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Rhenium-mediated dehydrogenative silylation and highly regioselective hydrosilylation of nitrile substituted olefins

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ABSTRACT

The rhenium (I) complex [Re(CH₃CN)₃Br₂(NO)] catalyzes the homogeneous hydrosilylation of a variety of substituted acrylonitriles, which were converted into the corresponding silyl-substituted alkanes with high regioselectivity of up to 94%. The products were analyzed by ¹H NMR and GC–MS. A rhenium specific mechanism is proposed for the hydrosilylation of olefins.

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1. Introduction

Hydrosilylation of carbon–carbon double bonds catalyzed by transition metals is of great importance in the production of silicon derived compounds and in the potential use of the transformation in organic synthesis [1]. A variety of methods can be applied to initiate this transformation in an atom-efficient way. Catalysts for the 1,2-addition of hydrosilanes to alkenes are mainly based on late transition metals including those with platinum, rhodium or ruthenium centers [2]. In comparison, middle transition metals such as rhenium are scarcely involved in such reactions simply due to their high tendency to obey the 18-electron rule. The metal ligand bonds are often too strong and not labilized for the initiation of metal-centered reactivity. Such drawbacks have to be overcome by proper tuning of the ancillary using for instance the cislabilization effect of π donor ligands (i.e. Br) or the trans influence effect of strong σ donors (i.e. NO) [2d].

Acrylonitrile is widely used in the production of acrylic and methacrylic fibers, resins and rubbers, and as a chemical intermediate [3]. Although there is an abundance of catalysts which are effective in promoting the addition of the Si–H bond across alkenes and alkynes, relatively few show significant activity in the hydrosilylation of acrylonitrile [3]. Agents such as amines, Raney nickel, amides and phosphines, normally result in β -addition of the silyl

moiety to the double bond of acrylonitrile [4]. The reaction between acrylonitrile and silane with prevailing formation of the α isomer was detected to occur with only a few catalysts, like peroxide compounds and platinum-based catalysts [5].

During our explorations on the feasibility of low-valent rhenium catalysts [6], we found that the nitrosyl rhenium complex $[Re(CH_3CN)_3Br_2(NO)]$ exhibited high catalytic activity and regioselectivity in the hydrosilylation of substituted alkenes. We present here the $[Re(CH_3CN)_3Br_2(NO)]$ catalyzed hydrosilylation of substituted olefins and acrylonitrile to give predominantly the α -addition product with a regioselectivity of up to 94% with a relatively low catalyst loading (1.5 mol %) at 115 °C in CH₃CN. As mentioned before, nitrile substituted olefins, in particular, are difficult substrates for hydrosilylations, because of a poisoning or partial poisoning of the catalysts by strong binding of the nitrile group to the metal center. However, in the $[Re(CH_3CN)_3Br_2(NO)]$ complex at least one nitrile ligand seemed to be labile, because it can easily be replaced by THF [6b]. This labile site is prone for acting as a catalytic site.

2. Results and discussion

2.1. Dehydrogenative silylation of substituted styrenes catalyzed by rhenium (I) complexes

We first examined the reactions of 4-methylstyrene with dimethylphenylsilane in the presence of various rhenium (I)





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complexes and solvents at 110–115 °C, which are summarized in Table 1. The progress of each reaction according to Table 1 was monitored by ¹H NMR, and the identity of the hydrosilylation product was assured by ¹H NMR spectroscopy.

Appropriate solvents were expected to have high boiling points and low polarity. Toluene turned out to be the solvent of choice, and it dissolves the rhenium catalyst $[Re(CH_3CN)_3Br_2(NO)]$ reasonably well at 110–115 °C. In toluene, $[Re(CH_3CN)_3Br_2(NO)]$ provided the best activity after 2 h with a conversion of 100% and a TOF value of 16.7 h⁻¹ (entry 1). The reaction took mainly the course of dehydrogenative silylation [7] and hydrosilylation (85/ 15). The reaction can also be carried out in polar solvents, but with loss in yield. In CH₂Cl₂, CH₃CN, THF and CHCl₃ yields of 66%, 59%, 45% and 50% were obtained (entries 2–5). Bromobenzene and DMSO gave the lowest yields in comparison with the other solvents (entries 6 and 7).

Screening the type of rhenium catalyst, $[Re(CH_3CN)_3Br_2(NO)]$ (entry 1) showed the best activity from the selection of the rhenium complexes given in Table 1. Various phosphine substituted complexes were tested for catalytic hydrosilylation. In the case of the rhenium complex $[Re(PTA)_2Br_2(NO)(CH_3CN)]$ (PTA = 1,3,5-triaza-7phospha-adamantane) containing two phosphine ligands, the reaction in toluene gave a yield of 47%, while in CH₃CN and dioxane very low yields were obtained after 24 h with TOF values of 0.7, 0.07 and 0.13 h⁻¹ (entries 8, 9 and 11). No conversion was observed when bromobenzene was used as a solvent (entry 10). $[Re(PTA)_3Br_2(NO)]$ gave only 6% yield of the desired product after 24 h (entry 12). The protonated species $[Re(PTAH)_2Br_2(NO)(CH_3CN)][Br]_2$, $[Re(PTAH)(PTA)Br_2(NO)-(CH_3CN)][Br]$, did not show any catalytic activity even after 24 h (entries 13–16).

Catalysts were generally employed at the 3 mol % level relative to the substrate. Lower catalyst loading could be used, but required longer. In the case of the rhenium complexes containing phosphine ligands such as PTA, PCy₃ and P^{*i*}Pr₃, even with much higher loadings (8–10 mol %), no obvious improvement of the yield was observed.

The scope of the dehydrogenative silvlation of substituted styrenes including both electron-rich and electron-deficient groups with dimethylphenylsilane was then investigated at 110-115 °C in toluene using [Re(CH₃CN)₃Br₂(NO)] (3 mol %) as a catalyst (Table 2). All the reactions were complete in 2–6 h with conversion of almost 100%, and no catalyst precipitation was observed and the color of the reaction solution color turned a little darker after reaction. For the substituted styrenes bearing electron-withdrawing groups, such as fluoro- and chloro-substitution, the dehydrogenative silvlation completed with conversion around 99% in 2–6 h and the relatively higher yields of 86%, 86% and 88% (entries 2, 6 and 7). A reaction time of 2 h was required for 4-methylstyrene, 3-methylstyrene and styrene to obtain yields of 85%, 82% and 83%, respectively (entry 4, 5 and 1). 3-Methoxystyrene gave the dehydrogenative silvlation products with relatively low yield of 78% in 2 h (entries 3). Among all the reactions, the ratios of the yields between dehydrogenative silylation and hydrosilylation stayed approximately constant at 85:15. The dehydrogenative silvlation of various substituted styrenes catalyzed by [Re(CH₃CN)₃Br₂(NO)] proceeded following the similar mechanism we reported before [7a].

Rhenium-mediated hydrosilylations of acrylonitrile and its derivatives with alkyl and aryl silanes in a 1:1 ratio.

As mentioned in the introductory part hydrosilylations of acrylonitrile and its derivatives often suffer from coordination of the acrylonitrile to the catalytic center. Perhaps it can even bind in an η^4 -fashion and thus attain affinity to the rhenium center higher than two separate acetonitrile ligands. We anticipated that for the [Re(CH₃CN)₃Br₂(NO)] molecule as a catalyst this blockage problem would be less significant owing to the fact that we deal with a labile nitrile substituted species.

We tested the hydrosilylation of acrylonitrile and its derivatives using this rhenium (I) catalyst in a sealed Young NMR

Table 1

Various rhenium complex-catalyzed dehydrogenative silylation of 4-methylstyrene with HSiMe₂Ph.^a

	(Cat.[Re] 3 mol %	SiMe ₂ l	Ph	SiMe ₂ Ph	<u>,</u>
4-MePh >> + H	1-SIMe ₂ Ph	solvent 110-115 °C	4-MePh	+ 4-MePh	+	4-MePh

Entry	Catalyst	Solvent	<i>t</i> (h)	Conversion (%) ^b	${{TOF}\atop{(h^{-1})^c}}$
1	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	Toluene	2	100	16.7
2	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	CH ₂ Cl ₂	12	66	1.8
3	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	CH ₃ CN	12	59	1.6
4	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	THF	12	45	1.2
5	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	CHCl ₃	12	50	1.3
6	$[Re(CH_3CN)_3Br_2(NO)]$	Bromobenzene	12	15	0.4
7	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	DMSO	12	<10	0.28
8	$[Re(PTA)_2Br_2(NO)]$	Toluene	24	47	0.7
	(CH ₃ CN)]				
9	$[Re(PTA)_2Br_2(NO)]$	CH ₃ CN	24	5	0.0
	(CH ₃ CN)]				
10	$[Re(PTA)_2Br_2(NO)]$	Bromobenzene	24	0	_
	(CH ₃ CN)]				
11	[Re(PTA) ₂ Br ₂ (NO)-	Dioxane	24	10	0.13
	(CH ₃ CN)]				
12	$[Re(PTA)_3Br_2(NO)]$	Toluene	24	6	0.08
13	[Re(PTAH) ₂ Br ₂ (NO)-	Toluene	24	0	-
	(CH_3CN) [Br] ₂				
14	[Re(PTAH)(PTA)Br ₂	Toluene	24	0	_
	(NO)(CH ₃ CN)][Br]				

^a All reactions were carried out with 4-methylstyrene (0.5 mmol), HSiMe₂Ph (0.25 mmol), and the rhenium catalyst (0.0075 mmol, 3 mol %) in the appropriate solvent (0.8 ml) at 110–115 °C for given time under a nitrogen atmosphere. Progress of the reactions was monitored by ¹H NMR spectroscopy.

^b Conversion of silane based on the integration of the ¹H NMR spectrum.

^c Defined as mol product per mol of catalyst per hour.

 Table 2

 Rhenium-mediated dehydro/hydro-silvlation of substituted olefins with HSiMe₂Ph.⁴

Entry	Substrate	<i>t</i> (h)	Conversion (%) ^b	Dehydro/hydro
1		2	100	83/17
2	F	2	100	86/14
3	MeO	2	100	78/22
4		2	100	85/15
5		2	100	82/18
6		4	99	86/14
7	CI	6	99	88/12

^a All reactions were carried out with the alkene (0.5 mmol), HSiMe₂Ph (0.25 mmol), and the rhenium catalyst [Re(CH₃CN)₃Br₂(NO)] (0.0075 mmol, 3 mol %) in toluene (0.8 ml) at 110–115 °C for given time under a nitrogen atmosphere. Progress of the reactions was monitored by ¹H NMR spectroscopy.

^b Conversion of silane based on the integration in ¹H NMR spectrum.

^c Ratio determined by the integration in ¹H NMR spectrum.

tube (Table 3). Various temperatures (60–115 °C) were applied and acetonitrile was regarded as the prime choice of solvent due to the high solubility of the rhenium catalyst. An alkyl silane (Et₃SiH) and aryl silanes (PhMe₂SiH, Ph₂MeSiH) were chosen as silyl reagents to examine the activity of the rhenium catalyst. The reaction times were dramatically prolonged with a decrease of

Table 4

Rhenium	mediated	hvdrosilvlati	on of acrvlo	onitrile in	various	solvents. ^a

Entry	Solvent	Silane	<i>t</i> (h)	Yield (%) ^b	TOF $(h^{-1})^{c}$
1	Isopropenylnitrile	PhMe ₂ SiH	36	90	1.7
2	Isopropenylnitrile	Et₃SiH	36	84	1.5
3	Isopropenylnitrile	ClMe ₂ SiH	36	78	1.4
4	2,4,5-Trimethylbenzonitrile	PhMe ₂ SiH	48	32	0.44
5	2,4,5-Trimethylbenzonitrile	Et₃SiH	48	20	0.28
6	2,4,5-Trimethylbenzonitrile	ClMe ₂ SiH	48	0	-
7	Benzonitrile	PhMe ₂ SiH	48	49	0.68
8	Benzonitrile	Et₃SiH	48	38	0.53
9	Benzonitrile	ClMe ₂ SiH	48	9	0.13

^a All reactions were performed with acrylonitrile (0.5 mmol), chlorosilane (0.6 mmol), and the rhenium complex [Re(CH₃CN)₃Br₂(NO)] (0.0075 mmol, 1.5 mol %) in the proper solvent (0.8 ml) at 115–120 °C for given time under a nitrogen atmosphere. Progress of the reaction was monitored by ¹H NMR spectroscopy. ^b Yield on the basis of GC–MS

^c Defined as mol product per mol of catalyst per hour.

the reaction temperatures from 115 °C to 60 °C when Et₃SiH was applied as a silane source (entries 1–3). Similar results were obtained for the cases of PhMe₂SiH (entries 4–6). The hydrosilylation of acrylonitrile required 48 h to achieve appropriate yields at 115 °C and when Ph₂MeSiH was used (entry 7). The hydrosilylation of 2-chloroacrylonitrile proceeded slowly and gave low yields even at 110 °C after 24 h and also in the case of Ph₂MeSiH (22%) after 24 h (entries 8–10). 2-Methylacrylonitrile provided a little better yields compared to 2-chloroacrylonitrile within 12 h of reaction time (entries 11–13). The highest TOF value (8.3) was obtained in the reaction between acrylonitrile and triethylsilane at 115 °C (entry 1).

Considering the results of Table 3, we concluded that the activity of the substrates is in the order of acrylonitrile > 2methylacrylonitrile > 2-chloroacrylonitrile, while the order for the silane activities is triethylsilane > dimethylphenylsilane > diphenylmethylsilane. The regioselectivity ratios of all the reactions were found to be α : $\beta \approx 3:1$ almost identical irrespective of the substrates, reaction temperature and reaction time. Also, various basic additives (TMEDA, KO^tBu, CF₃CO₃H, K₂CO₃, HCOONa and

0.6

4.5

4.0

2.0

75:25

73:27

73:27

73.27

Table 3

9

10

11

12

13

Rhenium-mediated hydrosilylation of acrylonitrile and its derivatives with alkyl and aryl silanes.^a

Ph₂MeSiH

PhMe₂SiH

Ph2MeSiH

Et₃SiH



Substrate	Silane	<i>T</i> (°C)	<i>t</i> (h)	Conversion (%) ^b	TOF $(h^{-1})^{c}$	Selectivity (α:β) ^d
Acrylonitrile	Et ₃ SiH	115	8	100	8.3	73:27
Acrylonitrile	Et ₃ SiH	90	9	95	7.0	73:27
Acrylonitrile	Et ₃ SiH	60	48	92	1.3	73:27
Acrylonitrile	PhMe ₂ SiH	115	10	100	6.7	73:27
Acrylonitrile	PhMe ₂ SiH	90	12	93	5.2	73:27
Acrylonitrile	PhMe ₂ SiH	60	48	80	1.1	73:27
Acrylonitrile	Ph ₂ MeSiH	115	48	95	1.3	73:27
2-Chloroacrylonitrile	Et ₃ SiH	110	24	66	1.8	75:25
2-Chloroacrylonitrile	PhMe ₂ SiH	110	24	53	1.5	75:25

24

12

12

12

22

80

72

36

^a All reactions were carried out with the substrate (0.5 mmol), HSiMe₂Ph (0.6 mmol), and the rhenium complex [Re(CH₃CN)₃Br₂(NO)] (0.0075 mmol, 1.5 mol %) in acetonitrile (0.8 ml) at proper temperature for given time under a nitrogen atmosphere. Progress of the reaction was monitored by ¹H NMR spectroscopy.

110

110

110

110

^b Yield on the basis of GC–MS.

^c Defined as mol product per mol of catalyst per hour.

2-Chloroacrylonitrile

2-Methylacrylonitrile

2-Methylacrylonitrile

2-Methylacrylonitrile

^d Selectivity was measured by GC-MS

pyridine) were introduced into the reactions. However, no obvious influence on the hydrosilylation was observed.

2.2. Solvent effects in the rhenium-mediated hydrosilylation of acrylonitrile

A variety of solvents, from polar to nonpolar, from aliphatic to aryl substituted ones were also examined in the hydrosilylation of acrylonitrile. However, it was found that only nitrile solvents worked in the hydrosilylation reactions to an acceptable extent.

We then tested various types of nitrile solvents to trace any refined influence on the hydrosilylation with a rhenium catalyst loading of 1.5 mol % (Table 4). Hydrosilylation of acrylonitrile was first attempted in isopropenylnitrile with various silanes. Relatively high yields were achieved after 36 h at 115 °C ranging from 78% to 90% (entries 1–3). 2,4,5-Trimethylbenzonitrile which possesses enhanced steric hindrance was then introduced into the reactions. Unfortunately, the hydrosilylation proceeded sluggishly to give yields lower than 32% after 48 h at 120 °C (entries 4-6). Benzonitrile provided relatively better yields compared to those in 2,4,5-trimethylbenzonitrile with yields between 49% and 9% at 120 °C after 48 h (entries 7–9). For the same solvent, PhMe₂SiH with medium hydridic and steric congestion gave the best conversion among all the three silane candidates (PhMe₂SiH, Et₃SiH and ClMe₂SiH). In contrast to the results of Table 1, acetonitrile revealed to be the best performing solvent for hydrosilylations.

2.3. Rhenium-catalyzed hydrosilylation of acrylonitrile with various silane ratios

Hydrosilylation of acrylonitrile in a cetonitrile in a ratio of 1:1 gave α and β silyl substituted products with a relatively constant

regioselectivity ratio of around 73:27, which was found to be independent of temperature (Table 3). To accomplish a better regioselectivity, we thought to test hydrosilylations also in 1:2 and 2:1 ratios with a rhenium catalyst loading of 1.5 mol % in acetonitrile at 60–115 °C for the given times (Table 5).

The ratios between acrylonitrile and PhMe₂SiH were varied from 4:1 to 1:4. When the ratio between substrate and PhMe₂SiH was 1:1. the regioselectivity of the reaction indeed remained practically constant independent of temperature and the silane source (entries 1–7). Higher regioselectivity (86:14) in favor of the silvl substitution and relatively high TOF values (14.5 and 11) were obtained when the hydrosilylation reactions were carried out with 1:2 or 2:1 ratios (entries 8 and 9). The reaction times were greatly reduced to 4.5 and 6 h. The regioselectivity of the hydrosilylation reaction changed also with unequal ratios of the substrates and could reach 92:8 and 94:6 when the reactants were loaded in a ratio of 1:4 and 4:1, respectively. In these cases the reaction times still decreased to 1.3 and 1.0 h (entries 10–14). These observations of accelerated catalyzes are however difficult to interpret, in particular with respect to the fact that the increase of the concentrations of both the unsaturated compound and the silane did not effect much better catalytic performance. This almost excludes the possibility of an influence of second order terms in the rate determining step or steps.

2.4. Investigation of the mechanism of the rhenium based hydrosilylation

A generalized catalytic cycle for the hydrosilylation with the rhenium complex [$Re(CH_3CN)_3Br_2(NO)$] is proposed in Scheme 1. [$Re(CH_3CN)_3Br_2(NO)$] takes the role of a pre-catalyst via primary dissociation of one of the CH₃CN ligands. In the ¹H NMR spectrum (CD₃CN) this dissociation became evident by a singlet at 1.98 ppm

Table 5

Rhenium mediated hydrosilylation of acrylonitrile in acetonitrile with various ratios.^a

$$\begin{array}{c|c} & & & \\ \hline \blacksquare N & + & R_3 SiH & \\ \hline \hline CH_3 CN & \\ \hline Ctat=[ReBr_2(NO)(CH_3 CN)_3] & (\alpha) & (\beta) \end{array}$$

Entry	Substrate: Silane (mmol)	Ratio	Silane	<i>T</i> (°C)	<i>t</i> (h)	Conversion (%) ^b	TOF $(h^{-1})^{c}$	Selectivity $(\alpha:\beta)^d$
1	0.5:0.5	1:1	Et₃SiH	115	8	100	8.3	73:27
2	0.5:0.5	1:1	Et₃SiH	90	9	95	7.0	73:27
3	0.5:0.5	1:1	Et₃SiH	60	48	92	1.3	73:27
4	0.5:0.5	1:1	PhMe ₂ SiH	115	10	100	6.7	72:28
5	0.5:0.5	1:1	PhMe ₂ SiH	90	12	100	5.6	72:28
6	0.5:0.5	1:1	PhMe ₂ SiH	60	48	90	1.3	72:28
7	0.5:0.5	1:1	Ph ₂ MeSiH	115	20	95	3.2	73:27
8	1:1	1:1	PhMe ₂ SiH	115	9.5	96	6.7	72:28
9	2:2	1:1	PhMe ₂ SiH	115	9	98	7.3	73:27
10	0.5:1.0	1:2	PhMe ₂ SiH	115	4.5	98	14.5	88:12
11	1.0:0.5	2:1	PhMe ₂ SiH	115	6.0	99	11	86:14
12	1.0:0.25	4:1	Ph ₂ MeSiH	115	2.0	99	33	88:12
13	1.0:0.25	4:1	Et₃SiH	115	0.9	99	73	90:10
14	1.0:0.25	4:1	Et₃SiH	115	1.2	99	55	89:11
15	0.25:1.0	1:4	PhMe ₂ SiH	115	1.1	100	51.3	92:8
16	1.0:0.25	4:1	PhMe ₂ SiH	115	1.0	99	66	94:6
17	1.5:0.25	6:1	PhMe ₂ SiH	115	1.2	99	55	90:10
18	0.25:1.5	1:6	PhMe ₂ SiH	115	1.5	99	44	88:12

^a All reactions were carried out with the substrate (0.5–1.0 mmol), silane (0.5–1.0 mmol), and the rhenium complex [Re(CH₃CN)₃Br₂(NO)] (0.0075 mmol, 1.5 mol %) in acetonitrile (0.8 ml) at proper temperature for given time under a nitrogen atmosphere. Progress of the reactions was monitored by ¹H NMR spectroscopy.

^b Conversion on the basis of integration of the ¹H NMR spectrum.
 ^c Defined as mol product per mol of catalyst per hour.

Decide as fill product per fill of catalyst

^d Based on GC-MS measurement.



Scheme 1. Proposed pathway for the hydrosilylation of an olefin, catalyzed by the $[Re(CH_3CN)_3Br_2(NO)]$ complex. R = Et, PhMe₂, Ph₂Me; R' = nitrile and nitrile containing groups.

assigned to the CH₃ group of free CH₃CN. Then an olefin molecule coordinates to the rhenium center of **2**, forming the olefin adduct **3**. The silanes are presumably then coordinated to the rhenium center with loss of another acetonitrile ligand giving species 4, which reacts subsequently with H transfer to the olefin ligand leading to the formation of complex 5. A ¹H-NOE experiment provided some evidence for the presence of a side-on rhenium bonded Si-H unit, since saturation of the dissociated acetonitrile methyl group at around 2 ppm gives rise to a very broad (>100 Hz) NOE signal, which was assigned to a Re attached Si-H group. α -Regioselectivity was preferred for R' = CN. We assume that the silane oxidatively adds to the rhenium center and a hydride is transferred to the incipient carbocationic end of the olefin [8]. Alternatively, we had to assume that the silane in **4** appears acidified by coordination initiating a proton transfer to the olefin. The α -regioselectivity would however not cope with the proton transfer step due to the expected opposite polarization of the olefin based on the stability of the intermediate incipient carbocation. The catalytic cycle "closes" with reductive elimination of the product 6 and re-formation of complex **2**. Attempts to isolate the η^2 -R₃SiH complex **4** were not successful presumably due to its instability. Further detailed studies are currently underway to achieve full understanding of the reaction mechanism.

A stoichiometric reaction between [Re(CH₃CN)₃Br₂(NO)] and 4methylstyrene (6 equiv.) was carried out in toluene- d_8 which afforded at 105 °C a yellow solution within 20 h ¹H NMR spectroscopy indicated the formation of a new species assigned to the 4methylstyrene coordinated Re(I) complex [Re(Br)₂(CH₃CN)₂(η^2 -CH₂ = CH(4-tolyl))(NO)]. The resonances of the alkene protons were observed as a doublet of doublet and a multiplet in the range of 4.99–5.10 and 3.92–4.01 ppm. The signals of the two acetonitrile ligands were observed as two singlets at 1.13 and 1.08 ppm due to different chemical environment caused by the coordinated 4methylstyrene suggesting a structure as shown in the catalytic cycle. The resonance of freed CH₃CN ligand was observed as a singlet at 0.73 ppm. One of the acetonitrile ligands of [Re(CH₃CN)₃Br₂(NO)] is apparently labilized and can be substituted by alkene. The stoichiometric reaction between [Re(CH₃CN)₃Br₂(NO)] and Et₃SiH (6 equiv.) was also examined. However, the reaction in toluene- d_8 afforded a dark brown solution and a dark precipitate within 1 h at 105 °C. ¹H NMR spectroscopy indicated the formation of several silane species in solution including a major one which most likely bears a Et₂HSi-unit. The Si-H signal is high-field shifted from 3.78 ppm (heptet) to 2.60 ppm (quart). A definite structural assignment of this major component failed, however. The reaction between [Re(CH₃CN)₃Br₂(NO)] and acrylonitrile (6 equiv.) was also investigated. At 110 °C for 1 h, a doublet of doublets at 3.69 ppm $({}^{3}J = 12 \text{ Hz}, {}^{3}J = 9 \text{ Hz})$ and two doublets at 3.42 ppm $({}^{3}J = 9 \text{ Hz})$ and 3.27 ppm (${}^{3}J$ = 12 Hz) were observed in ${}^{1}H$ NMR spectra, which are assigned to alkene protons. The high-field shift of the alkene resonance indicated the formation of an alkene coordinated rhenium species.

3. Conclusion

In summary, we have studied the reactions of silanes with various substituted styrenes proceeding in highly selective dehydrogenative silylation reactions affording vinyl silanes in good to excellent yields. Furthermore, we have developed a rheniummediated hydrosilylation of acrylonitrile and its derivatives, which often are reluctant to undergo hydrosilylation. The reactions were extensively investigated by evaluating various parameters in detail, such as solvents, stoichiometrics and various silanes. [Re(CH₃CN)₃Br₂(NO)] was found to be an effective catalyst for the reduction of acrylonitrile and its derivatives, when the reactions were carried out with aryl silanes in acetonitrile and in the ratios of 4:1 or 1:4. Excellent yields and high regioselectivity were observed. At higher temperatures (115 °C) the catalyst remained stable and provided even better performance.

4. Experimental section

4.1. General information

All manipulations were carried out using standard vacuum line, Schlenk and cannula techniques or in a dry box (M. Braun 150B-G-II) containing an atmosphere of purified nitrogen. Solvents were initially distilled under N₂ atmosphere using standard procedures and were degassed by freeze-thaw cycles prior to use. The following complexes: Re(NO)(PCy₃)₂(CH₃CN)Br₂] [6d], [Re(NO)(-PiPr₃)₂(CH₃CN)Br₂] [6d], [Re(NO)(CH₃CN)₃Br₂] [6b], [Re(PTA)₂Br₂(-NO)(CH₃CN)] [6b], [Re(PTA)₃Br₂(NO)] [9], Re(PTAH)₂Br₂(NO)- (CH_3CN) [Br]₂ [9], [Re(PTAH)(PTA)Br₂(CH₃CN)(NO)][Br] [9] were prepared according to known procedures. All other chemicals were purchased from Aldrich Chemical Co. or Fluka and, unless otherwise noted, used without further purification. ¹H and ¹¹B NMR spectra were recorded on a Varian Gemini 300 (300.08 MHz), or on a Varian Mercury 200 (199.96 MHz) spectrometer. GC-MS analysis were carried out on a CP-3800 Saturn 2000 MS/MS spectrometer (CP-Sil8CB low bleed/ MS 30m, ID 0.25 mm, OD 0.39 mm, Film thickness 0.25 µm from Chrompack).

4.2. General procedure for the catalytic hydrosilylations according to Tables 1-4

A solution of the appropriate substrate (0.5 mmol), the silane (0.6 mmol) and the proper catalytic amount of the rhenium

complex in the given solvent (0.8 ml) was stirred for an appropriate period of time at proper temperature under nitrogen atmosphere. Upon completion, the reaction mixture was filtered over Celite. The resulting solution was analyzed by NMR spectroscopy and GC-MS. The yields are listed in Tables 1–4.

4.3. General procedure for the catalytic hydrosilylations according to Table 5

Appropriate amounts of the acrylonitrile (0.5–1.0 mmol), dimethylphenylsilane (0.5–1.0 mmol) and catalytic amounts of the rhenium complex (1.5 mmol %) in acetonitrile were placed in a Young tap Schlenk tube according to the procedures of the hydrosilvlations of Tables 1–4. The reaction mixture was heated to the proper temperature and stirred for the required reaction time. Upon completion, the reaction mixture was filtered over Celite. The conversion and selectivity was analyzed by GC-MS. 3-(Dimethyl(phenyl)silyl)propanenitrile: ¹H NMR (300.08 MHz, toluene-*d*₈, ppm): δ 7.53 (m, 2H), 7.21 (m, 3H), 2.59 (t, 2H), 1.94 (t, 2H), 0.69 (s, 6H); m/z = 189.1, $t_R = 5.9$ min. 2-(dimethyl(phenyl)silyl)propanenitrile: ¹H NMR (300.08 MHz, toluene- d_8 , ppm): δ 7.51 (m, 2H), 7.16 (m, 3H), 2.73 (m, 1H), 1.28 (d, 3H), 0.61 (s, 6H); m/z = 189.1, $t_{\rm R} = 6.2$ min.

4.4. Stoichiometric reaction between Re(I) precursor and substrate

Reaction between [Re(Br)₂(CH₃CN)₃(NO)] (19 mg, 0.04 mmol) and 4-methylstyrene (31 μ L. 0.25 mmol) in toluene-d₈ afforded at 105 °C a vellow solution within 20 h. The reaction is slow due to the poor solubility of [Re(Br)₂(CH₃CN)₃(NO)] in toluene. ¹H NMR spectroscopy indicated the formation of a new species which was assigned to a 4-methylstyrene coordinated Re(I) complex $[\text{Re}(\text{Br})_2(\text{CH}_3\text{CN})_2(\eta^2-\text{CH}_2=\text{CH}(4-\text{MePh}))(\text{NO})]$. ¹H NMR (199.95 MHz, toluene-*d*₈, ppm): 4.99–5.10 (dd, ³*J*_(HH) = 13 Hz, ${}^{3}J_{(HH)} = 9.5$ Hz, 1H), 3.92–4.01 (m, 2H), 2.22 (s, 3H, Ph-CH3), 1.13 (s, CH₃CN), 1.08 (s, CH₃CN). ¹³C{¹H}NMR (75.5 MHz, CD₂Cl₂, ppm): 137.3, 137.2, 128.5, 127.2, 78.0, 52.9, 2.3, 1.9. The resonance of freed CH₃CN ligand is observed as a singlet at 0.73 ppm.

Reaction between [Re(Br)₂(CH₃CN)₃(NO)] (19 mg, 0.04 mmol) and Et₃SiH (38 µL, 0.25 mmol) in toluene-d₈ afforded at 105 °C a dark brown solution within 1 h with a dark precipitate. ¹H NMR spectroscopy indicated the formation of several uncharacterized silane species in solution including one which most likely bears a Et₂HSi-unit. ¹H NMR (199.95 MHz, toluene-*d*₈, ppm): 2.60 (quart, *J*_(HH) = 7.4 Hz, Si–H, 1H), 0.85 (t, *J*_(HH) = 7.4 Hz, 9H, CH₃), 0.56–0.67 (m, 6H, CH₂).

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