C–H and Si–C bond activation on diruthenium bridging methylene complexes: evidence for reversible oxidative addition of Si–C(sp^3) bonds

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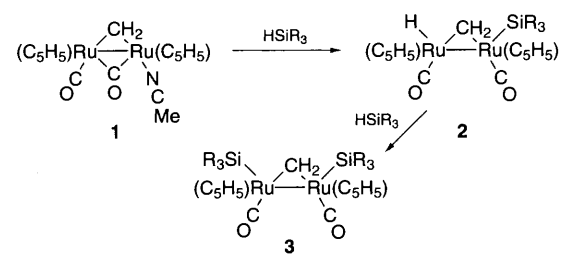
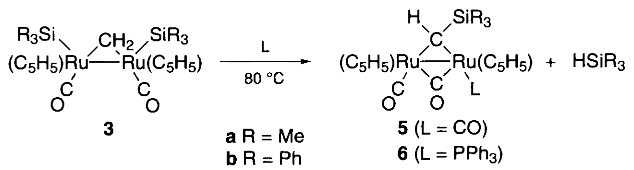
Interconversion between silyl-μ-methylene complexes $[(C_5H_5)_2Ru_2(\mu\text{-}CH_2)(H)(SiR_3)(CO)_2]$ and $[(C_5H_5)_2Ru_2(\mu\text{-}CH_2)(SiR_3)_2(CO)_2]$ and μ-silylmethylene complexes $[(C_5H_5)_2Ru_2(\mu\text{-}CHSiR_3)(\mu\text{-}CO)(CO)(L)]$ (L = CO, PPh_3) follows reversible oxidative addition–reductive elimination processes of C–H and Si–C(sp^3) bonds.

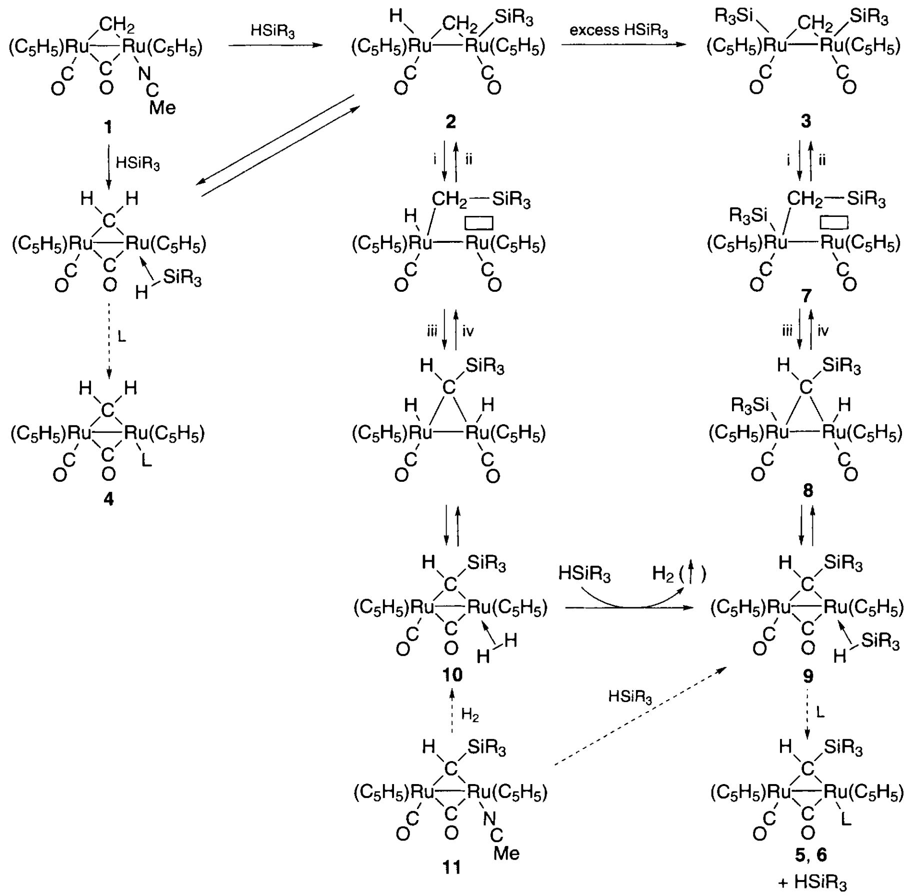
Activation of an Si–C bond induced by a transition-metal species has attracted much attention in connection with functionalization and catalytic transformation of organosilanes.[1] Although Si–C(sp^2) bond cleavage processes are often observed as typicaly illustrated by redistribution of arylhydrosilanes in the presence of a transition-metal species,[2] examples of Si–C(sp^3) bond cleavage on a discrete transition-metal complex are still quite rare.[3] Previously, we reported that treatment of the labile μ-methylene complex $[(C_5H_5)_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(MeCN)]$ **1** with hydrosilane resulted in sequential formation of the hydrido-silyl-μ-methylene complexes $[(C_5H_5)_2Ru_2(\mu\text{-}CH_2)(H)(SiR_3)(CO)_2]$ **2** and the disilyl-μ-methylene complexes $[(C_5H_5)_2Ru_2(\mu\text{-}CH_2)(SiR_3)_2(CO)_2]$ **3**



Scheme 1



Scheme 2

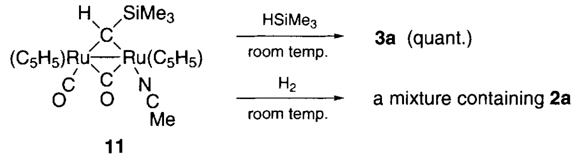


Scheme 3 i, Si–C coupling; ii, Si–C oxidative addition; iii, C–H oxidative addition; iv, C–H coupling; □, coordinatively unsaturated site; - - →, supporting experiments

(Scheme 1).[4] Both of the silylated μ-methylene complexes **2** and **3** exhibited quite complicated intra- and inter-molecular exchange reactions of the hydride, CH_2, and SiR_3 moieties. During the course of our study on the reaction mechanism we found that Scheme 1 and its related reactions involve intramolecular reversible oxidative addition–reductive elimination of Si–C(sp^3) bonds.

In order to determine the mechanism of the incorporation of the second equivalent of hydrosilane (**2** → **3**; Scheme 1), participation of coordinatively unsaturated intermediates was examined at first by treatment of the starting and resulting silylated μ-methylene complexes **2** and **3** with trapping agents (L = CO, PPh_3). While in the case of **2**, the reaction was reverted even at room temperature to give $[(C_5H_5)_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(L)]$ **4** with elimination of $HSiR_3$ as reported previously,[4] the reaction of **3** at 80 °C in C_6D_6 afforded isomeric mixtures of μ-silylmethylene complexes, *cis*- and *trans*-$[(C_5H_5)_2Ru_2(\mu\text{-}CHSiR_3)(\mu\text{-}CO)(CO)(L)]$ **5** (L = CO) and **6** (L = PPh_3), in quantitative yields accompanied by the elimination of $HSiR_3$ (1 equiv.) as observed by ^1H NMR spectroscopy (Scheme 2). One of the products, **6a** has been characterized by X-ray crystallography,† and the structure is in accord with the change in the coupling pattern of the bridging carbon signal {triplet (μ-CH_2 in **3**) → doublet [μ-$CHSiR_3$: δ_C in $CDCl_3$ 131.3 (J = 112 Hz) (**5a**), 115.4 (J = 116 Hz) (**5b**), 125.6 (J = 120 Hz) (**6a**), 112.8 (J = 117 Hz) (**6b**)} and the appearance of a ν(μ-CO) vibration [in CH_2Cl_2: 1973, 1938, 1782 (**5a**), 1983, 1942, 1777 (**5b**), 1917, 1747 (**6a**), 1917, 1747 cm^{-1} (**6b**)].‡ The most striking structural feature of **5** and **6** is that the SiR_3 group initially bonded to the Ru centre is transferred to the bridging methylene carbon. A plausible formation mechanism of **5** and **6** is given in Scheme 3. Thermolysis of **3** may induce reductive elimination of the methylene carbon and one of the two silyl groups to give a coordinatively unsaturated species **7**. Subsequent oxidative addition of a C(α)–H bond in the resultant silylmethyl functional group gives rise to the μ-silylmethylene intermediate **8**, which is finally converted to **5** and **6** *via* replacement of the η^2-coordinated silane ligand **9** by a trapping agent (L).

For further confirmation of the mechanism, the labile acetonitrile-coordinated μ-silylmethylene complex, $[(C_5H_5)_2Ru_2(\mu\text{-}CHSiMe_3)(\mu\text{-}CO)(CO)(MeCN)]$ **11**,[5] was treated with $HSiR_3$ and H_2 (Scheme 4) to generate the η^2-coordinated intermediates **9** and **10**. As expected, instantaneous reaction of hydrosilane took place at ambient temperature to furnish the silylated μ-methylene complex **3a** in quantitative yield. The formation of **3a** is interpreted in terms of the reverse process of that of **5** and **6** (*vide supra*), and oxidative addition of a CH_2–$SiMe_3$ bond is involved in the last stage of the reaction sequence (**7** → **3**). On the other hand, the reaction with H_2 afforded a complicated mixture containing only a small amount of **2a**,[6] which should be formed *via* a similar reaction pathway initiated by oxidative addition of the H–H bond.



Scheme 4

If the η^2-H_2 ligand in **10** is replaced by $HSiR_3$ (**10** → **9**), the reaction sequence summarized in Scheme 3 accounts for the mechanism of the conversion of **2** into **3** (Scheme 1). Thus the two silylated μ-methylene complexes **2** and **3** are interconverted by a combination of reversible oxidative addition–reductive elimination of Si–C and C–H bonds, and the conversion should be driven forward by diffusion of H_2 into the gas phase. The mechanism can also explain the intermolecular exchange of the CH_2 and SiR_3 groups in **3**,[4] which should be caused by substitution of the η^2-coordinated silane in **9** by externally added silane.

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Footnotes

† *Crystal data* for **6a**: $C_{34}H_{35}O_2PSiRu_2$, M = 736.9, triclinic, space group $P\bar{1}$, a = 11.407(5), b = 14.631(5), c = 9.750(2) Å, α = 79.20(2), β = 81.58(3), γ = 78.60(3)°, V = 1556.7(10) Å^3, Z = 2, D_c = 1.57 g cm^{-3}, $R(R_w)$ = 0.041 (0.043) for 4090 unique reflections with $I > 3\sigma(I)$ and 365 variables.

‡ *Selected ^1H NMR data* (in $CDCl_3$) for **5a**: (*cis*) δ 0.15 (9 H, s, $SiMe_3$), 5.21 [10 H, s, $(C_5H_5)_2$], 10.10 (1 H, s, CHSi); (*trans*) δ ($CDCl_3$) 0.23 (9 H, s, $SiMe_3$), 5.28, 5.36 [5 H × 2, 2 × s, $(C_5H_5)_2$], 9.15 (1 H, s, CHSi). For **5b**: (*cis*) δ 5.12 [10 H, s, $(C_5H_5)_2$], 10.32 (1 H, s, CHSi); (*trans*) δ 4.98, 4.99 [5 H × 2, 2 × s, $(C_5H_5)_2$], 9.15 (1 H, s, CHSi). For **6a**: (*trans*) δ 0.33 (9 H, s, $SiMe_3$), 4.44, 4.87 [5 H × 2, 2 × s, $(C_5H_5)_2$], 7.95 (1 H, d, J_{P-H} 13 Hz, CHSi). For **6b**: (first isomer) δ 4.24, 4.78 [5 H × 2, 2 × s, $(C_5H_5)_2$], 8.15 (1 H, d, J_{P-H} 13 Hz, CHSi); (second isomer) δ ($CDCl_3$) 4.45, 4.82 [5 H × 2, 2× s, $(C_5H_5)_2$], (the CHSi signal may overlap with the Ph signals).

References

1 *The Chemistry of Organosilicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, vols. 1 and 2; *Comprehensive Organometallic Chemistry I and II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1982, 1995.

2 See for example, L. G. Bell, W. A. Gustavson, S. Thanedar and M. D. Curtis, *Organometallics*, 1983, **2**, 740.

3 For intermolecular reactions, see: H. Yamashita, M. Tanaka and K. Honda, *J. Am. Chem. Soc.*, 1995, **117**, 8873, some examples of catalytic redistribution of functionalized alkylsilanes (*e.g.* halosilanes) are also known; M. D. Curtis and P. S. Epstein, *Adv. Organomet. Chem.*, 1981, **19**, 213. For intramolecular reactions, see: W. Lin, S. R. Wilson and G. S. Girolami, *Organometallics*, 1994, **13**, 2309.

4 M. Akita, T. Oku, R. Hua and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1993, 1670.

5 The MeCN adduct **11** was prepared from **5a** following the published synthetic procedure for **1**: N. M. Doherty, J. A. K. Howard, S. A. R. Knox, N. J. Terril and M. I. Yates, *J. Chem. Soc., Chem. Commun.*, 1989, 638.

6 Because the resulting **2** reacts with H_2 faster than does **11**, the reaction mixture may become complicated: R. Hua, M. Akita and Y. Moro-oka, unpublished results.

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