Ruthenium-catalysed Disproportionation between Vinylsilanes and Mono-substituted Alkenes *via* Silyl Group Transfer

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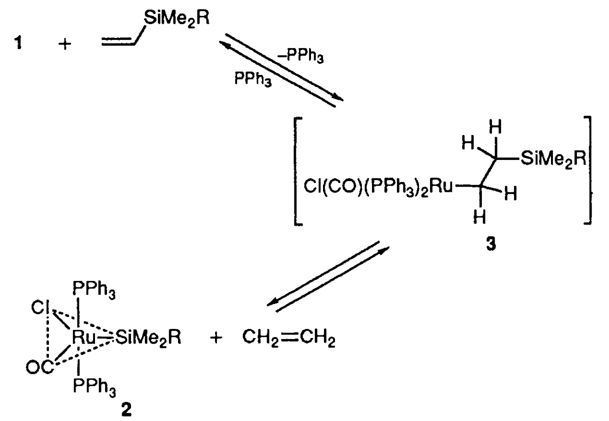
Selective cross-disproportion between vinylsilanes and various mono-substituted alkenes is catalysed by [RuCl(CO)H(PPh$_3$)$_3$] **1**; the mechanism of this reaction has been elucidated based on reactions of **1** with vinylsilanes as well as those of the resulting ruthenium–silyl complex with alkenes.

Alkenylsilanes have become increasingly important reagents in organic synthesis[1] but their transformation by alkene metathesis to more valuable forms has been found to be difficult. Typical alkene metathesis catalysts, MoO_3/Al_2O_3 and Re_2O_7/Al_2O_3, convert trimethyl(vinyl)silane to bis(trimethylsilyl)ethylene in only 10–15% yields.[2] Recent developments have involved the use of ruthenium and rhodium complexes. Marciniec and coworkers have shown that systems based on a combination of various ruthenium or rhodium complexes with a hydride donor and O_2 can catalyse self-metathesis of alkoxy(vinyl)silanes to ethylene and 1,2-bis(alkoxysilyl)ethylene in good yields.[3] A mechanism involving metal–carbene and metallacyclobutane intermediates has been proposed. Seki and coworkers have reported a similar disproportionation of trimethyl(vinyl)silane catalysed by $Ru_3(CO)_{12}$ and $HSiR_3$.[4] Cross-disproportionation with styrene has yielded (*E*)-PhCH=CHSiMe$_3$ together with an almost equal amount of the self-disproportionation product, Me$_3$SiCH=CHSiMe$_3$. Though no evidence was given, a mechanism whose key step is β-silyl elimination and successive



a; R = Me
b; R = OEt

Scheme 1

Table 1 Disproportionation of alkenes catalysed by **1**[a]

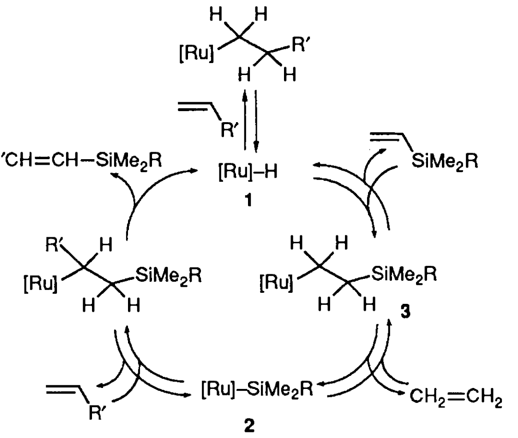
CH_2=$CHSiMe_2R$ R	CH_2=CHR′ R′	R′CH=$CHSiMe_2R$ Yield (%)[b]	R′CH=$CHSiMe_2R$ (*E*)/(*Z*)
Me	$SiMe_3$	38	44/56
Me	Me[c]	74	76/24
Me	Ph	66	99/1
Me	CO_2Me	59	93/7
Me	OBu^n	75	78/22
OEt	$SiMe_2OEt$	49	67/33
OEt	Ph	72	99/1
OEt	CO_2Me	70	83/17
OEt	OBu^n	84	84/16

[a] *Reaction conditions*: CH_2=$CHSiMe_2R$ (0.2 ml), CH_2=CHR′ (0.4 ml), **1** (20 mg), THF or toluene (2 ml), 140 °C, 14 h. [b] GC yields based on the vinylsilane. Each product from larger scale experiment was isolated by distillation and identified by elemental analyses and NMR spectra. [c] Carried out in a 50 ml autoclave, CH_2=CHMe (4.5 kg cm^{-2}) in toluene.

insertion of alkenes into the metal–Si bond has been discussed.[4] Insertion of alkenes into metal–Si bonds is also of recent interest in connection with the dehydrogenative silylation of alkenes, *i.e.* formation of alkenylsilanes under hydrosilation conditions.[5]

In this communication we report that a discrete ruthenium hydride complex, $[RuCl(CO)H(PPh_3)_3]$ **1**, cleanly undergoes insertion and β-Si elimination reactions with vinylsilanes and that it catalyses disproportionation of vinylsilanes without any additives. By use of this reaction system, the selective cross-disproportionation of vinylsilanes with mono-substituted alkenes has been realized for the first time.

The reaction of **1** with excess of CH_2=$CHSiMe_2R$ (R = Me or OEt) at 70 °C in tetrahydrofuran (THF) and subsequent work-up on column chromatography gave air-stable yellow crystals of $[RuCl(CO)(PPh_3)_2(SiMe_2R)]$ (**2a**; R = Me, **2b**; R = OEt) in 60–65% yields.† Evolution of ethylene was confirmed by conducting the reaction in C_6D_6 in a sealed NMR tube. ^{31}P NMR spectra indicate that the two phosphine ligands in **2a** and in **2b** are magnetically equivalent. That this reaction is reversible was demonstrated by the reaction of **2a** with ethylene (50 kg cm^{-2}) at 70 °C in the presence of an equimolar amount of triphenylphosphine: complex **1** was recovered in 61% yield while the yield of CH_2=$CHSiMe_3$ was determined by GLC to be 55%.



Scheme 2 [Ru] = $Cl(CO)(PPh_3)_2Ru$

These reactions are reasonably interpreted in terms of competitive β-H or β-Si elimination from the intermediate β-silylethylruthenium **3** (Scheme 1). Photo-induced β-Si and competitive β-H eliminations from $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2(CH_2CH_2SiMe_3)]$ have been documented by Randolph and Wrighton.[6] In reactions of propene with **2a** under conditions similar to those used for ethylene, complex **1** and $MeCH$=$CHSiMe_3$ [(*E*)/(*Z*) = 76/24] were obtained in almost quantitative yields.

The self-disproportionation of CH_2=$CHSiMe_2R$ and cross-disproportionation of CH_2=$CHSiMe_2R$ with CH_2=CHR′ were carried out in the presence of a catalytic amount of **1** at 120–140 °C (Table 1). In the latter reaction the self-disproportionation of vinylsilane can be suppressed completely by use of the vinylsilane and mono-substituted alkenes in a 1 : 2 ratio. Presumably, the presence of bulky triphenylphosphine ligands in intermediate **2** is responsible for the differentiation of incoming alkene bonds with bulky and less bulky substituents. Alkenes bearing electronically different kinds of substituents can successfully be employed as listed in Table 1, suggesting the synthetic versatility of the present system.

The reaction sequence in the catalytic cycle is illustrated in Scheme 2, evidence for which is provided by the stoichiometric reactions of the ruthenium complexes described above.

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† Complex **2a**: m.p. 159–161 °C (decomp.); IR (CH_2Cl_2) 1916 cm^{-1} (ν_{CO}); ^1H NMR (C_6D_6) δ 0.62 (s, 9H, $SiMe_3$); ^{31}P NMR ($CDCl_3$) δ 35.2 (s). Complex **2b**: m.p. 176–178 °C (decomp.); IR (CH_2Cl_2) 1922 cm^{-1} (ν_{CO}); ^1H NMR ($CDCl_3$) δ 3.27 (q, 2H, J_{HH} 7 Hz, OEt), 0.76 (t, 3H, OEt) and 0.25 (s, 6H, $SiMe_2$); ^{31}P NMR ($CDCl_3$) δ 36.1 (s). Satisfactory C and H analyses were obtained for **2a** and **2b**.

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