischer–Tropsch mechanism[12] in the following sequence.[13] At the diruthenium centre the CO ligand in **1** is reduced with hydrosilanes (an equivalent for dihydrogen) to methane (**4a**) [eqn. (2)]. To be noted is that the C and H atoms in methane originate from CO on Ru (**2**) and the hydrosilanes, respectively.



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¶ Details will be reported in a forthcoming full paper.

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