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New methyl group migration of a trimethylsilylmethylruthenium(IV) complex: an unprecedented reaction mode of a trimethylsilylmethyl transition metal bond

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Abstract

The novel allyl(trimethylsilylmethyl)ruthenium(IV) complex, $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)Br$ (**1**), was prepared by alkylation of the corresponding allyldibromocyclopentadienylruthenium(IV) complex with trimethylsilylmethylmagnesium chloride. When **1** was treated with silver fluoride or tetrafluoroborate, one of the methyl groups in the trimethylsilylmethyl moiety migrates from the silicon to the ruthenium atom to result in the formation of $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_3)(CH_2SiMe_2F)$.

The trimethylsilylmethyl group has been known to form stable alkyl transition metal complexes because its lack of β-hydrogen atoms does not induce the most familiar decomposition pathway, the β-elimination, of alkyl complexes [1]. One of the typical reactions of the trimethylsilylmethyl–transition metal bonds is the activation of a γ(C–H) bond to give the corresponding 3-silametallacyclobutane compounds (path a, Scheme 1) [2–5]. This process occurs particularly in bis(trimethylsilylmethyl) transition metal complexes, in which the elimination of tetramethylsilane facilitates the silametallacycle formation [4]. Another possibility is that the nucleophilic activation with fluoride or alkoxide anions may cleave the Me_3SiCH_2 bond to generate a transition metal methylene species (path b). There is, however, little evidence for this pathway, presumably because these nucleophiles attack the transition metal center more readily. Here, we report another new reaction mode of the trimethylsilylmethyl–transition metal bond (path c), in which the methyl group

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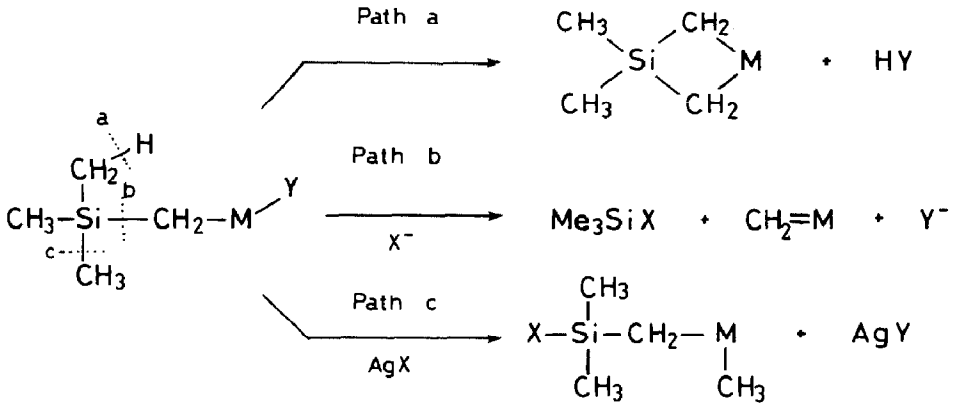
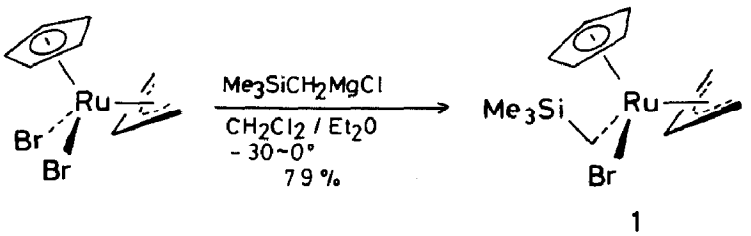


Scheme 1

of trimethylsilyl group, assisted simultaneously by the nucleophilic activation of the methyl–silicon bond, migrates to a cationic transition metal center.

Results and discussion

Treatment of the allyldibromo precursor $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)Br_2$ [6], with trimethylsilylmethylmagnesium chloride in dichloromethane gave trimethylsilylmethylruthenium(IV) complex, $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)Br$ (**1**), in 70–80% yield (Scheme 2).



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Scheme 2

The composition and structure of **1** were confirmed by elemental analysis and ^1H and ^{13}C NMR spectroscopy; the ^1H NMR data are collected in Table 1. The most important features of the ^1H NMR spectrum are the asymmetry of two allylic terminal proton signals, the two *anti* ones at δ1.89 and 2.76 ppm and the two *syn* ones at δ2.92 and 4.00 ppm, and that of the methylene protons at 1.37 and 0.85 ppm between which there is a geminal coupling of 12.82 Hz. The splitting of two *syn* protons at the C(1) and C(3) caused long range coupling ($J_{ss'}$) between them as shown in Table 1. This is strong evidence for a ruthenium atom which is asymmetric in that it has four different ligands.

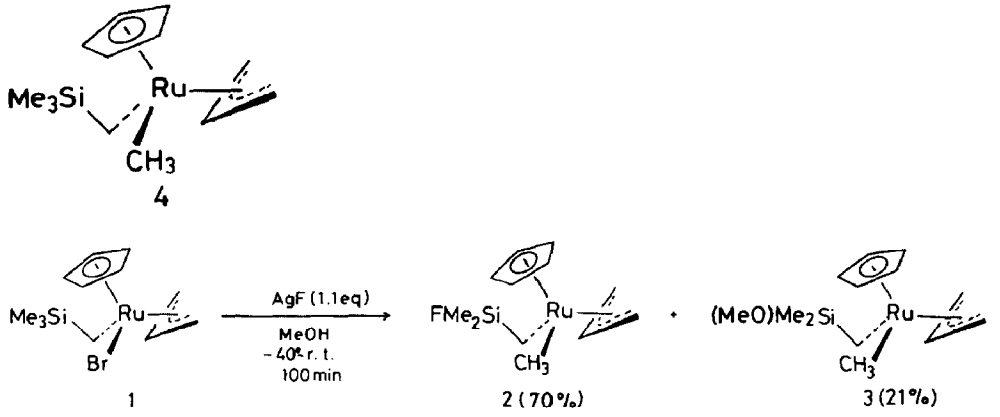
When **1** was treated with a stoichiometric amount of silver fluoride in methanol under mild conditions, two bis(alkyl)allylruthenium(IV) complexes, $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_3)(CH_2SiMe_2X)$, where X = F (**2**) and X = OCH_3, (**3**), were

Table 1

Proton NMR spectroscopic data for several organosilylmethylruthenium(IV) complexes

Assignment	Chemical shift (δ, ppm) and coupling constant (Hz)			
	$CpRu(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)Br$ (1)	$CpRu^3\text{-}C_3H_5)(CH_2SiMe_2F)(CH_3)$ (2)	$CpRu(\eta^3\text{-}C_3H_5)(CH_2SiMe_2OMe)(CH_3)$ (3)	$CpRu(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)(CH_3)$ (4)
CH_3–Si	0.30(s)	0.37(two d; J(HF) 7.32)	0.06(s)	0.28(s)
Si–CH_2–Ru	0.85(d) J_{gem} 12.82	−0.69(dd) J_{gem} 13.67	−0.98(d) J_{gem} 13.20	−0.59(d) J_{gem} 12.90
	1.37(d)	−0.56(dd) J(HF) 12.20, 8.79	−0.82(d)	−0.39(d)
CH_3–Ru	–	0.35(s)	0.07(s)	0.36(s)
Allyl *anti*	1.89(d) J_{trans} 9.89	2.14(s) J_{trans} 9.28	2.35(d) J_{trans} 9.76	2.17(d) J_{trans} 9.52
	2.76(d)	2.18(s)	2.45(d)	2.18(d)
Allyl *syn*	2.92(dd) J_{cis} 5.86	2.37(dd) J_{cis} 5.86	2.40(dd) J_{cis} 5.86	2.35(dd) J_{cis} 5.86
	4.00(dd) $J_{ss'}$ 3.30	2.55(dd) $J_{ss'}$ 2.93	2.51(dd) $J_{ss'}$ 2.93	3.55(dd) $J_{ss'}$ 2.93
Allyl center	4.08(tt)	2.89(tt)	2.80(tt)	2.89(tt)
Cyclopentadienyl	4.59(s)	4.66(s)	5.05(s)	5.05(s)
CH_3–O	–	–	3.39(s)	–
Solvent	C_6D_6	C_6D_6	$CDCl_3$	C_6D_6

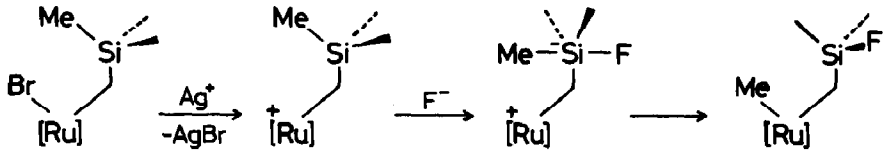
obtained unexpectedly. They were isolated as thermally unstable, oily compounds, in 70 and 21% yields, respectively (Scheme 3).



Scheme 3

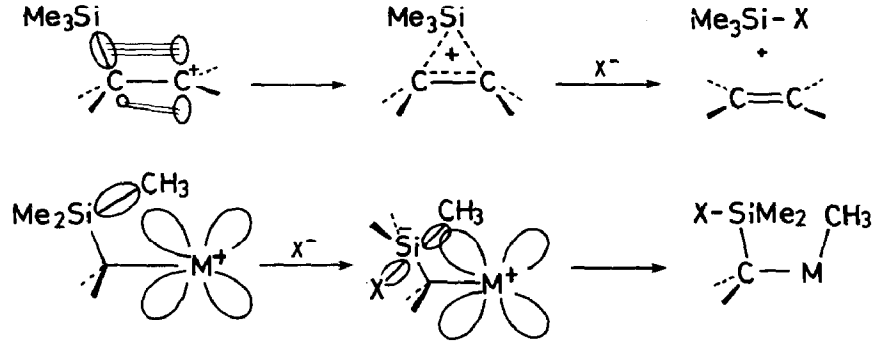
The fluorodimethylsilylmethyl complex (**2**) was also obtained in much lower yield (37%) on treatment of **1** with silver tetrafluoroborate (1.2 equiv.) in ether at room temperature, in addition the permethyl derivative, $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2\text{-}SiMe_3)(CH_3)$ (**4**; 21%) which probably formed by intermolecular migration of the methyl group was also isolated. Thermal instability of both **2** and **3** made satisfactory elemental analyses unsuccessful; however, the NMR spectroscopic results listed in Table 1 are completely consistent with the proposed structures. The organosilylmethylene signals for **2** appeared as two double doublets at -0.69 and -0.56 ppm with couplings both to the geminal (J(HH) 13.67 Hz) protons and to the introduced fluorine atom (J(HF) 12.20 Hz). The methyl proton signals of the fluorodimethylsilyl group are also split to give a doublet with coupling to the fluorine nuclei (J(HF) 7.32 Hz). The ^{13}C NMR spectrum of **2** also showed couplings with fluorine; J(FC) 17.6 for the methyl carbon signals and 15.7 Hz for that of methylene. Non-equivalence of the allylic terminals and the two silylmethylene protons was also evident for both **2** and **3** based on the appearance of the long range coupling $J_{ss'}$ for the former and that of the geminal coupling for the latter signals as shown in Table 1. Furthermore the ^1H NMR spectrum of the latter, compound **3**, indicates the presence of a methoxy proton signal at 3.39 ppm. The formation of the methoxy complex **3** is explained in terms of the replacement of the fluoride ion of **2** with methanol solvent, because the increase in the concentration (to 2 equiv.) of silver fluoride on the reaction with **1** completely inhibited the formation of **3**. By contrast, **3** becomes the predominant product (35% yield) in the reaction of **1** with sodium methoxide in methanol at room temperature. It is noteworthy that the medium of the reaction is an important factor. The formation of **2** became depressed (23%) when less polar dichloromethane was used as the solvent, and $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}CH_2SiMe_3)$ (**5**; 19%) was unexpectedly formed together with the intermolecularly rearranged product (**4**; 3%) as by-products. The mechanism of formation of **5** is not clear at present; but it can be explained in terms of the joining of the Me_3SiCH_2 group to the cyclopentadienyl ligand followed by the elimination of propene along with the intermolecular migration of a cyclopentadienyl moiety from decomposition products.

The migration of methyl group may occur intramolecularly via a five-coordinate fluoro- or methoxy-trimethylsilicate intermediate, since this new migration process always requires hard nucleophiles such as fluoride or methoxide anions. In fact, during treatment of **1** with silver trifluoromethanesulfonate there was no sign of the 1,3-migration of a methyl group, whereas other simple metal fluorides did induce methyl migration to give **2**; KF (23%) or CsF (30%). Similarly sodium methoxide gave **3** in 35% yield. In addition to nucleophilic activation with such hard nucleophiles, the efficient generation of a cationic ruthenium(IV) center is another important requirement for the generation of the rearranged products **2** or **3** in good yields. Silver ion is the most effective for this purpose. Consequently, this methyl migration process is assisted by both the cationic transition metal center and the hard nucleophilic reagents which have strong affinity for the organosilyl moiety (Scheme 4).



Scheme 4

In organosilicon chemistry it is well known that the organosilyl group present at the position β to the carbocation is stabilized by a $\sigma \rightarrow \pi$ interaction, and this concept has been applied to a number of organic synthetic reactions such as stereospecific olefin formations [7]. Attack of a nucleophile readily induces the selective cleavage of the silicon-carbon bond, at the β-position of the $Me_3SiCH_2C^+$ cation.



Scheme 5

The present finding, however, suggests that the cationic transition metal center (β to the silyl group), in a relatively high oxidation state with vacant *d* orbitals, induces the activation of γ-silicon–carbon bond, CH_3–$SiCH_2M^+$.

Experimental

General remarks. All preparative manipulations were carried out under argon or dinitrogen. Proton and carbon NMR spectra were recorded with a JEOL Model GX-270 spectrometer. Elemental analysis was achieved by use of a Yanagimoto Model MT-3 CHN Coder.

Preparation of $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)Br$ (1)

A solution (ca. 2*N*) of Me_3SiCH_2MgCl (0.41 ml; 2 equiv.) in ethyl ether was added at −30 °C to a stirred methylene chloride (79 ml) solution of $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)Br_2$ (150 mg, 0.409 mmol), which had been prepared by a previously published procedure [6]. The mixture was then kept at 0 °C for 15 min with stirring. After disappearance of the starting dibromide complex had been confirmed by TLC, a saturated aqueous ammonium chloride solution (ca. 0.6 ml) was added at that temperature and then stirred vigorously for a few minutes. The organic layer was dried over anhydrous magnesium sulfate and was filtered through a Celite C-545 column under a nitrogen stream. The solid residue was washed three times with 5 ml of dry methylene chloride (each 5 ml). The filtrate and washings were combined, and were concentrated under vacuum. The residue was absorbed onto the least amount of Celite C-545, and placed on top of a silica gel/hexane column. In the initial stages of elution, hexane was used. The yellowish-orange band was eluted with a mixed solvent, hexane/ether (1/1 vol. ratio). Removal of solvents gave **1** as yellow crystals (121.5 mg; 79.5% yield). **1**; Mp. 56.5 °C (dec); Anal. Found: C, 38.48; H, 5.68. $C_{12}H_{21}BrRuSi$ calcd.: C, 38.50; H, 5.65%. The proton NMR spectral data are collected in Table 1. ^{13}C NMR (C_6D_6); −0.66 (t, Si–CH_2–Ru), 3.80 (q, CH_3–Si), 52.33 and 56.72 (t, allylic terminal carbons), 96.07 (d, allylic central carbon), 89.39 (d, cyclopentadienyl carbon).

Reaction of $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)Br$ (1) with silver fluoride in methanol

A methanol (4 ml) solution of **1** (20 mg, 0.0535 mmol), which had been purified by column chromatography (silica gel/hexane: ether 1 : 1) immediately before use, was cooled at −40 °C in a shaded flask. A 1.1 equiv. of a methanol solution of silver fluoride (ca. 0.1 *N*) was added with stirring, and the temperature of the mixture was raised to 0 °C during 20 min. After the mixture had been stirred for 80 min the solvent was removed in vacuo, and the residue was extracted with ether.

The ether extract was filtered through a short column packed with Celite 545. The ether layer was concentrated, and the residual oily mixture was absorbed onto the least amount of Celite 545, which was placed on the top of a silica gel column packed with hexane. Elution was begun with hexane and was continued with ether. From the first fraction, an extremely small quantity of the intermolecularly rearranged product, **4**, whose identification will be described in the following section, were obtained as ivory crystals in 1.2% yield (0.2 mg). Concentration of the second yellow band under vacuum gave $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_2F)(CH_3)$ (**2**; 11.7 mg; 70.1%) as a thermally sensitive yellow oil. The ^1H NMR data of **3** are listed in Table 1. The ^{13}C NMR spectrum of **3** in C_6D_6 showed the following signals; 2.97 and 3.10 (dq. *J*(FC) 17.6 Hz, CH_3–Si), −4.15 (dt, *J*(FC) 15.7 Hz, Si–CH_2–Ru), −2.36 (q, CH_3–Ru), 45.86 and 49.38 (t, allylic terminal carbons), 91.48 (d, allylic central carbon), and 89.28 (d, cyclopentadienyl carbon).

$Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)[CH_2SiMe_2(OMe)](CH_3)$ (**3**; 3.6 mg; 20.1%), a metastable, pale yellow oil, was isolated from the third pale yellow band, and its ^1H NMR data are listed in Table 1.

*Reaction of **1** with silver tetrafluoroborate*

To (4.5 ml) solution of **1** (21.0 mg, 0.056 mmol) in ethyl ether was added a 0.09 *N* solution of silver tetrafluoroborate (1.2 equiv., 0.75 ml) in a mixed solvent (ether/acetone 10/1 vol ratio) at room temperature. The reaction was instantaneous and gave a precipitate of silver bromide. After 10 min, the mixture was filtered through a short column of Celite 545 under a dinitrogen stream. The filtrate was concentrated in vacuo, and the residue was separated by column chromatography (silica gel and pentane). Evaporation of the first band gave $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)(CH_3)$ (**4**; 3.7 mg; 21.3%). **4**: Mp. 51°C. Found: C, 50.23; H, 7.90. $C_{13}H_{24}RuSi$ calcd.: C, 50.45; H, 7.2%. The proton NMR data of **4** are listed in Table 1. ^{13}C NMR (CD_2Cl_2); 3.35 (q, CH_3Si), −0.91 (t, $Si\text{–}CH_2\text{–}Ru$), −1.89 (q, CH_3Ru), 45.91 and 48.68 (t, allylic terminal carbons), 93.65 (d, allylic central carbon), and 89.45 (d, cyclopentadienyl carbon).

The second yellow band, yielded the (fluorosilylmethyl)methyl complex, **2**, as an unstable yellow oil in 38.6% yield (6.8 mg). All spectroscopic data and the R_f value on TLC (silica gel; Merck 5715) were identical with those of an authentic sample of **2**.

*Reaction of **1** with silver fluoride in dichloromethane*

A mixture of freshly purified **1** (29.9 mg, 0.0799 mmol), AgF (27 mg, 0.213 mmol), and dichloromethane (3 ml) was stirred at room temperature for 13 h. The complete disappearance of **1** was confirmed by TLC, and the color of the suspension had turned from yellow to brown.

The mixture was evaporated under vacuum, and the residue obtained was extracted with pentane and ether. The combined extracts were separated by column chromatography on silica gel with hexane as eluent. The first fraction yielded **4** as an ivory solid (0.7 mg, 2.8%). The second fraction gave colorless crystals of $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}CH_2SiMe_3)$ (**5**); Mp. 74.0–74.5°C; Anal., Found: C, 52.79; H, 6.40. $C_{14}H_{20}RuSi$ calcd.: C, 52.97; H, 6.35%. ^1H NMR (C_6D_6); δ 0.08 (s, 9H, CH_3Si), 1.65 (s, 2H, CH_2 of the η^5-trimethylsilylmethylcyclopentadienyl ligand), 4.53–4.92 (m, 4H, aromatic protons of the trimethylsilylmethylcyclopentadienyl ligand), 4.60 ppm (s, 5H, cyclopentadienyl). ^{13}C NMR (C_6D_6), −1.72 (q, CH_3Si), 20.01 (t, $Me_3Si\text{–}CH_2$), 69.50 and 71.20 (d, the C–H carbons of trimethylsilylmethylcyclopentadienyl ligand), 90.26 (s, the $Me_3SiCH_2\text{-}C$ of the trimethylsilylmethylcyclopentadienyl ligand), 70.94 ppm (d, cyclopentadienyl carbon).

The third yellow band yielded **2** as an unstable oil (5.8 mg, 23.2% yield). The NMR spectra of both **2** and **4** were identical with those of samples prepared independently according to the previous sections.

Acknowledgement

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References

1 B. Wozniak, J.D. Ruddick, and G. Wilkinson, J. Chem. Soc., A, (1971) 3116. A review on silyl- and silylmethyl-transition metal compounds is available; C.S. Cundy, B.M. Kingston, and M.F. Lappert, Advances in Organometallic Chemistry, vol. 11, Academic Press, N.Y., 1973, p. 253–330.

2 R.A. Anderson, R.A. Jones, and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1978) 446.

3 T.H. Tulip and D.L. Thorn, J. Am. Chem. Soc., 103 (1981) 2448.

4 J.W. Bruno, T.J. Marks, and V.W. Day, J. Am. Chem. Soc., 104 (1982) 7357; J.W. Bruno, T.J. Marks, and V.W. Day, J. Organomet. Chem., 250 (1983) 237; G.M. Smith, J.D. Carpenter, and T.J. Marks, J. Am. Chem. Soc., 108 (1986) 6805.

5 L. Andreucci, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasia, and M. Nardelli, J. Chem. Soc., Dalton Trans., (1986) 477.

6 H. Nagashima, K. Mukai, and K. Itoh, Organometallics, 3 (1984) 1314.

7 I. Fleming, in D. Barton and W.D. Ollias (Eds.), Comprehensive Organic Chemistry, vol. 3, Pergamon Press, Oxford, 1979, p. 541; E. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981; P.D. Magnus, T. Sarkar, and S. Djuric, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 7, Pergamon Press, Oxford, 1982, p. 515; W.P. Weber, Silicon Reagents for Organic Synthesis, Springer Verlag, Berlin, 1983.