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

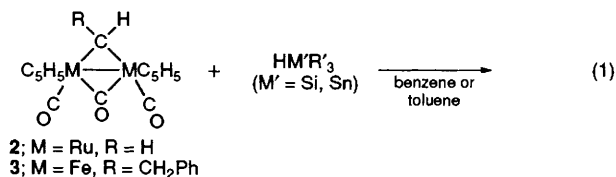Munetaka Akita,* Tomoharu Oku, Ruimao Hua and Yoshihiko Moro-oka*

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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 $[Ru_2(C_5H_5)_2\text{-}(\mu\text{-}CO)_2(CO)_2]$ **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
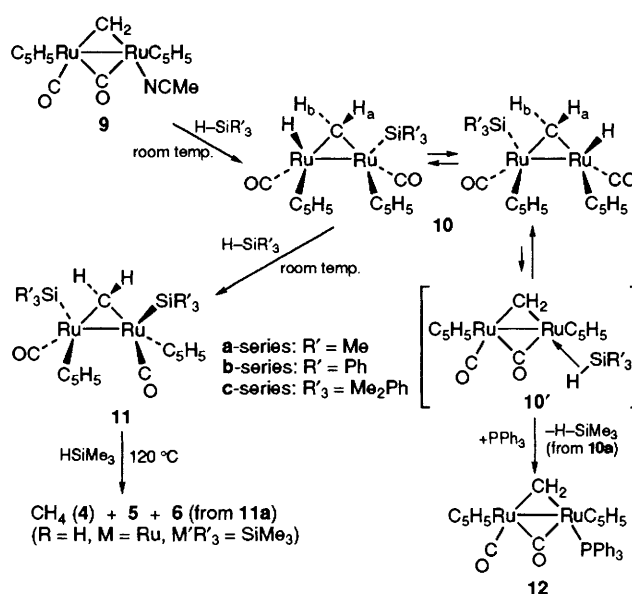
$$R\text{-Me} + R\text{-CH}_2\text{M}'\text{R}'_3 + M(C_5H_5)(H)(CO)(M'\text{R}'_3)_2 + M(C_5H_5)(CO)_2\text{-M}'\text{R}'_3$$

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$_5$H$_5$)$_2$(μ-CHR)(μ-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 [²H$_8$]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$_5$H$_5$)$_2$(μ-SiEt$_2$)(μ-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$_5$H$_5$)$_2$(μ-CH$_2$)(μ-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

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† *Spectral data* for **6** (M = Ru, M'R'$_3$ = SiMe$_3$): ¹H 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); ¹³C NMR (in C$_6$D$_6$ at 67 MHz at 27 °C) δ 201.9 (s, CO), 88.1 (d, ¹J$_{C-H}$ 177 Hz, C$_5$H$_5$), 10.3 (q, ¹J$_{C-H}$ 119 Hz, SiMe$_3$); IR 1942 cm⁻¹ (CH$_2$Cl$_2$). For **10a**: ¹H NMR (in CD$_2$Cl$_2$ at 90 MHz) at −60 °C δ 6.90, 6.80 (1H × 2, d × 2, ²J$_{H-H}$ 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$_{H-H}$ 3.6 Hz), 5.21 [10H, s, (C$_5$H$_5$)$_2$], 0.37 (9H, s, SiMe$_3$), −10.08 (1H, s, Ru–H); ¹³C NMR (in CDCl$_3$ at 67 MHz at 27 °C) δ 205.7, 203.3 (s × 2, 2CO), 110.0 (t, ¹J$_{C-H}$ 144 Hz, CH$_2$), 90.1 (d, ¹J$_{C-H}$ 178 Hz, C$_5$H$_5$), 88.6 (d, ¹J$_{C-H}$ 177 Hz, C$_5$H$_5$), 6.9 (q, ¹J$_{C-H}$ 119 Hz, SiMe$_3$); IR 1924 cm⁻¹ (CH$_2$Cl$_2$). For **10b**: ¹H 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**: ¹H 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$_3$); ¹³C NMR (in CDCl$_3$) δ 206.7 (s, CO), 117.0 (t, ¹J$_{C-H}$ 141 Hz, CH$_2$), 90.6 (d, ¹J$_{C-H}$ 178 Hz, C$_5$H$_5$), 3.9 (q, ¹J$_{C-H}$ 118 Hz, SiMe$_3$); IR 1904 cm⁻¹ (CH$_2$Cl$_2$). For **11b**: ¹H 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$_5$)]; ¹³C 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$_{C-H}$ 143 Hz, CH$_2$), 91.8 (d, ¹J$_{C-H}$ 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$_2$); ¹³C NMR (in CDCl$_3$) δ 207.2 (s, CO), 146.9, 133.8, 127.9, 127.1 (Ph), 120.8 (t, ¹J$_{C-H}$ 141 Hz, CH$_2$), 90.9 (d, ¹J$_{C-H}$ 177 Hz, C$_5$H$_5$), 5.9 (q, ¹J$_{C-H}$ 119 Hz, SiMe), 5.1 (q, ¹J$_{C-H}$ 120 Hz, SiMe); IR 1909 cm⁻¹ (CH$_2$Cl$_2$).

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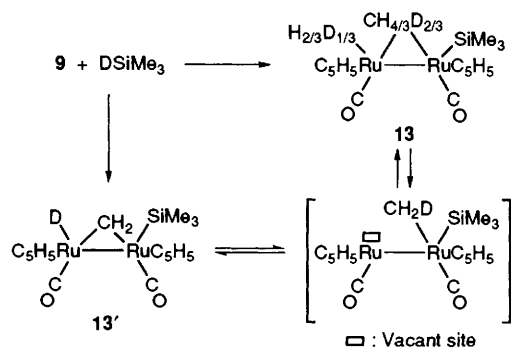

Scheme 1

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.

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 η¹-coordination of CO was confirmed by IR and ¹³C 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 (¹H 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 η²-coordination of the H–Si bond (10'),[10] no spectroscopic data supporting 10' [*e.g.* ¹J$_{1H-29Si}$ for Ru–H or the presence of μ-CO] was
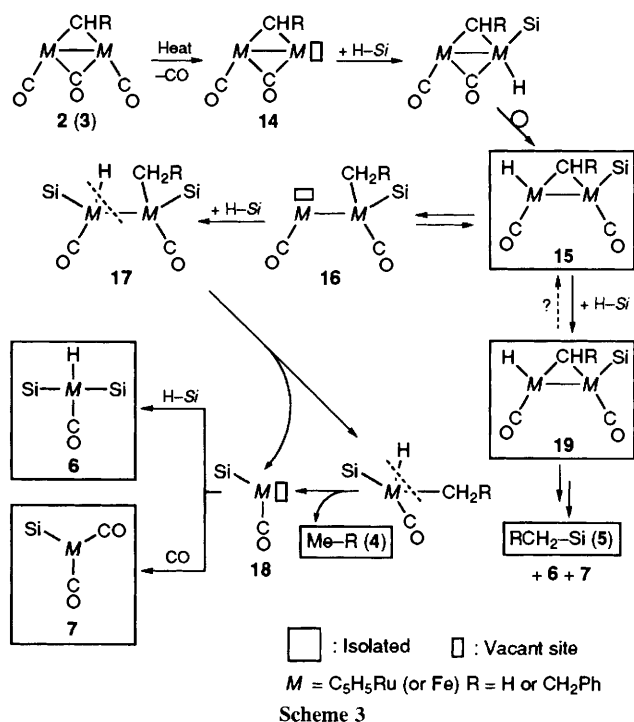
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§ At room temp. 10a was fluxional on the time-scale of ¹H NMR (90 MHz) but not fluxional on the time-scale of ¹³C NMR (67 MHz). Complex 10b was not fluxional even on the time-scale of ¹H NMR (90 MHz) at room temp., although the C$_5$H$_5$ signals were very broad.
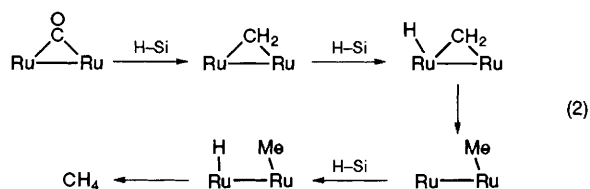
Scheme 2

M = C₅H₅Ru (or Fe)   R = H or CH₂Ph

Scheme 3

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 methylenation 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.

(2)

We thank Professor H. Tobita (Tohoku Univ.) for helpful correspondence on the synthesis of 8.[14]

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

¶ Details will be reported in a forthcoming full paper.

References

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8 The molecular structures of 11b, c were determined by X-ray crystallography. The C_2 axis passes through the methylene carbon atom and the midpoint of the Ru–Ru bond. M. Akita, T. Oku, R. Hua, M. Tanaka and Y. Moro-oka, unpublished results.

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