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PAPER

Probing the catalytic potential of chloro nitrosyl rhenium(I) complexes†

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The reduction of the mononitrosyl Re(II) salt $[NMe_4]_2[ReCl_5(NO)]$ (**1**) with zinc in acetonitrile afforded the Re(I) dichloride complex $[ReCl_2(NO)(CH_3CN)_3]$ (**2**). Subsequent ligand substitution reactions with PCy_3, $PiPr_3$ and $P(p\text{-tolyl})_3$ afforded the bisphosphine Re(I) complexes $[ReCl_2(NO)(PR_3)_2(CH_3CN)]$ (**3**, R = Cy **a**, *i*Pr **b**, *p*-tolyl **c**) in good yields. The acetonitrile ligand in **3** is labile, permitting its replacement with H_2 (1 bar) to afford the dihydrogen Re(I) complexes $[ReCl_2(NO)(PR_3)_2(\eta^2\text{-}H_2)]$ (**4**, R = Cy **a**, *i*Pr **b**). The catalytic activity of **2**, **3** and **4** in hydrogen-related catalyses including dehydrocoupling of $Me_2NH{\cdot}BH_3$, dehydrogenative silylation of styrenes, and hydrosilylation of ketones and aryl aldehydes were investigated, with the main focus on phosphine and halide effects. In the dehydrocoupling of $Me_2NH{\cdot}BH_3$, the phosphine-free complex **2** exhibits the same activity as the bisphosphine-substituted systems. In the dehydrogenative silylation of styrenes, **3a** and **4a** bearing PCy_3 ligands exhibit high catalytic activities. Monochloro Re(I) hydrides $[Re(Cl)(H)(NO)(PR_3)_2(CH_3CN)]$ (**5**, R = Cy **a**, *i*Pr **b**) were proven to be formed in the initiation pathway. The phosphine-free complex **2** showed in dehydrogenative silylations even higher activity than the bisphosphine derivatives, which further emphasizes the importance of a facile phosphine dissociation in the catalytic process. In the hydrosilylation of ketones and aryl aldehydes, at least one rhenium-bound phosphine is required to ensure high catalytic activity.

Introduction

Hydrogen-related catalyses, including those with activation of E–H (E = H,[1,2] B,[3] Si,[4] C [5]) bonds as key elementary steps, have attracted growing interest in both organic and inorganic chemistry. Recent studies on chemical hydrogen storage are often based on amine boranes,[6] and these require such H–E bond activation processes.[7,3a] So far, robust catalysts for such hydrogen-related catalyses are mostly limited to early and late transition metal compounds. In contrast, middle transition metal complexes appear to be less active due to their high tendency to stay as coordinatively saturated 18-electron species. The metal ligand bonds are usually too strong to admit ligand lability. Such drawbacks have to be overcome *via* the help of the ancillary ligand sphere using for instance the *cis*-labilization effect of π-donating ligands (*e.g.* Cl, Br) stabilizing dissociative transition states or intermediates of low coordination numbers.[8] A similar labilization effect was expected to originate from the *trans*-effect and *trans*-influencing ligands, like the NO moiety.[9] With this background our group has in recent years focused on the study of the chemistry of the middle transition element rhenium,[10] in particular with respect to applications in homogeneous hydrogen reactions.[11] For example, the mononitrosyl rhenium dibromides $[ReBr_2(NO)(PR_3)_2(CH_3CN)]$ (R = Cy **a**, *i*Pr **b**)[12] comprised of nitrosyl,[13] the π-donor bromide, and the additional presence of σ-donor phosphine ensure a certain degree of electron richness and simultaneously ligand lability. Such species exhibited for instance good catalytic activities toward the dehydrocoupling of $Me_2NH{\cdot}BH_3$ [14] and highly selective dehydrogenative silylation of alkenes,[15] *i.e.* in more general terms the activation of E–H bonds. Mechanistic studies implied the involvement of phosphine dissociation which was either promoted by the substrate (*e.g.* $Me_2NH{\cdot}BH_3$) or induced by the ancillary ligand sphere (*e.g.* in dehydrogenative silylation).[16] Also the phosphine-free but still π-donor and *trans*-influence/effect ligand containing Re(I) dibromide $[ReBr_2(NO)(CH_3CN)_3]$ was found to be active in hydrosilylation of ketones and aldehydes.[17] In extension of this work with respect to ligand tuning, we report here the preparation of the related mononitrosyl rhenium dichloride complexes bearing either no phosphine or two phosphine ligands and their application in the above-mentioned types of catalyses to trace the impact of phosphine and halide substitution on the catalytic performance of such mononitrosyl Re(I) systems.

Results and discussion

Synthesis of mononitrosyl Re(I) dichloride complexes

Chloride is a strong π-donor and therefore exerts a strong *cis*-labilization effect on neighboring ligands, even stronger than bromide.[18] This could result in enhanced ligand replacements or

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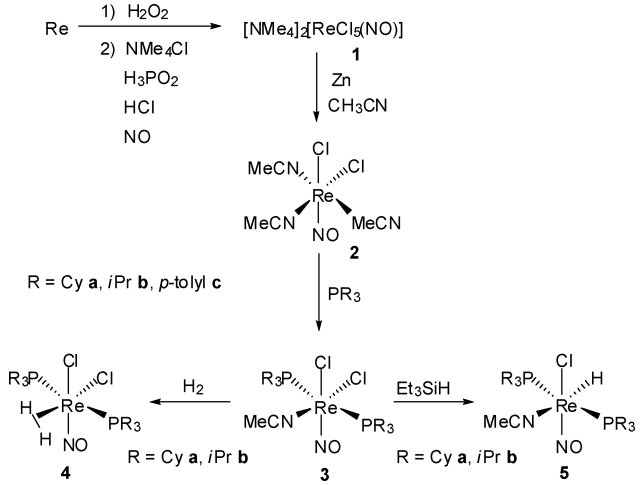
stabilization of unsaturated catalytic species. A synthetic pathway to suitable mononitrosyl rhenium dichloride complexes is depicted in Scheme 1, similar to the procedure in the preparation of related Re(I) dibromides.[11a]



Scheme 1 Synthetic pathways to various chloro nitrosyl Re(I) complexes.

Starting from rhenium metal, a two-step procedure furnished the mononitrosyl Re(II) salt $[NMe_4]_2[ReCl_5(NO)]$ (**1**) in 26% yield. This compound was previously reported in a lower yield (15%) by Guisto and co-workers *via* a complex procedure starting from $[K_2][ReCl_6]$.[19] Compound **1** is well soluble in H_2O but has a quite poor solubility in CH_3CN. Different from the bromide derivatives bearing $[NMe_4]^+$ and $[NEt_4]^+$ counter-ions,[19a] **1** was found to be insoluble in ethanol or methanol, even at elevated temperatures. This prevented the preparation of Re(I) bisphosphine complexes *via* a facile substitution route employing ethanol as both a solvent and reductant.[10b] Therefore we modified this procedure adding zinc as a reducing agent. Treatment of **1** with excess of zinc in CH_3CN at room temperature afforded within 5 days an orange solution, from which the Re(I) complex *mer*-$[ReCl_2(NO)(CH_3CN)_3]$ (**2**) was isolated in 51% yield. The IR spectra showed a strong ν(NO) absorption at 1697 cm^{-1}. In the ^1H NMR spectrum two resonances were observed for the $Me_{acetonitrile}$ groups at 3.00 and 2.93 ppm in a 1 : 2 ratio, confirming the *mer*-substitution pattern of the acetonitrile ligands.

Complex **2** turned out to be a suitable precursor for various ligand exchange reactions. Treatment of **2** with excess of phosphines such as PCy_3, $PiPr_3$ and $P(p\text{-tolyl})_3$ in acetonitrile at 70 °C afforded within 24 h the bisphosphine Re(I) dichloride complexes of the type [*trans*-$ReCl_2(NO)(PR_3)_2(CH_3CN)$] (**3**, R = Cy **a**, *i*Pr **b**, *p*-tolyl **c**) in 50% (**3a**), 16% (**3b**) and 76% (**3c**) isolated yield, respectively. Complexes **3a–c** were fully characterized by elemental analysis and various spectroscopic methods. In the IR spectra the coordinated NO ligands gave rise to ν(NO) bands at 1672 cm^{-1} (**3a**), 1668 cm^{-1} (**3b**) and 1688 cm^{-1} (**3c**), respectively. The $^{31}P\{^1H\}$ NMR spectra displayed singlet resonances at –11.10 (**3a**), –0.3 (**3b**) or –0.96 ppm (**3c**) accounting for the two chemically equivalent *trans*-phosphorus nuclei. In the ^1H NMR spectra the $Me_{acetonitrile}$ groups were observed as singlets at 3.09 (**3a**), 3.07 (**3b**) and 1.79 ppm (**3c**), which are comparable to those of the Re(I) dibromide derivatives.[11a] The molecular structures of complexes **3a** and **3c** were established by single-crystal X-ray diffraction studies, as shown in Fig. 1 and 2. Both molecules adopted a pseudo-octahedral geometry around the rhenium center with two *trans*-disposed phosphines. The two 2e ligands of **3c** are slightly bent toward one chloride with a P(1)–Re(1)–P(2) angle of 173.85(3)°. The $Re–N_{acetonitrile}$ distance is 2.0935(17) Å in **3a** and 2.075(3) Å in **3c**, close to the average value (2.098 Å) for such bonds.[10a] Apparently, the coordination mode of the phosphine, nitrosyl and acetonitrile ligands do not depend much on the nature of the halide, since only small variations of the Re–P, Re–N and NO bond lengths are found with respect to the bromide derivative.

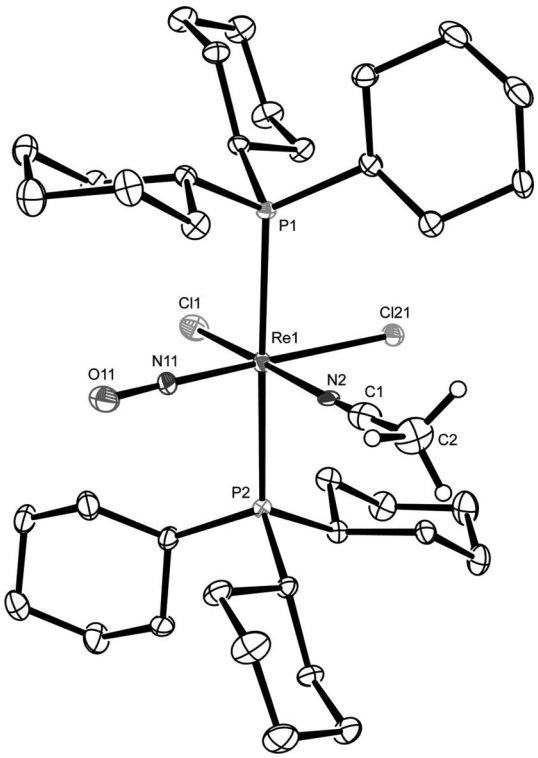


Fig. 1 ORTEP drawing of $[ReCl_2(NO)(PCy_3)_2(CH_3CN)]$ (**3a**) using 30% probability ellipsoids. The NO/Cl disorder and selected H atoms are omitted for clarity. Selected bond lengths (Å): Re(1)–N(11), 1.768(6); Re(1)–N(2), 2.0935(17); Re(1)–Cl(1), 2.4183(10); Re(1)–Cl(21), 2.4129(17); Re(1)–P(1), 2.5062(11); Re(1)–P(2), 2.5134(12); N(11)–O(11), 1.185(8). Selected bond angles (deg): N(11)–Re(1)–N(2), 87.31(17); N(2)–Re(1)–Cl(1), 177.46(10); P(1)–Re(1)–P(2), 177.02(5); O(11)–N(11)–Re(1), 176.4(5); N(11)–Re(1)–Cl(21), 174.43(15); N(11)–Re(1)–P(1), 93.79(15); Cl(21)–Re(1)–Cl(1), 91.08(5).

The acetonitrile ligand of **3** is substitutionally labile. Treatment of **3a** with 1 bar of H_2 in CH_2Cl_2 at room temperature afforded within 24 h the dihydrogen Re(I) complex $[ReCl_2(NO)(PCy_3)_2(\eta^2\text{-}H_2)]$ (**4a**) in 85% isolated yield. Complex **4a** was fully characterized by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR spectroscopy. The IR spectrum showed a strong ν(NO) absorption at 1674 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra displayed a singlet at δ 14.5 ppm, which is shifted low-field in comparison with that of **3a**. In the ^1H NMR spectra, the resonance of the dihydrogen ligand was observed as a broad triplet at 2.61 ppm ($^2J_{(PH)}$ = 18 Hz, T_1 = 39 ms) due to coupling with the two phosphorus nuclei.[10b] In the same manner **3b** was also reacted with H_2 but affording a mixture containing 84% of the dihydrogen complex $[ReCl_2(NO)(PiPr_3)_2(\eta^2\text{-}H_2)]$ (**4b**) and 16% of the starting material

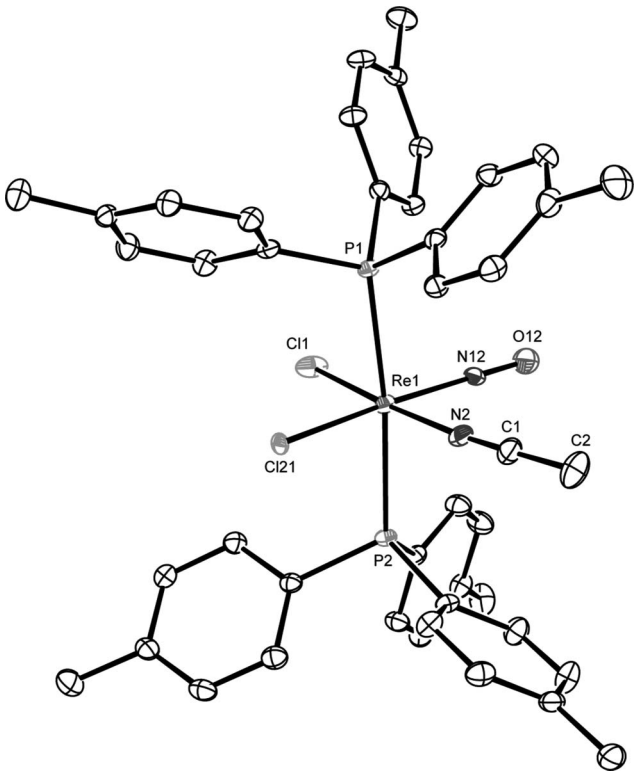


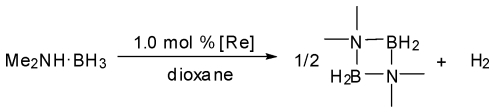
Fig. 2 ORTEP drawing of $[ReCl_2(NO)\{P(p\text{-tolyl})_3\}_2(CH_3CN)]$ (**3c**) using 30% probability ellipsoids. The NO/Cl disorder and all H atoms are omitted for clarity. Selected bond lengths (Å): Re(1)–N(12), 1.862(7); Re(1)–N(2), 2.075(3); Re(1)–Cl(21), 2.360(2); Re(1)–Cl(1), 2.4137(8); Re(1)–P(1), 2.4636(8); Re(1)–P(2), 2.4771(9); N(12)–O(12), 1.055(9). Selected bond angels (deg): P(1)–Re(1)–P(2), 173.85(3); N(12)–Re(1)–Cl(21), 170.5(3); N(2)–Re(1)–Cl(1), 175.03(8); O(12)–N(12)–Re(1), 177.1(9); Cl(1)–Re(1)–P(1), 87.37(3); Cl(21)–Re(1)–P(1), 88.50(6).

3b. T_1 measurement was also carried out for the triplet signal at 2.49 ppm ($^2J_{(PH)}$ = 18 Hz) of **4b** in ^{1}H NMR and the short T_1 value of 87 ms indicated the coordination of dihydrogen ligand to rhenium. No reaction at all occurred between **3c** and H_2 even at elevated temperatures, presumably caused by the lower electron-donating ability of the *p*-tolyl phosphine. H_2 binding is known to require a certain degree of electron richness of the metal center.[1]

Application of chloro nitrosyl rhenium(I) complexes to hydrogen-related catalysis

1. Dehydrocoupling of $Me_2NH{\cdot}BH_3$. The bisphosphine dichloride complexes **3a–c** and **4a** were tested as catalysts in the dehydrocoupling of $Me_2NH{\cdot}BH_3$. The observed turnover frequencies (TOFs) are listed in Table 1. In a typical run, 0.25 mmol of $Me_2NH{\cdot}BH_3$ and 1.0 mol% of **3a** were mixed in 0.5 mL of dioxane. The solution was kept at 85 °C with continuous release of hydrogen. After 4 h, the ^{11}B NMR spectra indicated the formation of the dehydrocoupled cyclic product $[Me_2N{-}BH_2]_2$ in 97% yield displaying a characteristic triplet at 4.5 ppm (J_{BH} = 112 Hz).[14f] Except for trace amounts of $(Me_2NH)_2BH$ (δ 28.0 ppm, d, J_{BH} = 132 Hz), no evidence was found for the formation of the cyclic trimer $[Me_2N{-}BH_2]_3$ or the linear dimer $[Me_2NH{-}BH_2{-}NMe_2{-}BH_3]$. The stoichiometric reaction between **3a** and 5 equiv. of $Me_2NH{\cdot}BH_3$ proved the formation of the phosphine-abstracted adduct $Cy_3P{\cdot}BH_3$. Similar results were obtained by applying **3b** and **3c** as catalysts. Complex **4a** turned out to be slightly less active, probably due to its lower solubility in dioxane. In comparison with the dibromide derivatives, the chloride complexes **3a** and **3b** did not show higher activity. When the reaction catalyzed by **3a** or **4a** was carried out at lower temperatures, such as 23 °C or 45 °C, the TOFs decreased considerably.

Table 1 Dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by chloro nitrosyl Re(I) complexes[a]



Entry	[Re]	T (°C)	t (h)	Yield (%)[b]	TOF (h)
1	**3a**	23	24	14	1
2	**3a**	23	4	25	6
3	**3a**	85	4	97	24
4	**3b**	85	4	93	23
5	**3c**	85	4	95	24
6	**4a**	45	2	7	4
7	**4a**	85	4	79	20
8	**2**	85	4	96	24
9[c]	**2**	80	4	11	3
10[c]	**3a**	80	4	<1	—

[a] Reactions were performed with 0.25 mmol of $Me_2NH{\cdot}BH_3$ in 0.5 mL of dioxane. [b] On the basis of integration of ^{11}B-NMR spectrum (96 MHz) of the reaction mixture. [c] In acetonitrile.

Interestingly, the phosphine-free Re(I) dichloride precursor **2** exhibited the same catalytic activity in the dehydrocoupling of $Me_2NH{\cdot}BH_3$ in dioxane. It should be noted that **2** is almost insoluble in dioxane and during the catalysis it quickly turned from orange to black within 15 min. The formed dark residue was found to act as a heterogeneous catalyst in the dehydrocoupling reaction, reaching a conversion of 96% within 4 h, which corresponds to a TOF value of 24 h^{-1}. The stoichiometric reaction between **2** and $Me_2NH{\cdot}BH_3$ (5 equiv.) demonstrated the formed black residue to be insoluble in almost any organic solvent and only poorly soluble in water. In the IR spectrum, a weak and broad absorption at 1644 cm^{-1} indicated the presence of a NO group.

The performance of the dehydrocoupling catalysis was found to be quite solvent-dependent. When the reaction was catalyzed by **2** in acetonitrile at 80 °C for 4 h, only 11% of $[Me_2N{-}BH_2]_2$ was obtained along with the formation of 6% of $(Me_2NH)_2BH$. Under the same conditions, the dehydrocoupling reaction catalyzed by **3a** in acetonitrile afforded merely a trace amount of $[Me_2N{-}BH_2]_2$ and $(Me_2NH)_2BH$ (less than 1% of the total). These results suggest the involvement of rhenium intermediates bearing vacant sites regardless of the type of the coordinated ligand (PR_3 or CH_3CN).

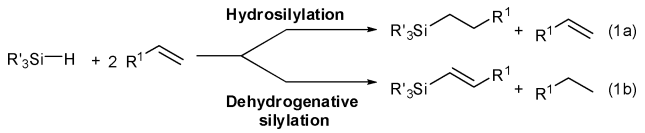
2. Dehydrogenative silylations of styrenes. Simultaneous activation of sp^2C–H and Si–H bonds by transition metal complexes to form new Si–C bonds is one of the key steps of organosilicon chemistry. Besides the well-developed hydrosilylation reaction, which has found various industrial applications,[20] the competitive dehydrogenative silylation reaction, which permits the direct production of unsaturated silyl compounds from olefins and silanes, has drawn much attention during the last two decades.[21] Hydrosilylations and dehydrogenative silylations are related by a formal transfer hydrogenation process (eqns 1a and 1b). However,

Table 2 Dehydrogenative silylation of styrenes catalyzed by chloro nitrosyl Re(I) complexes[a]

Entry	R′	R[1]	[Re]	T(°C)	t (h)	Conv. (%)[b]	Ratio dehydro (E/Z) : hydro[c]
1	Et	*p*-$MeOC_6H_4$	**3a**	70	28	99	99 (99/1) : 2
2	Ph	*p*-$MeOC_6H_4$	**3a**	100	24	91	95 (99/1) : 5
3	Et	*p*-$MeOC_6H_4$	**3b**	70	24	9	—
4	Et	*p*-$MeOC_6H_4$	**3b**	100	24	99	97 (98/2) : 3
5	Et	*p*-$MeOC_6H_4$	**3c**	70	28	<5	—
6	Et	*p*-$MeOC_6H_4$	**3c**	100	24	92	96 (96/4) : 4
7	Et	*p*-MeC_6H_4	**3a**	70	24	87	98 (>99/1) : 2
8	Et	*p*-MeC_6H_4	**3c**	100	24	97	97 (99/1) : 3
9	Et	*p*-ClC_6H_4	**3a**	100	24	99	96 (99/1) : 4
10	Et	*p*-FC_6H_4	**3a**	70	24	39	—
11	Et	*p*-FC_6H_4	**3a**	100	24	98	97 (99/1) : 3
12	Et	*p*-$MeOC_6H_4$	**4a**	70	24	99	98 (99/1) : 2
13	Et	*p*-MeC_6H_4	**4a**	70	24	99	98 (>99/1) : 2
14	Et	H	**3a**	100	24	99	80 : 20
15	Et	H	**3c**	100	24	99	80 : 20
16	Et	*p*-MeC_6H_4	**2**	110	2	99	94 (>99/1) : 6
17	Et	*p*-$MeOC_6H_4$	**2**	110	2	99	93 (>99/1) : 7
18	Et	Ph	**2**	110	1.5	71	95 (>99/1) : 5[d]
19	Et	*p*-FC_6H_4	**2**	110	1.5	56	95 (>99/1) : 5
20	Et	*m*-ClC_6H_4	**2**	110	9	99	97 (>99/1) : 3
21	Et	*m*-MeC_6H_4	**2**	110	1.5	66	93 (>99/1) : 7
22	Et	*o*-FC_6H_4	**2**	110	1.5	51	94 (>99/1) : 6
23	Me_2Ph[e]	*p*-MeC_6H_4	**2**	110	3	99	87 (>99/1) : 13
24	Me_2Ph[e]	*m*-MeC_6H_4	**2**	110	1.5	69	85 (>99/1) : 15
25	Me_2Ph[e]	*o*-FC_6H_4	**2**	110	3	64	90 (>99/1) : 10
26	Ph	*p*-MeC_6H_4	**2**	110	2	98	98 (>99/1) : 2

[a] Reactions were carried out with 0.25 mmol of silane and 0.50 mmol of styrenes. [b] Calculated based on the silane consumption. [c] On basis of the integration of the ^{1}H NMR spectrum. [d] The selectivities decreased with prolonged reaction time. [e] With Me_2PhSiH as the silane substrate.

a major drawback of the dehydrogenative silylation is that it is usually accompanied by hydrosilylation byproduct. Thus highly selective processes are desired.[22,15a,15c–d]



In continuation of the exploration of the respective catalytic potential, the performance of complexes **2**, **3a–c** and **4a** in the dehydrogenative silylation of styrenes was examined. Table 2 lists the dehydrogenative silylation reactions studied under catalytic conditions with various Re(I) dichlorides. For the sake of comparison the reaction of Et_3SiH (0.25 mmol) with *p*-methoxystyrene (0.5 mmol) in toluene-d_8 was carried out for at least 24 h in the presence of 1.0 mol% of the Re(I) catalyst. Compared to the dibromide analogues, the Re(I) dichlorides **3b** and **3c** bearing P*i*Pr$_3$ or P(*p*-tolyl)$_3$ ligands did not show improved activities. Somewhat higher temperatures of 100 °C were required which, however, did not affect the selectivities for the dehydrogenative silylations over the hydrosilylations, with (*E*)-1-(*p*-methoxystyryl)-2-(triethylsilyl)ethylene remaining the dominant product. In contrast, complexes **3a** and **4a** bearing PCy_3 ligands turned out to be better catalysts than the respective bromides, since the reaction temperature could be decreased to 70 °C, affording even slightly better selectivities. However, this positive tuning effect was restricted to the case of *p*-methoxy and *p*-methylstyrene. Reactions with substrates, such as *p*-chloro- and *p*-fluorostyrene, with silanes using **3a** or **4a** as catalysts had to be carried out at 100 °C for the benefit of both high conversions and selectivities. In the case of ethylene, a high yield, but lower dehydro/hydro selectivities (about 4 : 1) were observed. The reactions with the less hydridic Ph_3SiH catalyzed by **3a** turned out to be sluggish at low temperature, but could be accelerated at the higher temperature of 100 °C. All these reactions, despite that trace amount of (*Z*)-vinylsilane products were always found, showed no branched "side-products" of the dehydrogenative silylations.

We also investigated the stoichiometric reactions of **3** in the presence of Et_3SiH. The reaction of **3a** or **3b** with Et_3SiH in toluene-d_8 at 100 °C afforded within 1 h a deep-pink solution, which quickly turned light-brown accompanied by some oily residue when cooled to ambient temperature. The NMR spectra indicated the formation of chloro Re(I) hydride complexes [Re(Cl)(H)(NO)$(PR_3)_2(CH_3CN)$] (**5**, R = Cy **a**, *i*Pr **b**) in 98% (**5a**) or 99% (**5b**) *in situ* yields. When the reactions were carried out at 70 °C, the conversions became rather poor, pointing to significant catalyst degradation at longer reaction times. Both compounds **5a** and **5b** were characterized in solution. For example, the $^{31}P\{^1H\}$ NMR spectra showed singlets at δ 21.2 for **5a** and at 31.6 ppm for **5b**. In the ^{1}H NMR spectra triplet resonances at δ –1.51 ppm ($^2J_{(HP)}$ = 20.0 Hz) for **5a** and –1.75 ppm ($^2J_{(HP)}$ = 20.0 Hz) for **5b** were assigned to the H_{Re} proton. The $Me_{acetonitrile}$ groups were observed as singlets at 1.11 ppm for **5a** and 1.08 ppm for **5b**. Isolation of pure **5a** and **5b** was attempted, but elemental analyses of the obtained solids were not satisfactory. In the IR spectra one ν(NO) band was observed at 1648 (**5a**) and at 1637 cm^{-1} (**5b**). In contrast, no reaction occurred between **3c** and Et_3SiH at 100 °C even at longer times (48 h), which presumably can be attributed to the lower electron-donating ability of the P(*p*-tolyl)$_3$ ligands.

Interestingly, the phosphine-free complex **2** proved to be an even better catalyst than those of type **3** and **4** in such silane catalyses. For example, when a mixture of 0.50 mmol of *p*-methylstyrene and

0.25 mmol of Et_3SiH were treated with 1.0 mol% of **2** in toluene-d_8 and kept at the higher temperature of 110 °C, conversions of 99% were achieved within 2 h accompanied by a high selectivity of 94% for dehydrogenative silylation over hydrosilylation. Other styrenes, such as *p*-methoxystyrene, *m*-methylstyrene also afforded satisfactory conversions catalyzed by **2** at 110 °C within 1.5–3 h giving high selectivities of over 9 : 1 between dehydrogenative silylations and hydrosilylations. The reactions of styrenes bearing electron-withdrawing substituents such as *p*-fluorostyrene, *m*-chlorostyrene and *o*-fluorostyrene were found to proceed slower than those with electron-donating substituents of the aromatic rings. Variations in the silanes were additionally tested in reactions catalyzed by **2**. While Ph_3SiH still afforded reasonable conversions and selectivities for dehydrogenative silylation, the reaction of dimethylphenylsilane with various styrene derivatives afforded somewhat lower selectivities (<9 : 1) under the same conditions as in the cases of Ph_3SiH and Et_3SiH as the silyl component. It should also be pointed out that in these catalyses of **2** always black residues were formed, which were isolated and proved to be catalytically inactive. The improved activity of **2** over **3** and **4** suggests that **3** and **4** are pre-catalysts which operate on the basis of loss of phosphine ligands to form the active species. Phosphine dissociation might even participate in the rate-determining step(s).[12b]

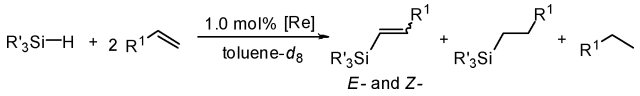
The stoichiometric reaction of **2** with 5 equiv. of *p*-methylstyrene afforded within 5 h at 110 °C a yellow solution, in which the formation of *p*-methylstyrene-coordinated Re(I) complex $[ReCl_2(NO)(CH_3CN)_2(\eta^2\text{-}CH_2{=}CHPh(p\text{-}Me))]$ could be traced. The ^1H NMR resonances of the alkene protons were observed as two doublets of doublets at 4.85 and 3.81 ppm in a 1 : 2 ratio. The signals of the two acetonitrile ligands were observed as two singlets at 1.12 and 1.09 ppm suggesting their *cis*-position. The resonance of free CH_3CN ligand is detected as a singlet at 0.71 ppm.

Kinetic measurements were carried out for **2** (1.0 mol%) catalyzed dehydrogenative silylation of *p*-methylstyrene and Et_3SiH. The rate law was determined, and showed first-order dependence in the concentration of each substrate:

$$\text{rate} = 0.048\ (\text{min L mol}^{-1}) \times [Et_3SiH][p\text{-methylstyrene}]$$

3. Hydrosilylation of ketones and aryl aldehydes. When ketones and aryl aldehydes were employed as substrates, the reactions with silane catalyzed by **3** and **4** furnished hydrosilylation and formation of silyl ether products, as depicted in Table 3. When benzophenone and 1.1 equiv. of Et_3SiH were mixed with 1 mol% of **3a** in 0.5 mL of chlorobenzene-d_5 and kept at 80 °C for 4 h, the ^1H NMR spectra indicated almost complete hydrosilylation (yield > 99%). Similar results were obtained using **3b** and **4a** as catalysts. Complex **3c** bearing P(*p*-tolyl)$_3$ ligands led to only moderate yields after 4 h, thus showing lower activity than the complexes bearing alkylphosphine ligands. Other ketones, such as acetophenone, 3,3-dimethylbutan-2-one, cyclopentanone and cyclohexanone also afforded the corresponding hydrosilylation products in high yields under similar conditions as for benzophenone. Aryl aldehydes, including benzaldehyde and 1-naphthaldehyde, can also be reduced to silyl ethers by the reaction with Et_3SiH. It was further proven that the type of silane has a great influence on the catalytic performance. Et_3SiH turns out to be the most efficient silane source for hydrosilylations. The reaction of Ph_3SiH with benzophenone or cyclopentanone afforded only moderate yields even at elevated temperature. In the case of iPr_3SiH, no conversion was observed at all, presumably due to its steric congestion being too high.

Table 3 Hydrosilylation of ketones and aryl aldehydes catalyzed by chloro nitrosyl Re(I) complexes[a]



		Carbonyl substrate					
Entry	R′	R^1	R^2	[Re]	*T* (°C)	*t* (h)	Yield (%)[b]
1	Et	Ph	Ph	**3a**	80	4	99
2	Et	Ph	Ph	**3a**	23	15	14
3	Et	Ph	Ph	**3b**	80	4	99
4	Et	Ph	Ph	**3c**	80	4	74
5	Et	Ph	Ph	**4a**	80	4	99
6	Et	Ph	Me	**3a**	80	5	91
7	Et	Me	*t*Bu	**3a**	80	5	87
8	Et	Cyclohexanone		**3a**	80	4	99
9	Et	Cyclohexanone		**3a**	80	4	99
10	Et	*p*-MeC_6H_4	H	**3a**	80	5	99
11	Et	1-Naph	H	**3a**	80	4	95
12	Ph	Ph	Ph	**3a**	100	4	69
13	Ph	Cyclohexanone		**3a**	80	4	74
14	*i*Pr	Ph	Ph	**3a**	80	4	0
15	*i*Pr	Cyclohexanone		**3a**	80	4	0
16	Et	Ph	Ph	**2**	110	4	34
17	Et	Ph	Me	**2**	110	4	81
18	Et	Me	*t*Bu	**2**	110	5	47
19	Et	*p*-$MeOC_6H_4$	H	**2**	110	2	99
20	Et	*p*-FC_6H_4	H	**2**	110	4	99
21	Et	1-Naph	H	**2**	110	4	95
22	Et	Cyclohexanone		**2**	110	3	96
23	Et	Cyclohexanone		**2**	110	4	87

[a] Reactions were performed with 0.28 mmol of silane and 0.25 mmol of ketones or aldehydes. [b] On the basis of the integration of the ^1H-NMR spectrum.

In comparison to the dehydrogenative silylation reactions with **3** and **4**, the phosphine-free compound **2** showed lower performance in the hydrosilylation of ketones and aryl aldehydes. When the reaction of benzophenone (0.25 mmol) and Et_3SiH (0.28 mmol) with 1 mol% of **2** was carried out at 80 °C, a conversion of less than 10% was achieved within 4 h. Raising the temperature to 110 °C indeed accelerated the catalysis affording a yield of 34% within 4 h, which however is much lower than that from the catalyses of **3** or **4** at 80 °C. Similar low activities were also observed with 3,3-dimethylbutan-2-one and cyclopentanone as substrates. Generally, the reactions with aryl aldehydes are faster than those with ketones. A high yield of over 95% could be achieved at 110 °C within 2-4 h in the hydrosilylation of anisaldehyde, *p*-fluorobenzaldehyde and 1-naphthaldehyde.

The catalytic behavior of **2** differing from **3** or **4** in the dehydrogenative silylations and hydrosilylations suggests divergent underlying reaction paths. The stoichiometric reaction of **3a** with 5 equiv. of acetophenone and Et_3SiH afforded at 80 °C within 10 min the acetonitrile-coordinated Re(I) hydride **5a** in 75% yield, along with hydrosilylation products. The hydrosilylation was completed at 80 °C within 1 h with **5a** as the major remaining organometallic species. This demonstrates that the Re(I) hydrides **5** are generated even in the initial pathway in bisphosphine Re(I) dichloride catalyzed hydrosilylations. In contrast, the reaction of **2** with acetophenone and Et_3SiH proceeded relatively slowly and

no obvious hydrosilylation occurred at 110 °C within 10 min. Kinetic measurements for the hydrosilylation of acetophenone with Et_3SiH catalyzed by **2** (2.0 mol%) indicated a second-order behavior, first-order with respect to both silane and ketone:

$$\text{rate} = 0.062\ (\text{min L mol}^{-1}) \times [Et_3SiH][PhCOCH_3]$$

It is most likely that in these hydrosilylations the rhenium catalyst (**5** or **2**) functions as a Lewis acid coordinating the ketones or aryl aldehydes, in which the activated carbon atom of the C═O bond is further attacked from "outside" by the hydride of the silane affording the final hydrosilylation product.[23] Another possible pathway would be the initial activation of the Si–H bond at the rhenium center, then the polarized silicon atom is attacked by the carbonyl group.[24] The rate-determining step is presumed to be the dissociation of one acetonitrile ligand. This would explain why the reactions catalyzed by **3** or **4** are faster than that by **2**, as the acetonitrile ligands in the bisphosphine Re(I) hydrides **5** are more labile than those of **2**.

Conclusions

In summary, we have demonstrated synthetic access to chloro nitrosyl Re(I) complexes and their utility in hydrogen-related catalyses including dehydrocoupling of $Me_2NH{\cdot}BH_3$, dehydrogenative silylation of styrenes, and hydrosilylation of ketones and aryl aldehydes. An influence of the type of phosphine substitution and a halide effect could be demonstrated. In the dehydrocoupling of $Me_2NH{\cdot}BH_3$, the phosphine-free Re(I) complex **2** exhibited the same activities as the bisphosphine ones. In dehydrogenative silylation reactions, the catalytic activities are only slightly enhanced in the case of **3a** and **4a** when bromide and chloride derivatives are compared. This might be interpreted in terms of different *cis*-labilization effects exerted by different halide ligands that facilitates phosphine dissociation. However, the substitution of one halide by a hydride in the initiation step largely suppresses this halide effect. Interestingly, **2** exhibited higher activity toward dehydrogenative silylation than **3** or **4**, which implies that two acetonitrile ligands must dissociate from the rhenium center and that such two-ligand dissociations are more reluctant to occur with complexes of type **3** and **4**. In the hydrosilylation of ketones and aryl aldehydes, the phosphine-free complex **2** proved to be less effective than the bisphosphine derivatives **3** and **4**. The different catalytic performance indicates a different mechanism. Presumably the rhenium center operates as a Lewis acid to the carbonyl group and the rate-determining step is the substitution of acetonitrile ligand by the substrate. All these types of reactions have in common a strong propensity of Re(NO) centers to activate E–H bonds (E = B, Si), which in this respect resemble isoelectronic RuL units (L = $2e^-$ donor).

Experimental details

General

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze–thaw cycles prior to use. The deuterated solvents were dried with sodium/benzophenone (toluene-d_8, benzene-d_6) or CaH_2 (CD_2Cl_2), and vacuum-transferred for storage in Schlenk flasks fitted with Teflon valves. ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR data were recorded on a Varian Gemini-300, Varian Mercury 200, or Bruker DRX 500 spectrometers using 5-mm diameter NMR tubes equipped with Teflon valves, which allow degassing and further introduction of gases into the probe. Chemical shifts are expressed in parts per million (ppm). ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual proton or ^{13}C resonances of the deuterated solvent. All chemical shifts for the $^{31}P\{^1H\}$ NMR data are reported downfield in ppm relative to external 85% H_3PO_4 at 0.0 ppm. Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were obtained by using ATR methods with a Bio-Rad FTS-45 FTIR spectrometer. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich. Et_3SiH, Ph_3SiH, Me_2PhSiH, different styrene derivatives, ketones and aryl aldehydes were purchased from Fluka and Aldrich and used without further purification.

Caution: When generating hydrogen gas in Young-tap NMR tubes, the tubes should be vented for safety reasons every 30 min during experiments.

$[NMe_4]_2[ReCl_5(NO)]$ (1). In a 500 mL round-bottom flask, H_2O_2 (20 mL, 30%) was added dropwise to Re powder (6.0 g, 32.2 mmol) at 0 °C. $[NMe_4]Cl$ (5.60 g, 51.09 mmol) was then added and the mixture was stirred for 15 h at room temperature until the solution became relatively homogenous. The mixture was dried by rotary evaporation. After that, additional part of $[NMe_4]Cl$ (5.60 g, 51.09 mmol) was added, and the mixture was dissolved in 220 mL of HCl (32%) and 10 mL of H_3PO_2 (50%). NO gas was bubbled through the solution at 110 °C, and the solution turned green after 2 h. 15 h later, the reaction mixture was cooled down to room temperature and was filtered. The filtrate was dried by rotary evaporation giving green solid, which was further washed with acetone (3 × 20 mL) and dried *in vacuo*. Yield: 4.50 g, 26%. IR (ATR, cm^{-1}): ν (NO) 1715. Anal. Calcd for $C_8H_{24}Cl_5N_3ORe$ (541.77): C, 17.74; H, 4.47; N, 7.76. Found: C, 18.23; H, 4.35; N, 7.75.

***mer*-$[ReCl_2(NO)(CH_3CN)_3]$ (2).** In a 250 mL round-bottom flask, 1.14 g of **1** (2.10 mmol) was dissolved in 100 mL of CH_3CN. Then an excess of Zn (1.2 g, 18.46 mmol) was added and the mixture was stirred at room temperature for 5 days. The dark-orange supernatant solution was filtered and the solvent was evaporated *in vacuo*. The residue was extracted with CH_3CN (5 × 10 mL) to remove most of $[NMe_4]Cl$ and $[NMe_4]_2[ZnCl_4]$ salt. The extracted solution was dried *in vacuo* and was further extracted with CH_2Cl_2 (5 × 20 mL) to afford orange solid. Yield: 440 mg, 51%. IR (ATR, cm^{-1}): ν (NO) 1697. ^{1}H NMR (300.1 MHz, CD_3CN, ppm): 3.00 (s, 3H, CH_3CN), 2.93 (s, 6H, CH_3CN). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 134.2 (s, CH_3CN), 132.7 (s, CH_3CN), 4.3 (s, CH_3CN). Anal. Calcd for $C_6H_9Cl_2N_4ORe$ (410.27): C, 17.56; H, 2.21; N, 13.66. Found: C, 17.60; H, 2.53; N, 13.57.

$[ReCl_2(NO)(PCy_3)_2(CH_3CN)]$ (3a). In a 50 mL Young-tap Schlenk, **2** (82 mg, 0.2 mmol) and excess of PCy_3 (280 mg, 1.0 mmol) were dissolved in 10 mL of CH_3CN. The solution was stirred at 70 °C for 15 h. During the reaction, a bright

yellow precipitate was gradually formed. After cooling down to room temperature, the supernatant solution was removed and the precipitate was further washed with CH_3CN (2 × 10 mL) and hexane (3 × 5 mL), dried again *in vacuo*. Yield: 91 mg, 50%. IR (ATR, cm^{-1}): *ν* (C–H) 2917, 2842, *ν* (NO) 1672. ^1H NMR (300.1 MHz, CD_2Cl_2, ppm): 3.09 (s, 3H, CH_3CN), 1.24–2.53 (m, 66H, $P(C_6H_{11})_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 34.3 (t, $J_{(PC)}$ = 10.1 Hz, P-C), 29.3, 28.6, 27.2. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, ppm): −11.10 (s). Anal. Calcd for $C_{38}H_{69}Cl_2N_2OP_2Re$ (889.03): C, 51.34; H, 7.82; N, 3.15. Found: C, 50.99; H, 7.56; N, 3.06.

[ReCl$_2$(NO)(P*i*Pr$_3$)$_2$(CH$_3$CN)] (3b). In a 50 mL Young-tap Schlenk, **2** (235 mg, 0.56 mmol) and excess of P*i*Pr$_3$ (0.50 mL, 2.20 mmol) were dissolved in 10 mL of CH_3CN and the solution was stirred at 70 °C for 24 h. The resulting dark-brown solution was dried *in vacuo* and the residue was extracted with CH_2Cl_2/pentane (1/20 v/v, 5 × 5 mL). The extracted yellow solution was dried *in vacuo*. Yield: 57 mg, 16%. IR (ATR, cm^{-1}): *ν* (NO) 1668. ^1H NMR (300.1 MHz, CD_2Cl_2, ppm): 3.07 (s, 3H, CH_3CN), 2.54 (m, 6H, P–C*H*$(CH_3)_2$), 1.34–1.43 (m, 36H, P–CH$(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 24.3 (t, $J_{(PC)}$ = 10.6 Hz, P–*C*H$(CH_3)_2$), 19.8 (s), 19.6 (s); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, ppm): −0.30 (s). Anal. Calcd for $C_{20}H_{45}Cl_2N_2OP_2Re$ (648.19): C, 37.03; H, 6.99; N, 4.32. Found: C, 37.20; H, 7.11; N, 4.13.

[ReCl$_2$(NO){P(*p*-tolyl)$_3$}$_2$(CH$_3$CN)] (3c). In a 50 mL Young-tap Schlenk, **2** (126 mg, 0.3 mmol) and an excess of P(*p*-tolyl)$_3$ (307 mg, 1.0 mmol) were dissolved in 10 mL of CH_3CN and the mixture was stirred at 70 °C for 8 h. During the reaction, an orange-yellow precipitate was gradually formed. After cooling down to room temperature, the supernatant solution was removed. The residue was washed with CH_3CN (4 × 5 mL) and dried *in vacuo*. Yield: 215 mg, 76%. IR (ATR, cm^{-1}): *ν* (CH_3CN): 2276, *ν* (NO) 1688. ^1H NMR (300.1 MHz, CD_2Cl_2, ppm): 7.20–7.66 (m, 24H, Ph), 2.37 (s, 18H, Ph–C*H*$_3$), 1.79 (s, 3H, CH_3CN); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 140.6, 135.0, 129.2, 21.6, 3.5. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, ppm): −0.96 (s). Anal. Calcd for $C_{44}H_{45}Cl_2N_2OP_2Re$ (936.90): C, 56.41; H, 4.84; N, 2.99. Found: C, 56.02; H, 4.43; N, 2.70.

[ReCl$_2$(NO)(PCy$_3$)$_2$(η^2-H$_2$)] (4a). In a 50 mL Young-tap Schlenk, **3a** (58 mg, 0.065 mmol) was dissolved in 10 mL of CH_2Cl_2. The nitrogen atmosphere was replaced with 1 bar of H_2 by using a freeze–pump–thaw cycle. The mixture was stirred at room temperature for 24 h. The resulting brown solution was dried *in vacuo* and washed with toluene (1 × 2 mL), dried again *in vacuo*. Yield: 48 g, 85%. IR (ATR, cm^{-1}): *ν* (C–H): 2925, 2852, *ν* (NO) 1674. ^{1}H-NMR (300.1 MHz, CD_2Cl_2, ppm): 2.61 (t, $^2J_{(PH)}$ = 18 Hz, T_1 = 39 ms, η^2-H$_2$), 2.56–1.33 (m, 66H, $P(C_6H_{11})_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 33.3 (t, $J_{(PC)}$ = 11 Hz, P–C), 29.6, 27.9, 26.8. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, ppm): 14.5 (br). Anal. Calcd for $C_{36}H_{68}Cl_2NOP_2Re$ (865.03): C, 50.87; H, 8.06; N, 1.65; Found: C, 50.40; H, 7.56; N, 1.25.

Preparation of [ReCl$_2$(NO)(P*i*Pr$_3$)$_2$(η^2-H$_2$)] (4b). In a 3 mL Young-tap NMR tube, **3b** (13 mg, 0.02 mmol) was dissolved in 0.5 mL of CD_2Cl_2. The nitrogen atmosphere was replaced with 1 bar of H_2 by using a freeze–pump–thaw cycle. The mixture was kept at room temperature for 24 h. NMR spectroscopy indicated that **4b** was formed in 84% yield with 16% of **3b** remained. At elevated temperatures (40 °C), the yield of **4b** doesn't improve. ^1H NMR (300.1 MHz, CD_2Cl_2, ppm): 2.87 (m, 6H, P-C*H*$(CH_3)_2$), 2.49 (t, $^2J_{(PH)}$ = 18 Hz, T_1 = 87 ms, η^2-H$_2$), 1.33–1.43 (m, 36H, P-CH(C*H*$_3$)$_2$). $^{31}P\{^1H\}$ NMR (80.9 MHz, CD_2Cl_2, ppm): 23.7 (br). IR (ATR, cm^{-1}): *ν* (C–H) 2929, 2852, *ν* (CH_3CN) 2259, *ν* (Re–H) 2002, *ν* (NO) 1648.

Preparation of [Re(Cl)(H)(NO)(PCy$_3$)$_2$(CH$_3$CN)] (5a). In a 3 mL Young-tap NMR tube, **3a** (24 mg, 0.027 mmol) and Et_3SiH (20 μL, 0.12 mmol) were dissolved in 0.5 mL of toluene-d_8. The solution was kept at 100 °C for 1 h affording a pink-violet solution, which quickly turned light-brown when it was cooled to room temperature. Some oily residue was also observed. NMR spectroscopy indicated the formation of **5a** in 98% yield with 2% of free PCy_3 ligand. ^1H NMR (300.1 MHz, benzene-d_6, ppm): 1.25–2.59 (m, 66H, $P(C_6H_{11})_3$), 1.11 (s, 3H, CH_3CN), −1.51 (t, $^2J_{(PH)}$ = 20 Hz, 1H, Re–H). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 35.1 (t, $J_{(PC)}$ = 10 Hz, P-C), 30.0 (s), 29.9 (s), 28.4 (m), 27.6 (s), 2.0 (s, *C*H$_3$CN). $^{31}P\{^1H\}$ NMR (121.5 MHz, benzene-d_6, ppm): 21.2 (s). IR (ATR, cm^{-1}): *ν* (C–H) 2929, 2852, *ν* (CH_3CN) 2259, *ν* (Re–H) 2002, *ν* (NO) 1648.

Preparation of [Re(Cl)(H)(NO)(P*i*Pr$_3$)$_2$(CH$_3$CN)] (5b). In a 3 mL Young-tap NMR tube, **3b** (20 mg, 0.03 mmol) and Et_3SiH (20 μL, 0.12 mmol) were dissolved in 0.5 mL of toluene-d_8. The solution was kept at 100 °C for 1 h affording a pink-violet solution, which quickly turned light-brown when it was cooled to room temperature. NMR spectroscopy indicated the formation of **5b** in over 99% yield. ^1H NMR (300.1 MHz, benzene-d_6, ppm): 2.72 (m, 6H, CH), 1.33–1.48 (m, 36H, CH_3), 1.08 (s, 3H, Re–CH_3CN), −1.75 (t, $^2J_{(PH)}$ = 20 Hz, 1H, Re–H). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 25.1 (t, $J_{(PC)}$ = 10 Hz, P-*C*H$(CH_3)_2$), 19.7 (s), 19.5 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, benzene-d_6, ppm): 31.6 (s). IR (ATR, cm^{-1}): *ν* (C–H) 2963, 2878, *ν* (CH_3CN) 2259, *ν* (Re–H) 2106, *ν* (NO) 1637.

Catalytic dehydrocoupling of Me$_2$NH·BH$_3$ by chloro nitrosyl Re(I) complexes. In a 3 mL Young-tap NMR tube, $Me_2NH{\cdot}BH_3$ (15 mg, 0.25 mmol) and 0.0025 mmol of Re(I) chloride catalyst (**2**, 1.0 mg; **3a**, 2.2 mg; **3b**, 1.6 mg, **3c**, 2.3 mg; **4a**, 2.1 mg) were mixed in 0.5 mL of dioxane or acetonitrile. The mixture was stirred at the given temperatures (23, 45, 80, 85 °C) for appropriate reaction times (2, 4, 24 h). When the reaction was carried out at 85 °C, bubbles of H_2 were released vigorously during the reaction and the NMR tube was vented every 30 min. After the reaction, the yield of $[Me_2N–BH_2]_2$ and other byproducts were determined by the integration of the ^{11}B NMR spectrum. ^{11}B NMR (96.28 MHz, ppm): *δ* −14.4 (q, J_{BH} = 96 Hz, $Me_2NH{\cdot}BH_3$), 4.5 (t, J_{BH} = 112 Hz, $[Me_2N–BH_2]_2$), 28.0 (d, J_{BH} = 132 Hz, $(Me_2NH)_2BH$).

Dehydrogenative silylation of styrenes with silanes catalyzed by chloro nitrosyl Re(I) complexes. In a 20 mL Young-tap Schlenk, 0.25 mmol of silane (Et_3SiH, 38 μL; Me_2PhSiH, 38 μL; Ph_3SiH, 65 mg), 0.5 mmol of various styrenes (*p*-methoxystyrene, 67 μL; *p*-methylstyrene, 66 μL; *p*-chlorostyrene, 60 μL; *p*-fluorostyrene, 60 μL; styrene, 57 μL; *m*-chlorostyrene, 63 μL; *m*-methylstyrene, 66 μL; *o*-fluorostyrene, 59 μL) and 0.0025 mmol of Re(I) chloride catalyst (**2**, 1.0 mg; **3a**, 2.2 mg; **3b**, 1.6 mg, **3c**, 2.3 mg; **4a**, 2.1 mg) were mixed in toluene-d_8 (0.5 mL). The mixture was kept stirring in the closed system at the given temperatures (70, 100, 110 °C).

After appropriate reaction times the yield and product distribution were determined by ^{1}H NMR spectroscopy according to the characteristic chemical shifts (with typical coupling constants) of (*E*)-CH=C*H*SiR′$_3$, (*Z*)-CH=C*H*SiR′$_3$, CH_2=C*H*Ar and -CH_2–CH_2SiR′$_3$ moieties of known products. The data determined by NMR were further verified by GC–MS and proved to be quite reliable. The work-up procedures and spectroscopic data of unreported products are listed below:

(*E*)-1-(*m*-methylstyryl)-2-(triethylsilyl)ethylene. In a 30 mL Young-Schlenk tube, catalytic amount of **2** (4 mg, 0.01 mmol), substrate Et_3SiH (152 μL, 1.00 mmol) and *m*-methylstyrene (264 μL, 2.00 mmol) were added. The solution was mixed in toluene-d_8 (0.8 mL) and kept stirring in the open system at 110 °C for 18 h. NMR spectroscopy indicated 100% conversion of the starting material to the vinylsilane product. The solvent was evaporated *in vacuo* and the residue was chromatographed on a silica gel column. Pure (*E*)-1-(*m*-methylstyryl)-2-(triethylsilyl)ethylene was isolated (140 mg, 60%) as colorless oil using 1 : 50 EtOAc/petroether mixture as eluent. ^{1}H-NMR (300.1 MHz, $CDCl_3$, ppm): δ 6.78–7.08 (m, 4H, Ar*H*), 6.81 (d, $^3J_{(HH)trans}$ = 18 Hz, 1H, *trans*-Ar–C*H*=CH), 6.36 (d, $^3J_{(HH)trans}$ = 18 Hz, 1H, *trans*-CH=C*H*–Si), 2.10 (s, 3H, Ar–CH_3), 0.98 (t,^3J = 6 Hz, 9H, CH_3), 0.62 (q,^3J = 6 Hz, 6H, CH_2). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, ppm): δ 144.9, 138.5, 138.0, 128.7, 128.4, 127.0, 125.6, 123.5, 21.4, 7.4, 3.5. GC-MS: *m*/*z*: 203.3 [M – Et]$^{+\cdot}$.

(*E*)-1-(*m*-chlorostyryl)-2-(triethylsilyl)ethylene. By a similar procedure (Et_3SiH, 152 μL; *m*-chlorostyrene, 252 μL; 110 °C, 24 h, 1 : 100 EtOAc/petroether), pure (*E*)-1-(*m*-chlorostyryl)-2-(dimethylphenylsilyl)ethylene was isolated in 38% yield (96 mg). ^{1}H-NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.23–7.45 (m, 4H, Ar*H*), 6.84 (d, $^3J_{(HH)trans}$ = 19 Hz, 1H, *trans*-Ar–C*H*=CH), 6.47 (d, $^3J_{(HH)trans}$ = 19 Hz, 1H, *trans*-CH=C*H*–Si), 1.03 (t,^3J = 6 Hz, 9H, CH_3), 0.72 (q,^3J = 6 Hz, 6H, CH_2). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, ppm): δ 143.2, 140.3, 134.5, 129.7, 128.0, 127.7, 126.2, 124.6, 7.4, 3.5. GC-MS: *m*/*z*: 223.1 [M – Et]$^{+\cdot}$.

(*E*)-1-(*m*-methylstyryl)-2-(dimethylphenylsilyl)ethylene. By a similar procedure (Me_2PhSiH, 152 μL; *m*-methylstyrene, 264 μL; 110 °C, 24 h, 1 : 80 EtOAc/petroether), pure (*E*)-1-(*m*-methylstyryl)-2-(dimethylphenylsilyl)ethylene was isolated in 75% yield (192 mg). ^{1}H-NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.34–7.70 (m, 9H, Ar*H*), 7.03 (d, $^3J_{(HH)trans}$ = 21 Hz, 1H, *trans*-Ar–C*H*=CH), 6.68 (d, $^3J_{(HH)trans}$ = 21 Hz, 1H, *trans*-CH=C*H*–Si), 2.46 (s, 3H, Ar–CH_3), 0.57 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, ppm): δ 145.5, 138.1, 134.0, 129.1, 129.0, 128.5, 127.9, 127.2, 126.8, 123.8, 21.5, –2.4. GC-MS: *m*/*z*: 252.2 [M]$^{+\cdot}$.

(*E*)-1-(*o*-fluorostyryl)-2-(dimethylphenylsilyl)ethylene. By a similar procedure (Me_2PhSiH, 152 μL; *o*-fluorostyrene, 240 μL; 110 °C, 24 h, 1 : 80 EtOAc/petroether), pure (*E*)-1-(*o*-fluorostyryl)-2-(dimethylphenylsilyl)ethylene was isolated in 47% yield (119 mg).^{1}H-NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.15–7.65 (m, 9H, Ar*H*), 7.25 (d, $^3J_{(HH)trans}$ = 19 Hz, 1H, *trans*-Ar–C*H*=CH), 6.72 (d, $^3J_{(HH)trans}$ = 19 Hz, 1H, *trans*-CH=C*H*–Si), 0.53 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, ppm): δ 161.9, 136.8, 133.9, 130.0, 129.5, 129.4, 129.2, 127.9, 126.8, 124.1, 115.9, 115.6, –2.5. GC-MS: *m*/*z*: 241.2 [M – Me]$^{+\cdot}$.

Hydrosilylation of ketones and aryl aldehydes with silanes catalyzed by chloro nitrosyl Re(I) complexes. In a 3 mL Young-tap NMR tube, 0.25 mmol of ketone (benzophenone, 45 mg; acetophenone, 30 μL; 3,3-dimethylbutan-2-one, 31 μL; cyclopentanone, 22 μL; cyclohexanone, 26 μL) or 0.25 mmol of aryl aldehyde (*p*-tolualdehyde, 30 μL; 1-naphthaldehyde, 27 μL; *p*-methoxybenzaldehyde, 30 μL; *p*-fluorobenzaldehyde, 27 μL) was mixed with 0.28 mmol (1.1 equiv.) of silane (Et_3SiH, 43 μL; iPr_3SiH, 57 μL; Ph_3SiH, 73 mg) and 0.0025 mmol (1 mol% to ketone or aryl aldehyde) of the Re(I) chloride complex (**2**, 1.0 mg; **3a**, 2.2 mg; **3b**, 1.6 mg, **3c**, 2.3 mg; **4a**, 2.1 mg) in chlorobenzene-d_5 (0.5 mL). The mixture was kept at an appropriate temperature (23, 80, 100, 110 °C). Progress of the reaction was monitored by ^{1}H NMR spectroscopy.

Kinetic measurements. The kinetic test for **2** catalyzed dehydrogenative silylation was carried out in a Young–Schlenk flask loaded with 4 mg of **2** and 1.5 mL of toluene-d_8 and kept at 110 °C under N_2. Solutions were prepared by mixing Et_3SiH and *p*-methylstyrene in different ratios: **I** (Et_3SiH, 152 μL; *p*-methylstyrene, 266 μL), **II** (Et_3SiH, 152 μL; *p*-methylstyrene, 532 μL), **III** (Et_3SiH, 304 μL; *p*-methylstyrene, 266 μL). Samples were taken from the solution every 5 min and studied by ^{1}H NMR ($CDCl_3$) to determine the ratios between reactants and products.

The kinetic test for **2** catalyzed hydrosilylation was carried out in a Young–Schlenk flask loaded with 4 mg of **2** and 1.0 mL of toluene-d_8 and kept at 110 °C under N_2. Solutions were prepared by mixing Et_3SiH and acetophenone in different ratios: **I** (Et_3SiH, 86 μL; PhCOMe, 60 μL), **II** (Et_3SiH, 86 μL; PhCOMe, 120 μL), **III** (Et_3SiH, 172 μL; PhCOMe, 60 μL). Samples were taken from the solution every 5 min and studied by ^{1}H NMR ($CDCl_3$) to determine the ratios between reactants and products.

X-ray diffraction analyses

Relevant details about the structure refinements are given in Table 4, and selected geometrical parameters are included in the captions of the corresponding figures (Fig. 1 and 2). Intensity data were collected at 183(2) K with an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector, and a single wavelength Enhance X-ray source with MoKα radiation, λ = 0.71073 Å).[25] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption corrections [26] were performed with the Oxford program suite CrysAlisPro.[27] The crystal structures were solved with SHELXS-97 [28] using direct methods. The structure refinements were performed by full-matrix least-squares on F^2 with SHELXL-97.[28] All programs used during the crystal structure determination process are included in the WINGX software.[29] The program PLATON [30] was used to check the result of the X-ray analyses. CCDC 783380 (**3a**) and 783381 (**3c**) contain the supplementary crystallographic data (excluding structure factors) for this paper.†

In the crystal structure of **3a**, the *trans*-nitrosyl and chloride ligand are substitutionally disordered over two positions with site-occupancy factors of 0.747(3) and 0.253(3). The Checkcif report detected additional pseudo-symmetry elements which would lead to the space group $P2_1/c$. The Flack parameter of 0.521(6)

Table 4 Crystallographic data for compounds **3a** and **3c**[a]

	3a	**3c**
Empirical formula	$C_{38}H_{69}Cl_2N_2OP_2Re$	$C_{44}H_{45}Cl_2N_2OP_2Re$
Formula weight (g mol^{-1})	889	936.87
Temperature (K)	183(2)	183(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$
a (Å)	9.5051(1)	10.8035(4)
b (Å)	16.2268(1)	12.5280(5)
c (Å)	13.0872(1)	15.6262(6)
α (deg)	90	79.631(3)
β (deg)	95.074(1)	86.029(3)
γ (deg)	90	75.399(3)
Volume (Å^3)	2010.63(3)	2012.59(14)
Z, density (calcd) (Mg m^{-3})	2, 1.468	2, 1.546
Abs coefficient (mm^{-1})	3.265 mm	3.268 mm
F(000)	916	940
Crystal size (mm^3)	0.35 × 0.25 × 0.20	0.43 × 0.28 × 0.13
θ range (deg)	2.49 to 33.14	2.25 to 30.51
Reflections collected	63 043	35 112
Reflections unique	15 310/R_{int} = 0.031	12 287/R_{int} = 0.049
Completeness to θ (%)	100	99.9
Absorption correction	Semi-empirical from equivalents	
Max/min transmission	0.538 and 0.423	0.654 and 0.369
Data/restraints/parameters	13 893/3/428	8670/0/486
Goodness-of-fit on F^2	1.036	0.981
R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0296, 0.0635	0.0345, 0.0733
R_1 and wR_2 indices (all data)	0.0351, 0.0658	0.0526, 0.0767

[a] The unweighted R-factor is $R_1 = \sum(F_o - F_c)/\sum F_o$; $I > 2\sigma(I)$ and the weighted R-factor is $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

speaks also indicates a centrosymmetric space group. Nevertheless, the solution in $P2_1/c$ imposes the metal center to lie on a crystallographic center of inversion and consequently the four ligands in the equatorial plane (NO, 2Cl and $NCCH_3$) to be disordered over two positions with site-occupancy factor of 0.5. The determination in $P2_1$ clearly shows that only the *trans* NO and Cl ligands are disordered and in a ratio different than 0.5. Furthermore, many atoms are non-positive definite in $P2_1/c$ or exhibit elongated ellipsoids. It seems to be a typical case of pseudo-symmetry, and we consider ultimately that $P2_1$ is the best choice. In the crystal structure of **3c**, the *trans*-nitrosyl and chloride ligands are also substitutionally disordered over two positions with site-occupancy factors of 0.501(1) and 0.499(1). No classical hydrogen bonding was found in both crystal structures.

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