

A Convenient and Efficient Rhenium-Catalyzed Hydrosilylation of Ketones and Aldehydes

Hailin Dong^a and Heinz Berke^{a,*}

^a Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland
Fax: (+41)-1-63-568-02; phone: (+41)-1-63-546-81; e-mail: hberke@aci.uzh.ch

Received: April 9, 2009; Published online: July 27, 2009

Abstract: The easily available rhenium(I) complex $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$ catalyzes the homogeneous hydrosilylation of a great variety of organic carbonyl compounds (ketones and aldehydes). The reaction is quite sensitive to the solvent applied. Chlorobenzene was found to be superior over all the other solvents used. Various aliphatic and aromatic silanes were tested. Excellent yields were achieved at 85 °C in chlorobenzene using triethylsilane, the reaction affording TOF values of up to 495 h^{-1} . A possible reaction mechanism for the hydrosilylation is presented.

Keywords: aldehydes; homogeneous catalysis; hydrosilylation; ketones; reaction mechanism; rhenium

Transition metal-catalyzed hydrosilylations are useful alternatives to hydrogenations and transfer hydrogenations of C=C and carbon-heteroatom multiple bonds.^[1] In recent years hydrosilylation of various organic carbonyl compounds has made considerable progress and became a major tool of synthetic organic chemistry and organosilicon chemistry as well as providing efficient and versatile access to new compounds.^[1p,q] Asymmetric hydrosilylations with high enantioselectivities are also been well documented.^[1b,d,m,n] In industry hydrosilylation has become also an appropriate method to produce organosilicon compounds, in particular with respect to the functionalization of polymers.^[2]

Exploring rhenium complexes for their use as catalysts, our early work has led to the development of several efficient systems for transfer hydrogenation, dehydrogenative silylation and hydrosilylation.^[3] Recently, hydrosilylation reactions using various metals such as zinc,^[4] iron,^[5] rhodium^[6] and copper^[7] have been reported, including the work of other authors with rhenium catalysts.^[8] Toste et al.^[8a-c] and Abu-Omar et al.^[8d-g] proposed new mechanisms for the hy-

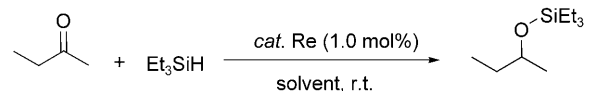
dro-silylation using high oxidation state rhenium oxo complexes as catalysts.

We report here the efficient hydrosilylation of various ketones and aryl aldehydes catalyzed by a phosphine-free rhenium(I) system. The reaction was carried out at room temperature with relatively low catalyst loading (0.2–1.0 mol%) giving good to excellent yields. The TOF values of the reaction can be greatly enhanced by elevating the reaction temperature to 85 °C.

Several rhenium complexes were examined in various solvents at room temperature for the hydrosilylation of butanone with triethylsilane as a model reaction (Table 1). In this reaction butanone was converted to the corresponding silyl ether. The yield of *sec*-butoxytriethylsilane was dramatically affected by the type of the rhenium complexes and solvents used in the reaction. $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$ proved to be the most reactive complex the reaction going to completion in 1.5 h (entry 1). $[\text{Re}(\text{THF})(\text{CH}_3\text{CN})_2\text{Br}_2(\text{NO})]$ gave a good yield, but the reaction time required was 2.5 h (entry 9). Other rhenium complexes containing various phosphines gave only modest yields after 1–2 h (entries 11–14). Several water-soluble rhenium complexes showed very little or no activity (entries 15–17). The rhenium complexes, such as $[\text{Re}(\text{CH}_3\text{CN})_3\text{Cl}_2(\text{NO})]$, $[\text{Re}(\text{TACN})(\text{CO})_2\text{Br}]$, did not exhibit any activity at all (entries 10 and 18).

When the reaction was carried out in coordinating solvents such as THF and CH_3CN , only modest yields were obtained (entries 3 and 4). When aromatic hydrocarbons, such as benzene and toluene were used as solvents, the reaction proceeded very slowly. In solvents of higher polarity, like DMF and DMSO, the yields were also very low. Dichloromethane and dioxane were therefore proper choices of reaction solvents (entries 1–2).

In order to understand the influence of the silane applied in the catalytic hydrosilylation, the reactions of a variety of silanes were tested with butanone in dichloromethane at room temperature (Table 2). It appeared that the choice of the silane had a significant influence on the outcome of the reaction. Triethylsi-

Table 1. Rhenium-catalyzed hydrosilylation of butanone with triethylsilane.^[a]


Entry	Catalyst	Solvent	<i>t</i> [h]	Yield [%] ^[b]
1	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	CH ₂ Cl ₂	1.5	99
2	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	Dioxane	1.5	90
3	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	THF	1.5	69
4	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	CH ₃ CN	1.5	45
5	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	DMF	1.5	50
6	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	Benzene	1.5	75
7	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	DMSO	1.5	10
8	[Re(CH ₃ CN) ₃ Br ₂ (NO)]	Toluene	1.5	8
9	[Re(THF)(CH ₃ CN) ₂ Br ₂ (NO)]	CH ₂ Cl ₂	2.0	75
10	[Re(CH ₃ CN) ₃ Cl ₂ (NO)]	CH ₂ Cl ₂	10	0
		Dioxane		
11	[Re(PTA) ₂ Br ₂ (NO)(CH ₃ CN)] ^[c]	CH ₂ Cl ₂	10	0
		Dioxane		
12	[Re(PPh ₃) ₂ Br ₂ (NO)(CH ₃ CN)]	CH ₂ Cl ₂	18	5
13	[Re(PCy ₃) ₂ Br ₂ (NO)(CH ₃ CN)]	CH ₂ Cl ₂	18	37
14	[Re(P ^{<i>i</i>} Pr ₃) ₂ Br ₂ (NO)(CH ₃ CN)]	CH ₂ Cl ₂	18	40
15	[Re(PTA) ₃ Br ₂ (NO)]	CH ₂ Cl ₂	10	1.3
		Dioxane		0.8
16	[Re(PTAH) ₂ Br ₂ (NO)(CH ₃ CN)][Br] ₂	CH ₂ Cl ₂	10	0
		Dioxane		
17	[Re(PTAH)(PTA)Br ₂ (NO)(CH ₃ CN)][Br]	CH ₂ Cl ₂	10	0
		Dioxane		
18	[Re(TACN) ^[d] (CO) ₂ Br]	CH ₂ Cl ₂	10	0
		DMSO		

^[a] All reactions were carried out with butanone (0.5 mmol), Et₃SiH (0.6 mmol), and the rhenium complex (1.0 mol%) in the appropriate solvent (0.8 mL) at room temperature under a nitrogen atmosphere. Progress of the reaction was monitored by ¹H NMR.

^[b] Yield on the basis of the integration of the ¹H NMR spectrum.

^[c] PTA = 1,3,5-triaza-7-phosphaadamantane.

^[d] TACN = 1,4,7-triazacyclononane.

lane proved to be the most suitable silane source for the reaction with yields of 99% in 1.5 h (entry 1). In general, aliphatic silanes led to better yields in comparison with arylsilanes. An exception was *i*-Pr₃SiH, which gave a low yield, presumably due to its bulky substituents, as also did HSi(SiMe₃)₃ (entries 5 and 10). Secondary silanes, alkoxysilanes and polysilanes also did not provide satisfactory yields (entries 7–9).

A variety of ketones were reduced to the corresponding silyl ethers catalyzed by the [Re(CH₃CN)₃Br₂(NO)] complex (Table 3). In most cases the reactions were complete within 2 h or less with excellent yields (entries 1–8). Substrates containing bulky groups, such as 3, 4-dihydro-1(2*H*)-naphthalenone, 9-fluorenone and 2-decanone, required 3 h for

Table 2. Hydrosilylation of butanone catalyzed by the [Re(CH₃CN)₃Br₂(NO)] complex.^[a]

Entry	Silane	<i>t</i> [h]	Yield [%] ^[b]
1	HSiEt ₃	1.5	99
2	PhSiH ₃	2	31
3	Ph ₂ MeSiH	2	54
4	PhMe ₂ SiH	2	51
5	(<i>i</i> Pr) ₃ SiH	2	10
6	(<i>n</i> Bu) ₃ SiH	2	67
7	Ph ₂ SiH ₂	2	26
8	HSi(OMe) ₃	2	25
9	PMHS ^[c]	2	29
10	HSi(SiMe ₃) ₃	2	10

^[a] Reaction conditions: 1.0 mol% of the complex [Re(CH₃CN)₃Br₂(NO)], 0.5 mmol of butanone and 1.2 equiv. of appropriate silanes in dichloromethane (0.8 mL) at room temperature for the given time, under a nitrogen atmosphere.

^[b] Yield on the basis of the integration of the ¹H NMR spectrum.

^[c] Polymethylhydrosiloxane.

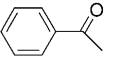
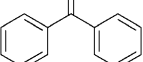
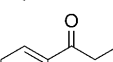
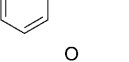
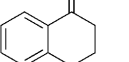
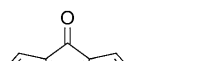
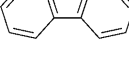
obtaining similar yields (entries 9–11). 2, 2-Dimethyl-1-phenylpropan-1-one was converted to the silyl ether with the yield of 58% after 8 h presumably due to the hindrance of the bulky isopropyl group.

Trying to extend the scope of the rhenium-catalyzed hydrosilylation, a screening of various aldehyde substrates was initiated bearing a variety of substituents at varying aromatic positions (Table 4). Benzaldehyde, 2-phenylpropanal and 4-methylbenzaldehyde gave high yields of 95%, 99% and 98%, respectively (entries 1–3). The reaction proceeded smoothly independent of the position of the aryl substitution (*ortho*, *meta* or *para*), which did not affect the reaction rate to a great extent. Substrates with methyl or chlorine substitution required relatively longer reaction times to render satisfactory yields. The catalyst showed great tolerance for electron-withdrawing and electron-donating substitution on the aryl rings (entries 7–12). The aliphatic ketones worked better than aromatic ones presumably because of their higher electron-donating abilities and consequently their better ligand properties.

To improve the catalytic activity (TOFs) and for appropriate practical purposes, higher temperatures and lower catalyst loadings were tested. Representative yields for the hydrosilylation of various organic carbonyl compounds with triethylsilane are summarized in Table 5. Low catalyst loadings (0.2 mol%) and relatively shorter reaction times (1–2 h) were successful when the reactions were carried out in chlorobenzene at 85 °C.

A possible mechanism for the hydrosilylation of ketones catalyzed by the [Re(CH₃CN)₃Br₂(NO)] complex is proposed in Figure 1. [Re(CH₃CN)₃Br₂(NO)]

Table 3. $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$ -catalyzed hydrosilylation of ketones with triethylsilane.^[a]

Entry	Substrate	<i>t</i> [h]	Yield [%] ^[b]
1		1.5	98 ^[c]
2		1.5	99 ^[c]
3		1.5	95 ^[c]
4		1.5	99
5		1.5	98 ^[c]
6		1.5	93
7		1.5	99 ^[c]
8		2	96
9		5	90
10		3	95
11		3	92
12		8	58

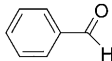
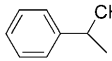
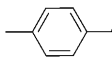
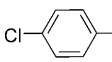
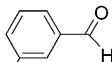
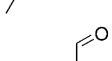
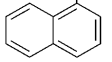
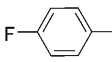
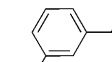
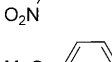
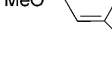
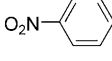
^[a] Reaction conditions: 1.0 mol% of the complex $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$, 0.5 mmol of ketone and 1.2 equiv. of HSiEt_3 in dichloromethane (0.8 mL) at room temperature for given time, under nitrogen atmosphere.

^[b] Yield on the basis of the integration of the ^1H NMR spectrum.

^[c] Yield measured by GC-MS, based on the ketone.

takes the role of a pre-catalyst *via* primary dissociation of one of the CH_3CN ligands. In the ^1H NMR spectrum this dissociation became evident by a singlet at 1.98 ppm assigned to the CH_3 group of free CH_3CN . Then a silane molecule coordinates to the rhenium center of complex **2**, forming the $\eta^2\text{-R}_3\text{SiH}$ complex **3**. The ^1H -NOE experiment provides 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 could be assigned to an Re attached Si-H group. For the alternative structure of an oxidatively added silane with

Table 4. $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$ -catalyzed hydrosilylation of aldehydes with HSiEt_3 ^[a]

Entry	Substrate	<i>t</i> [h]	Yield [%] ^[b]
1		1.5	95
2		2	99
3		2	98
4		2	94
5		2	93
6		2	91
7		4	89
8		4	87
9		6	99
10		8	95
11		8	95
12		8	90

^[a] Reaction conditions: 1.0 mol% of the complex $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$, 0.5 mmol substrate, and 1.2 equiv. of HSiEt_3 in dichloromethane (0.8 mL) at room temperature, under nitrogen atmosphere. Progress of the reaction was monitored by ^1H NMR.

^[b] Yield on the basis of the integration of the ^1H NMR spectrum.

a classical $\text{Re}(\text{silyl})\text{hydride}$ structure a sharp line (<1 Hz) would be expected for the H_{Re} group. In addition a long range C,H -correlation experiment was carried out in support of the simultaneous presence of a classical rhenium hydride and acetonitrile in the ligand sphere. However, the NMR response was negative, since scalar coupling between H_{Re} and NC-CH_3 was not observed. This latter experiment does not allow the conclusion that oxidative addition would not take place. We take two alternative pathways into consideration, which are direct inter-ligand transfer of a hydride from the silane to the C_{ketone} atom or indeed oxidative addition of the silane and then β -hydride

Table 5. $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$ -catalyzed hydrosilylation of organic carbonyl compounds.^[a]

$\text{R}-\text{C}(=\text{O})-\text{R}' + \text{H}-\text{SiEt}_3 \xrightarrow[\text{chlorobenzene, 85}^\circ\text{C}]{\text{cat. Re}} \text{R}-\text{CH}(\text{H})-\text{SiEt}_3$				
Entry	Substrate	<i>t</i> [h]	Yield [%] ^[b]	TOF ^[c]
1		1	95	475
2		1	99	495
3		1	71	355
4		1.5	94	313
5		1.5	95	317
6		1	89	445
7		1	90	450
8		1.5	90	300
9		1.5	92	307
10		1.5	85	283
11		2	88	220

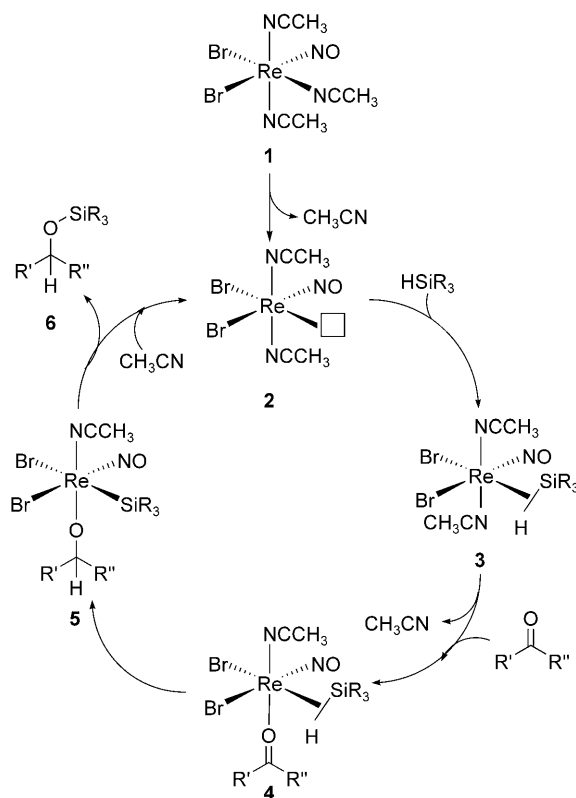
^[a] Reaction conditions: 0.2 mol% of the complex $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$, 2.5 mmol of substrate, and 1.5 equiv. of HSiEt_3 in chlorobenzene (2.0 mL) at 85°C for the given time, under nitrogen atmosphere.

^[b] Yield on the basis of the integration of the ^1H NMR spectrum.

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

transfer to form in either case the organyloxy complex **5**. The catalytic cycle “closes” with reductive elimination of the siloxy product **6** and re-formation of complex **2**. Attempts to isolate the $\eta^2\text{-R}_3\text{SiH}$ complex **3** were not successful, presumably due to its instability. The solution turns black after removal of the solvent under vacuum. Further detailed studies are currently underway to achieve full understanding of the mechanism.

In summary, we have successfully explored a quite generally applicable phosphine-free rhenium(I) hydrosilylation catalysis utilizing the easily available $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$ complex. A great variety of silyl ethers derived from ketones and aryl aldehydes were accessed in excellent yields at room temperature

**Figure 1.** Proposed pathway for the hydrosilylation of a ketone, $\text{R}'\text{R}''\text{C}=\text{O}$, catalyzed by the $[\text{Re}(\text{CH}_3\text{CN})_3\text{Br}_2(\text{NO})]$ complex

or 85°C and with reasonable activities of the catalyst. A plausible mechanism for this hydrosilylation has been put forward, which follows a course with primary addition of the silane to the rhenium center and consecutive H-shift and silyl transfer, the latter step *via* reductive elimination to generate the silyl ethers. This catalysis is suggested to function so well, because of a facile $\text{Re}(\text{I})$ and $\text{Re}(\text{III})$ redox interplay in the given ligand environment. Further studies regarding the detailed mechanism and the extension of this rhenium-mediated catalysis to the hydrosilylation of olefins are in progress.

Experimental Section

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 N_2 atmosphere using standard procedures and were degassed by freeze-thaw cycles prior to use. The following rhenium complexes: $[\text{Re}(\text{NO})(\text{PPh}_3)_2(\text{CH}_3\text{CN})\text{Br}_2]$,^[9] $[\text{Re}(\text{NO})(\text{PCy}_3)_2(\text{CH}_3\text{CN})\text{Br}_2]$,^[9] $[\text{Re}(\text{NO})(\text{P}^i\text{Pr}_3)_2(\text{CH}_3\text{CN})\text{Br}_2]$,^[9] $[\text{Re}(\text{NO})(\text{CH}_3\text{CN})_3\text{Br}_2]$,^[10] $[\text{Re}(\text{THF})(\text{CH}_3\text{CN})_2\text{Br}_2(\text{NO})]$,^[10]

$[\text{Re}(\text{PTA})_2\text{Br}_2(\text{NO})(\text{CH}_3\text{CN})]$,^[10] $[\text{Re}(\text{PTA})_3\text{Br}_2(\text{NO})]$,^[11] $[\text{Re}(\text{PTAH})_2\text{Br}_2(\text{NO})(\text{CH}_3\text{CN})][\text{Br}]_2$,^[11] $[\text{Re}(\text{PTAH})(\text{PTA})\text{Br}_2(\text{CH}_3\text{CN})(\text{NO})][\text{Br}]$,^[11] $[\text{Re}(\text{CH}_3\text{CN})_3\text{Cl}_2(\text{NO})]$,^[12] and $[\text{Re}(\text{TACN})\text{Br}(\text{CO})_2]$ ^[13] were prepared according to known procedures. Except for the rhenium compounds, all the chemicals were purchased from Aldrich Chemical Co. or Fluka. Unless otherwise noted all commercial materials (silanes, ketones and aldehydes) were used without purification. ^1H , ^{11}B , ^{31}P and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Gemini 300 (299.78 MHz), or on a Varian Mercury 200 (199.78 MHz) spectrometer. GC-MS analyses were carried out on a CP-3800 Saturn 2000 MS/MS spectrometer (CP-Sil8CB low bleed/MS 30 m, ID 0.25 mm, OD 0.39 mm, Film thickness 0.25 μm from Chrompack).

General Procedure for the Catalytic Hydrosilylations according to Tables 1–4

A solution of the appropriate substrates (0.5 mmol) and the silanes (0.6 mmol) and the given catalytic amount of the rhenium complex in the given solvent (0.8 mL) was stirred for an appropriate period of time at room temperature under a nitrogen atmosphere. Upon completion, the reaction mixture was filtered over celite. The resulting solution was analyzed by NMR spectroscopy or GC-MS. The obtained NMR data of the silyl ethers were identical to those of the literatures.^[3d,8a,f,g] The yields are listed in Table 1, Table 2, Table 3 and Table 4. The GC-MS analysis furnished the retention time listed in the following (t_{R} = retention time, CH_2Cl_2 was used as the solvent): triethyl(isopropoxy)silane: m/z = 174.1, t_{R} = 2.73 min; *sec*-butoxytriethylsilane: m/z = 188.2, t_{R} = 3.43 min; triethyl(3-methylbutan-2-yloxy)silane: m/z = 202.2, t_{R} = 5.17 min; cyclopentyl-oxytriethylsilane: m/z = 200.2, t_{R} = 4.63 min; benzhydryloxytriethylsilane: m/z = 298.2, t_{R} = 9.02 min.

General Procedure for the Catalytic Hydrosilylations of Table 5

Appropriate amounts of the substrate (2.5 mmol), silane (3.75 mmol) and catalytic amounts of the rhenium complex (0.2 mmol%) in chlorobenzene were placed a Young tap Schlenk tube according to the procedures of the hydrosilylations of Tables 1–4. The reaction mixture was heated to 85 °C and stirred for the required reaction time. Upon completion, the reaction mixture was filtered over Celite. The resulting solution was analyzed by NMR spectroscopy. The found resonances were in accord with those of the literature. The yields were determined by integration of the ^1H NMR signals.

Acknowledgements

We gratefully acknowledge financial support from the Swiss National Science Foundation and the funds of the University of Zurich.

References

- a) F. Buch, J. Brettar, S. Harder, *Angew. Chem.* **2006**, *118*, 2807–2811; *Angew. Chem. Int. Ed.* **2006**, *45*, 2741–2745; b) A. Corma, C. Gonzalez-Arellano, M. Iglesias, F. Sanchez, *Angew. Chem.* **2007**, *119*, 7966–7968; *Angew. Chem. Int. Ed.* **2007**, *46*, 7820–7822; c) A. Heufling, F. Pohlki, I. Bytschkov, S. Doye, *Angew. Chem.* **2005**, *117*, 3011–3013; *Angew. Chem. Int. Ed.* **2005**, *44*, 2951–2954; d) N. S. Shaikh, S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 2531–2535; *Angew. Chem. Int. Ed.* **2008**, *47*, 2497–2501; e) B. Tao, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4048–4050; *Angew. Chem. Int. Ed.* **2002**, *41*, 3892–3894; f) H. Ito, T. Kato, M. Sawamura, *Chem. Asian J.* **2007**, *2*, 1436–1446; g) O. Buisine, G. Berthon-Gelloz, J. F. Briere, S. Sterin, G. Mignani, P. Branlard, B. Tinant, J. P. Declercq, I. E. Marko, *Chem. Commun.* **2005**, 3856–3858; h) A. C. Fernandes, R. Fernandes, C. C. Romao, B. Royo, *Chem. Commun.* **2005**, 213–214; i) H. Nishiyama, A. Furuta, *Chem. Commun.* **2007**, 760–762; j) B. M. Wile, M. Stradiotto, *Chem. Commun.* **2006**, 4104–4106; k) M. D. Fryzuk, B. A. MacKay, B. O. Patrick, *J. Am. Chem. Soc.* **2003**, *125*, 3234–3235; l) P. B. Glaser, T. D. Tilley, *J. Am. Chem. Soc.* **2003**, *125*, 13640–13641; m) J. W. Han, N. Tokunaga, T. Hayashi, *J. Am. Chem. Soc.* **2001**, *123*, 12915–12916; n) J. F. Jensen, B. Y. Svendsen, T. V. Cour, H. L. Pedersen, M. Johannsen, *J. Am. Chem. Soc.* **2002**, *124*, 4558–4559; o) B. H. Lipshutz, K. Noson, W. Chrisman, A. Lower, *J. Am. Chem. Soc.* **2003**, *125*, 8779–8789; p) T. Shimada, K. Mukaide, A. Shinohara, J. W. Han, T. Hayashi, *J. Am. Chem. Soc.* **2002**, *124*, 1584–1585; q) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2005**, *127*, 17644–17655; r) B. M. Trost, Z. T. Ball, T. Joge, *J. Am. Chem. Soc.* **2002**, *124*, 7922–7923.
- J. W. Sprengers, M. de Greef, M. A. Duin, C. J. Elsevier, *Eur. J. Inorg. Chem.* **2003**, 3811–3819.
- a) Y. Jiang, H. Berke, *Chem. Commun.* **2007**, 3571–3573; b) W. J. Huang, H. Berke, *Chimia* **2005**, *59*, 113–115.
- a) V. Bette, A. Mortreux, D. Savoia, J. F. Carpentier, *Adv. Synth. Catal.* **2005**, *347*, 289–302; b) B. M. Park, S. Mun, J. Yun, *Adv. Synth. Catal.* **2006**, *348*, 1029–1032.
- S. Gaillard, J. L. Renaud, *ChemSusChem* **2008**, *1*, 505–509.
- M. Anada, M. Tanaka, K. Suzuki, H. Nambu, S. Hashimoto, *Chem. Pharm. Bull.* **2006**, *54*, 1622–1623.
- a) S. Diez-Gonzalez, H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *J. Org. Chem.* **2005**, *70*, 4784–4796; b) S. Diez-Gonzalez, E. D. Stevens, N. M. Scott, J. L. Petersen, S. P. Nolan, *Chem. Eur. J.* **2008**, *14*, 158–168.
- a) J. J. Kennedy-Smith, K. A. Nolin, H. P. Gunterman, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 4056–4057; b) K. A. Nolin, R. W. Ahn, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 12462–12463; c) K. A. Nolin, J. R. Krumper, M. D. Pluth, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 14684–14696; d) L. W. Chung, Y. D. Wu, B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2003**, *125*, 11578–11582; e) G. Du, M. M. Abu-Omar, *Curr. Org. Chem.* **2008**, *12*, 1185–1198; f) G. Du, P. E. Fanwick, M. M. Abu-Omar, *Inorg. Chim. Acta*

- 2008, 361, 3184–3192; g) G. D. Du, M. M. Abu-Omar, *Organometallics* **2006**, 25, 4920–4923; h) P. M. Reis, B. Royo, *Catal. Commun.* **2007**, 8, 1057–1059; i) E. A. Ison, E. R. Trivedi, R. A. Corbin, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2005**, 127, 15374–15375.
- [9] A. Choualeb, O. Blacque, H. W. Schmalle, T. Fox, T. Hildebrand, H. Berke, *Eur. J. Inorg. Chem.* **2007**, 33, 5246–5261.
- [10] A. Choualeb, E. Maccaroni, O. Blacque, H. W. Schmalle, H. Berke, *Organometallics* **2008**, 27, 3474–3481.
- [11] E. Maccaroni, *Dissertation*, University of Zurich, **2007**.
- [12] Y. Jiang, *Dissertation*, University of Zurich, **2009**.
- [13] F. Zobi, B. Spingler, R. Alberto, *Dalton Trans.* **2008**, 5287–5289.
-