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Stereoselective synthesis of amides possessing a vinylsilicon functionality via a ruthenium catalyzed silylative coupling reaction

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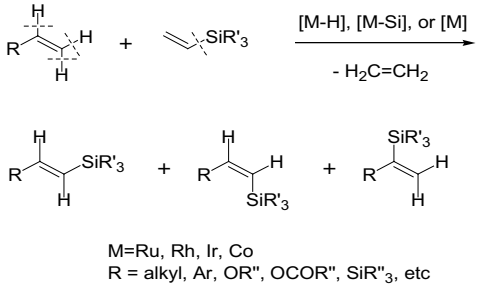
Abstract—An effective stereoselective synthesis of *E*-*N*-2-(silyl)vinylamides via silylative coupling of vinyl amides such as *N*-vinylpyrrolidinone, *N*-vinylphthalimide, and *N*-vinylformamide with vinyltrisubstituted silanes catalyzed by $[RuH(Cl)(CO)(PCy_3)_2]$ **I** is described.

Substituted vinylsilanes are widely used as synthetic reagents for the preparation of a variety of organic compounds.[1] However, only a few procedures for their stereoselective synthesis have been reported. During the last 15 years we have developed a new type of transition metal catalyzed reaction of vinyl substituted organosilicon monomers and polymers with a variety of olefins, known as the silylative coupling, *trans*-silylation or silyl group transfer, which has become a useful reaction for the functionalization of vinyl-silicon groups to give novel and well-known silicon-containing olefins (for a review see Ref. 2). The reaction occurs via cleavage of the =C–H bond of the olefin and the C–Si bond of the vinylsilane in contrast to cross-metathesis, which uses the same substrates and ends up with the same products through cleavage of the C=C bonds (Scheme 1).



Scheme 1.

The catalytic cycle of this new type of silyl olefin transfer involves a migratory insertion of the olefin into the M–H bond followed by β-H (and β-Si) transfer to the metal atom with elimination of the products. Recently, we have shown that $[RuH(Cl)(CO)(PPh_3)_3]$ **I** effectively catalyzes the *trans*-silylation of vinylsilanes with vinyl alkyl ethers to give β-alkoxy-substituted vinylsilanes, which are difficult to prepare via other TM-catalyzed reactions, for example, hydrosilylation.[3] The functionalization of vinyl-substituted cyclosiloxane and cyclosilazane[4] as well as the preparation of novel starburst compounds based on highly stereo- and regioselective reactions of tris(dimethylvinylsilyl)hexene with *p*-substituted styrenes[5] to give a new core for dendritic compounds are recent examples of this new synthetic route catalyzed by ruthenium complexes.

On the other hand, our recent study on the highly efficient cross-metathesis of vinyltrialkoxy- and vinyltrisiloxysilanes with various olefins, for example, styrene[6a,b] as well as allyl ethers[7a] and esters[7b] have opened a new opportunity for the use of olefin cross-metathesis in the synthesis of unsaturated organosilicon compounds (for a review see Refs. 2a, 8). However, alkyl substituted vinylsilanes appear to be quite inactive in the first generation Grubbs' complex-catalyzed cross-metathesis.[6] In this letter we report examples of very effective stereoselective silylative couplings of vinylmethyl-substituted silanes with vinyl-β-amides in the presence of

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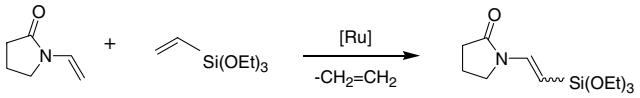
Table 1. Reaction of 1-vinylpyrrolidone-2-one with vinyltriethoxysilane catalyzed by Ru-complexes **I–IV**



Entry	Catalyst	Vinylsilane conversion	Yield (%)	E/Z (%)
1	$[RuH(Cl)(CO)(PPh_3)_3]$	28	25	3/1
2	$[RuH(Cl)(CO)(PPh_3)_3]$ (air)	36	32	4/1
3	$[RuH(Cl)(CO)(PCy_3)_2]$ (**I**)	97	97	>99/1
4	$[RuH(Cl)(CO)(PCy_3)_2]$ (**I**)[a]	90	68 (10)[d]	99/1
5	$[RuH(Cl)(CO)(PCy_3)_2]$ (**I**)[c]	92	90	98/2
6	$[Ru(SiMe_3)(Cl)(CO)(PPh_3)_3]$ (**II**)	65	64	8/1
7	$[RuH(OAc)(CO)(PPh_3)_3]$	32	30	10/1
8	$[RuCl_2(=CHPh)(PCy_3)_2]$ (**III**)[b]	Traces	Traces	—
9	$[(H_2IMes)RuCl_2(=CHPh)PCy_3]$ (**IV**)[b]	Traces	Traces	—

Reaction conditions: 110 °C, 24 h, argon (air), toluene.
Molar concentration ratios:
[a] $[Ru]/[CH_2{=}CHSi{\equiv}]/[CH_2{=}CHN{=}] = 10^{-2}/1/1$.
[b] $[Ru]/[CH_2{=}CHSi{\equiv}]/[CH_2{=}CHN{=}] = 10^{-2}/5/1$, 40 °C, CH_2Cl_2. $[Ru]/[CH_2{=}CHSi{\equiv}]/[CH_2{=}CHN{=}] = 10^{-2}/1/5$.
[c] 80 °C.
[d] Bis(silyl)ethene.

$[RuH(Cl)(CO)(PCy_3)_2]$ **I** as the catalyst, in comparison with the catalytic activity of Grubbs' catalysts $[RuCl_2(=CHPh)(PCy_3)_2]$ **III** and $[(H_2IMes)RuCl_2(=CHPh)PCy_3]$ **IV** in cross-metathesis reactions. β-Trimethylsilylethenyldiphenylamine is the only β-nitrogen-substituted vinylsilane, which has been reported but prepared via efficient silylation of *N*-phenyl-*N*-ethynylamine with $[(Me_3Si)_2CuCN]Li_2$.[9]

The reaction of vinyl-trisubstituted silanes with vinylamides proceeds in the presence of several ruthenium complexes initially containing Ru–H and/or Ru–Si bonds over a wide temperature range (120 °C). The catalytic data on the reaction of an exemplary amide, 1-vinyl-2-pyrrolidone with vinyltriethoxysilane catalyzed by these complexes as well as by first and second generation Grubbs' catalysts are presented in Table 1.

The reaction course was tested in an open system (under atmospheric pressure), so enabling the ethylene to be removed.

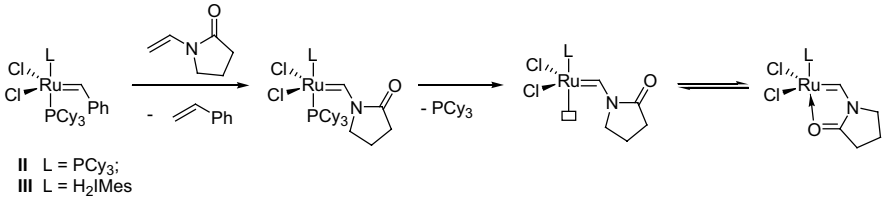
The inactivity of ruthenium carbenes has already been reported[10] in the ring-closing metathesis (RCM) of diethyl diallylmalonate and explained by intramolecular coordination of the carbonyl group blocking the coordination site of the Ru-complex according to Scheme 2.

In contrast to ruthenium-carbenes, ruthenium-hydride (or silyl) complexes catalyze the silylative coupling reaction and $[RuH(Cl)(CO)(PCy_3)_2]$ **I** appeared to be the most efficient, and above all, the most stereoselective catalysts for the *E*-products.

The equimolar reaction of vinylsilanes with vinyl-2-pyrrolidone yields 10% of the bis(silyl)ethene (Table 1). Since vinylamides are inactive in the silylative coupling, they can be used in excess to minimize the self-silylative coupling of vinylsilanes. A fivefold excess of vinyl pyrrolidone appears to be sufficient to suppress the formation of bis(silyl)ethene as a by-product to less than 1%.

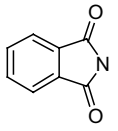
The above example of the stereoselective synthesis of an *E*-*N*-amido-silylethene shows that the limitations encountered using the cross-metathesis procedure can be overcome by employing complex **I**, which effectively catalyzes the silylative coupling of vinylamides with vinyltrisubstituted silanes (using a fivefold excess of the vinylamide), as shown in Table 2.

Most of the reactions proceed with high stereoselectivity with strong preference for the formation of the *E*-isomer (accompanied by traces, less than 1%, of the *Z*-isomer, which was detected by GC–MS analysis). Moreover, it was observed that extended heating of the reaction



Scheme 2.

Table 2. Silylative coupling of vinyltrisubstituted silanes with vinylamides catalyzed by **I**

CH_2=$CHSiR_3$	CH_2=CHX	Yield of silylative coupling (%)
SiR_3	X	(isolated)
$SiMe_3$		12 (81)[a]
$SiMe_2Ph$		93 (90)
$Si(OEt)_3$		97 (80)
$SiMe_2$		20 (88)[a]
$SiMe_2Ph$		91
$Si(OEt)_3$		89 (85)
$SiMe_3$		29
$SiMe_2Ph$		96
$Si(OEt)_3$		95

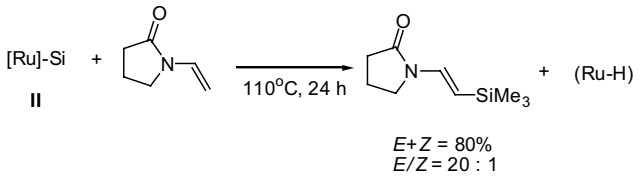
Reaction conditions: 110 °C, argon, toluene [**I**]/[CH_2=$CHSiR'_3$]/[CH_2=CHN=] = 10^{-2}/1/5.
[a] Reaction conditions: 60 °C, argon, toluene [**I**]/[CH_2=$CHSiR'_3$]/[CH_2=CHN=] = 10^{-2}/5/1.

mixture allowed exclusive isolation of the *E*-isomer due to $Z \rightarrow E$ isomerization of the product.

As can be seen from Table 2, the yields of the products obtained when using trimethylvinylsilane are much lower, which is a consequence of the fact that the reaction was conducted in a closed system because of the low boiling point of the silane (55 °C). As it is impossible to remove ethylene the reaction is slower than when it is run in an open system. Therefore, the synthesis of products in the presence of trimethylvinylsilane was conducted under specific conditions, that is, an excess of vinylsilane was employed to give the main product *E*-*N*-amido-vinylsilane accompanied by products of self-coupling of the vinylsilane.

The catalytic results provide a basis for a synthesis of silyl derivatives of vinylamides. Selected synthetic procedures are described in Ref. 11.

To shed light on the mechanism of the process, the reactions of equimolar amounts of the Ru–Si complex **II** with the vinylamide were carried out yielding 1-silyl-2-*N*-amido-ethene (Scheme 3).

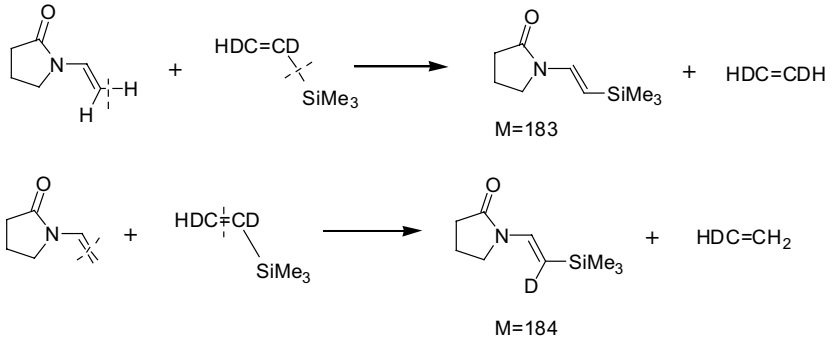


Scheme 3.

As in the previously reported reaction with styrene[12] and with vinyl *n*-propyl ether,[3] ^{1}H NMR examination did not confirm formation of a complex containing the Ru–H bond even in the presence of an excess of vinylamide. This is presumably due to the high activity of the Ru–H complex with vinylamides and vinylsilanes. The above experiment provides convincing evidence for the migratory insertion of the vinylamide into the Ru–Si bond, the step responsible for the silylative coupling reaction.

As in previous studies, the experiment with deuterium-labeled vinylsilane was performed to distinguish the two possible mechanisms.[3,12] The reaction of HDC=CDSiMe$_3$ with *N*-vinylpyrrolidone catalyzed by **I** was studied by GC–MS. If the reaction proceeded according to the non-metallacarbene silylative coupling mechanism the product formed in the first stage of the reaction would contain no deuterium atom. However, if the reaction occurred according to the metallacarbene mechanism, the cross-metathesis process would take place leading to exclusive formation of the d_1-product (Scheme 4).

GC–MS analysis of the reaction mixture after 10% reaction showed exclusive formation of the d_0-product [$m/z = 183$ (M^+)]. This fact strongly confirms the non-metallacarbene mechanism of the process. In conclusion, the efficient and highly stereoselective silylative coupling of vinylamides with vinylsilanes in the presence of small amounts of **I** offers an attractive route to the synthesis of amides possessing a vinylsilicon functionality, compounds which are important intermediates in organic synthesis. Well-defined ruthenium complexes **III/IV** appear to be completely inactive in this process. Labeling experiments using HDC=CDSiMe$_3$ confirm the mechanism of silylative coupling.



Scheme 4.

Acknowledgements

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11. Representative procedure for the silylative coupling reactions. All reactions were carried out under argon. All solvents and chemicals were dried and distilled under argon prior to use. An oven-dried 20 mL flask equipped with a magnetic stirrer bar and a condenser connected with a bubbler was charged with toluene (0.5 mL), vinyldimethylphenylsilane, or vinyltriethoxysilane (6.82 mmol), vinyl amide (34.13 mmol), and [RuH(Cl)-(CO)(PCy_3)$_2$] (0.068 mmol). The reaction mixture was stirred and heated at 110 °C for 24 h. No standard was added. The product was isolated by distilling all the volatiles under vacuum and the residue was chromatographed on a silica gel column (deactivated with triethylamine) using hexane/ethyl acetate (50/1). The crude product was distilled under vacuum.

In the case of the vinyltrimethylsilyl derivative of the product vinyltrimethylsilane (34.13 mmol), vinylamide (6.82 mmol), and [RuH(Cl)(CO)(PCy_3)$_2$] (0.068 mmol) were stirred and heated under gentle reflux (about 55 °C) for 24 h.

(*E*)-*N*-((2-Trimethylsilyl)vinyl)pyrrolidinone. Collected fraction: 95–98 °C/1 mmHg. ^{1}H NMR (300 MHz, C_6D_6) δ ppm 0.14 (9H, s), 1.17 (2H, m, $J_{H-H} = 7.9$), 1.96 (2H, t, $J_{H-H} = 7.9$), 2.78 (2H, t, $J_{H-H} = 7.4$), 4.56 (1H, d, $J_{H-H} = 17.3$), 7.51 (1H, d, $J_{H-H} = 17.3$); ^{13}C NMR (75 MHz, C_6D_6) δ ppm 0.36, 17.37, 31.49, 104.24, 134.99, 171.95; ^{29}Si NMR (60 MHz, C_6D_6) δ ppm −6.13; EIMS [*m*/*z* (rel int)] 183 (M, 5), 168 (100), 142 (62), 112 (5), 100 (7), 83 (5), 75 (12); HRMS M (obsd) 183.10792, M (calcd) 183.10794. Anal. Elem. (obsd) C, 58.61; H, 9.46; (calcd) C, 58.96; H, 9.35.

(*E*)-*N*-((2-Dimethylphenylsilyl)vinyl)pyrrolidinone. Collected fraction: 155–160 °C/1 mmHg. ^{1}H NMR (300 MHz, C_6D_6) δ ppm 0.36 (6H, s, $J_{H-H} = 7.9$), 1.14 (2H, m), 1.95 (2H, t, $J_{H-H} = 7.4$), 2.73 (2H, t), 4.65 (1H, d, $J_{H-H} = 17.3$), 7.21–7.29, 7.54–7.59 (5H, m), 7.59 (1H, d, $J_{H-H} = 17.3$); ^{13}C NMR (75 MHz, C_6D_6) δ ppm −2.09, 17.07, 31.24, 43.97, 102.35, 129.32, 134.13, 136.02, 139.37, 172.15; ^{29}Si NMR (60 MHz, C_6D_6) δ ppm 10.14; EIMS [*m*/*z* (rel int)] 245 (M, 8), 244 (6), 230 (100), 212 (11), 204 (24), 186 (8), 168 (38), 154 (8), 152 (8), 145 (6), 142 (10), 135 (5), 121 (8), 105 (5); HRMS M (obsd) 245.12377, M (calcd) 245.12360. Anal. Elem. (obsd) C, 67.86; H, 7.43; (calcd) C, 68.52; H, 7.80.

(*E*)-*N*-((2-Triethoxysilyl)vinyl)pyrrolidinone. Collected fraction: 151–157 °C/1 mmHg. ^{1}H NMR (300 MHz, C_6D_6) δ ppm 1.06 (2H, m), 1.22 (9H, t, $J_{H-H} = 6.9$), 1.86 (2H, t, $J_{H-H} = 7.7$), 3.70 (6H, t, $J_{H-H} = 6.9$), 4.43 (1H, d, $J_{H-H} = 17.3$), 7.93 (1H, d, $J_{H-H} = 17.03$); ^{13}C NMR (75 MHz, C_6D_6) δ ppm 18.55, 31.09, 43.75, 104.24, 58.71, 94.57, 139.04, 172.36; ^{29}Si NMR (60 MHz, C_6D_6) δ ppm −54.23; EIMS [*m*/*z* (rel int)] 273 (M, 8), 229 (100), 200 (32), 185 (12), 172 (22); HRMS M (obsd) 273.13768, M (calcd) 273.13965 Anal. Elem. (obsd) C, 52.41; H, 8.62; (calcd) C, 52.72; H, 8.48.

(*E*)-*N*-((2-Triethoxysilyl)vinyl)phthalimide. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (9H, t, $J_{H-H} = 6.8$), 3.90 (6H, q, $J_{H-H} = 6.9$), 6.84 (2H, q, $J_{H-H} = 7.53$), 6.92 (1H, d, $J_{H-H} = 17.6$), 7.32 (2H, q, $J_{H-H} = 7.52$), 7.64 (1H, d, $J_{H-H} = 17.6$); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 18.52, 58.84, 106.26, 123.38, 131.83, 133.00, 133.98, 166.22; ^{29}Si NMR (60 MHz, $CDCl_3$) δ ppm −56.476; EIMS [*m*/*z* (rel int)] 335 (M, 36), 291 (100), 264 (13), 263 (15), 249 (7), 248 (8), 234 (11); HRMS M (obsd) 335.11868, M (calcd) 335.11890. Anal. Elem. (obsd) C, 57.01; H, 6.10; (calcd) C, 57.29; H, 6.31.

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