Rare-Earth Catalysis

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[(NHC)Yb{N($SiMe_3$)$_2$}$_2$]-Catalyzed Cross-Dehydrogenative Coupling of Silanes with Amines**

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Silylamines are important silicon compounds that have been used as silylation and coupling agents, ligands for organometallic compounds, and precursors for Si, N polymeric materials.[1] Catalytic cross-dehydrogenative coupling [CDC; Eq. (1)] of amines with silanes presents the most attractive and atom-economic synthetic approach for silylamines because the only by-product is hydrogen. Several well-defined metal complexes including metal carbonyls,[2] f-element, early-transition-metal,[3] and magnesium complexes[4] have been successfully employed for catalytic Si–N coupling reactions. However, the control of the selectivity for Si–N coupling has proved to be problematic because the reactions can lead to several products with different Si/N ratios, including polysilazanes, as a result of multiple dehydrogenative-coupling steps; this issue is especially common for the coupling of primary silanes and amines. Thus, the development of highly reactive and selective catalytic systems for reactions of various amines and silanes is highly desirable.

$$PhSiH_3 + HNR_2 \xrightarrow[-H_2]{\text{cat.}} PhH_2Si{-}NR_2 \qquad (1)$$

Homoleptic rare-earth-metal silylamides [Ln{N($SiMe_3$)$_2$}$_n$] ($n = 2,3$) are readily available in large amounts and feature reactive Ln−N bonds for σ-bond metathesis and insertion reactions.[5] Therefore, they are ideal choice for catalytic applications and have been successfully employed as catalysts for ring-opening polymerization reactions of lactones, intramolecular hydroamination, hydroxygenation reactions of unsaturated hydrocarbons, as well as several others.[6] To modify the catalytic performance and extend the catalytic applications of rare-earth-metal amides, various bulky anionic ligands have been designed for the preparation of ligand-supported amides.[7] Immobilization of these amide catalysts has also been studied by the research groups of Anwander and Montreux.[8] Given the excellent catalytic performance of ubiquitous N-heterocyclic carbenes (NHCs) in transition metal catalysis,[9] it is surprising that the catalytic applications of NHC adducts of rare-earth amides have been virtually unexplored. Despite the fact that a large number of rare-earth complexes having NHC-functionalized anionic ligands have been reported,[10] there are only a couple of reports on NHC adducts of rare-earth amides.[11] We recently reported the dehydrosilylation reaction of [(thf)$_2$Yb{N($SiMe_3$)$_2$}$_2$] (**1**) with an aminosilane $ArNHSiH_3$; in this reaction the Yb−N bond undergoes σ-bond metathesis with the silane under mild reaction conditions, thus leading to the Si–N coupling and the formation of the first ytterbium silaimine complex.[12] The results suggested that ytterbium silylamide **1** might be a suitable catalyst for Si–N coupling reactions. Herein, we report the catalytic cross-dehydrogenative-coupling reactions of silanes with amines by [(NHC)Yb{N($SiMe_3$)$_2$}$_2$] adducts. Remarkably, the catalytic activity and selectivity can be modulated by NHCs.

Initially, the stoimetric reaction of **1** with $PhSiH_3$ in C_6D_6 at room temperature was investigated. ^{1}H NMR analysis disclosed the almost quantitative formation of $PhSiH_2N$($SiMe_3$)$_2$, thus indicating a clean Si–N coupling. Therefore, we conducted the reactions of $PhSiH_3$ with equimolar amounts of three secondary amines (HN($SiMe_3$)$_2$, HN(iPr)$_2$, and $HNEt_2$) and 5 mol% loading of catalyst **1**. However, the reactions of the two bulky amines yielded the expected 1:1 coupling products only in very low conversions of 24% and 3%, respectively, whereas the reaction of $HNEt_2$ gave the two products $PhSiH_2NEt_2$ and PhSiH(NEt_2)$_2$ with an almost quantitative conversion. These preliminary studies indicate that **1** is not a satisfactory catalyst for the coupling reactions and some modifications to the catalyst should be made to improve the activity and selectivity. It was found that the combination of **1** with a suitable N-heterocyclic carbene constitutes an efficient catalytic system for the Si–N coupling reactions. Thus, it was essential to study the reactions of **1** with NHCs to probe the roles of NHCs in the catalytic reaction. As we expected, the reactions of **1** with one equivalent of 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene (IiPr) and 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) yielded the NHC adducts **2** and **3**, respectively, in high yield (Scheme 1). Adducts **2** and **3** were fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, and elemental analysis. The ^{31}C NMR spectra of **2** and **3** display C_{NHC} resonances at $\delta = 197.9$ and 205.4 ppm, respectively, which are very similar to those for the reported NHC adducts of cyclopentadienyl ytterbium complexes.[13] The molecular structure of **3** was determined by single-crystal X-ray analysis.

Single crystals of **3** suitable for X-ray single-crystal analysis were obtained from toluene solution at −40°C, and the structure is shown in Figure 1 together with selected bond distances and angles. Complex **3** is monomeric with a three-coordinate ytterbium atom. The Yb−C_{NHC} bond length of 2.600(3) Å in **3** is only marginally longer than those observed in NHC adducts of substituted ytterbocenes (2.552(4) and

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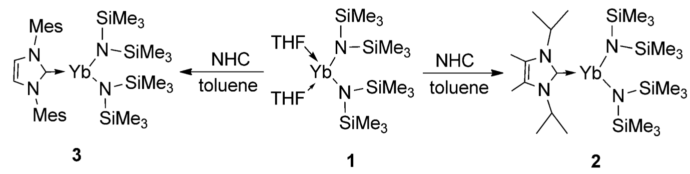


Scheme 1. Synthesis of **2** and **3**. Mes = 2,4,6-$Me_3C_6H_2$.

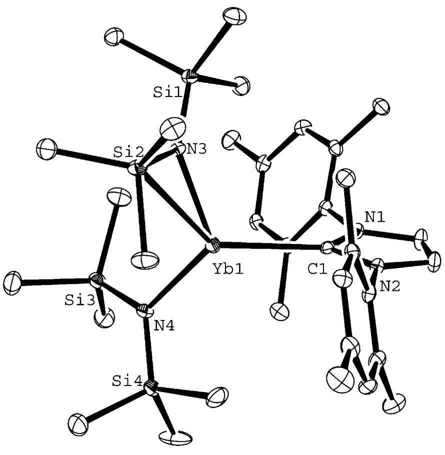
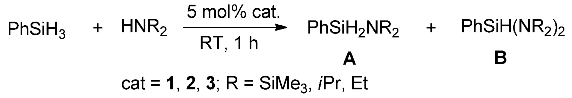


Figure 1. Ortep drawing of **3** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1–N4 2.317(3), Yb1–N3 2.323(2), Yb1–C1 2.600(3); N4-Yb1-N3 122.21(9), N4-Yb1-C1 114.24(9), N3-Yb1-C1 117.28(10).[15]

2.598(3) Å).[13] Adduct **3** is thermally stable in solution even at 120 °C but **2** slowly decomposed at this temperature.



Scheme 2. Dehydrogenative coupling catalyzed by **1**, **2**, and **3**.

The NHC Ytterbium silylamide complexes **2** and **3** were examined as catalysts for the dehydrogenative-coupling reactions of the three secondary amines $HN(SiMe_3)_2$, $HN(iPr)_2$, and $HNEt_2$ with one equivalent of $PhSiH_3$ (Scheme 2) to evaluate the steric effects of NHCs on the catalytic reactions. These results were compared with those for the reaction with **1** as the catalyst under the same conditions (Table 1). For the coupling of $PhSiH_3$ with the two bulky secondary amines $HN(SiMe_3)_2$ and $HN(iPr)_2$, the NHC complexes **2** and **3** show increased catalytic activity compared to that of **1**, and complex **3** with the bulky *N*-Mes-substituted NHC displays the highest activity with almost complete conversion in 1 hour (Table 1). For $HNEt_2$, the three catalysts showed comparable activity but only catalyst **3** produced the diaminosilane **B** as a sole product. Furthermore, in the cases with **1** and **2** as catalysts, noticeable amounts of Ph_2SiH_2 and SiH_4 were detected by NMR analysis. These results indicate that the NHC-containing complexes are far superior to silylamide **1** and steric factors of NHC have significant influence on the activity and selectivity for the catalytic reactions.

As complex **3** gave the best results for the Si–N coupling of the above-mentioned reactions, the coupling reactions of several primary and secondary amines with $PhSiH_3$ catalyzed by **3** (5 mol%) were investigated. In general, **3** is highly active for the reactions of the selected amines, as the reactions showed very high conversions after 1 h. Notably, no efficient catalysts for the coupling of the bulky amines $HN(SiMe_3)_2$, $HNiPr_2$, and $DippNH_2$ with silanes have been reported previously. The reaction products are largely dependent on the steric factors of amines. The reactions with bulky primary amines can be controlled by changing the molar ratios of the two reactants to give a single product (Table 2). The reaction with 4 equivalents of $iPrNH_2$ afforded the tris(amino)silane $PhSi(NHiPr)_3$ (Table 2, entry 4), whereas reactions with the more-bulky amines, $tBuNH_2$ and $DippNH_2$ (Dipp = 2,6-$iPr_2C_6H_3$), yielded bis(amino)silanes (Table 2, entries 5 and 6). Conversely, reactions of these amines with 2.2 equivalents of $PhSiH_3$ yielded disilazanes (Table 2, entries 7–9). Reactions of the bulky secondary amines $(SiMe_3)_2NH$ and iPr_2NH catalyzed by **3** gave mono(amino)silanes in nearly quantitative yield (Table 2, entries 1 and 2), whereas when 3 equivalents of Et_2NH was used the bis(amino)silane $PhSiH(NEt_2)_2$ was obtained as single product in excellent yield. However, the reaction of the aryl-substituted secondary amine Ph_2NH with $PhSiH_3$ catalyzed by **3** proved to be sluggish. Instead, this

Table 1: Comparison of activity and selectivity of catalysts **1**, **2**, and **3** for the coupling of $PhSiH_3$ with $(SiMe_3)_2NH$, iPr_2NH, and $HNEt_2$.

Cat.[a]	R = $SiMe_3$ product [%]	R = *i*Pr product [%]	R = Et product [%]
1	**A** (24)	**A** (3)	**A** (11) + **B** (89)
2	**A** (58)	**A** (13)	**A** (50) + **B** (50)
3	**A** (98)	**A** (100)	**A** (0) + **B** (100)

[a] Reaction conditions: amine (0.18 mmol, 1.2 equiv), silane (0.15 mmol, 1.0 equiv), catalyst (5.0 mol%), C_6D_6 (0.5 mL), room temperature, 1 h. Conversions were obtained on the basis of the consumption of $PhSiH_3$ from integration of signals in the ^{1}H NMR spectra.

Table 2: Reactions of various amines with $PhSiH_3$ catalyzed by **3** (5 mol%).[a]

Entry	$PhSiH_3$ (equiv)	Amine (equiv)	Product	Yield [%][b]
1	1	$(SiMe_3)_2NH$	$PhSiH_2N(SiMe_3)_2$	98 (85)
2	1	iPr_2NH	$PhSiH_2NiPr_2$	100 (89)
3	1	Et_2NH (3.0)	$PhSiH(NEt_2)_2$	100 (90)
4[c]	1	$iPrNH_2$ (4.0)	$PhSi(NHiPr)_3$	99 (83)
5	1	$tBuNH_2$ (4.0)	$PhSiH(NHtBu)_2$	100 (94)
6[d]	1	$DippNH_2$ (4.0)	$PhSiH(NHDipp)_2$	95 (59)
7	2.2	$iPrNH_2$	$(PhSiH_2)_2NiPr$	95 (75)
8	2.2	$tBuNH_2$	$(PhSiH_2)_2NtBu$	100 (77)
9[d]	2.2	$DippNH_2$	$(PhSiH_2)_2NDipp$	90 (64)

[a] Reaction conditions: **3** (5 mol%) in benzene or C_6D_6. [b] NMR yields, the values in paentheses refer to the yield of isolated product. [c] Reaction time: 6 h. [d] Reaction time: 24 h.

reaction can be catalyzed by **2** at 40 °C in C_6D_6 (NMR scale) to give the aminosilane Ph_2NSiH_2Ph in 61 % yield in 15 h.

The reactions of the secondary silanes Ph_2SiH_2 and $PhMeSiH_2$ with primary amines and secondary amines catalyzed by **3** (5 mol %) gave 1:1 coupling products, exclusively, in high yields (Table 3). The reaction of the bulky primary silane $MesSiH_3$ (Mes = 2,4,6-$Me_3C_6H_2$) with tBuNH$_2$ gave the 1:1 coupling product $MesSiH_2$(NHtBu) (Table 3, entry 9). However, **3** is not an effective catalyst for the coupling reactions of the secondary silanes with the bulky amines, that is, $(SiMe_3)_2NH$ and iPr$_2$NH. Interestingly, the reaction of Ph_2SiH_2 with the bulky secondary amine iPr$_2$NH can catalyzed by **2** to give the 1:1 coupling product in high yield (Table 3, entry 3). The results indicated that the steric factors of both substrates and the NHCs have significant effects on the coupling products and reaction conditions that were required. The coupling of $PhSiH_3$ with primary amines proved to be complicated, and yielded a mixture if the ratios of the two reactants were not optimized. However, polymeric silazanes were not detected in these reactions.

Table 3: Reactions of bulky silanes with amines catalyzed by **3** (5 mol %).[a]

Entry	Silane	Amine	Product	Yield [%][b]
1	Ph_2SiH_2	Et_2NH	$Ph_2Si(H)NEt_2$	100 (85)
2	$PhMeSiH_2$	Et_2NH	$PhMeSi(H)NEt_2$	87 (86)
3[c]	Ph_2SiH_2	iPr$_2$NH	$Ph_2Si(H)N$$iPr_2$	82 (73)
4	Ph_2SiH_2	iPrNH$_2$	Ph_2SiH(NHiPr)	100 (87)
5	$PhMeSiH_2$	iPrNH$_2$	$PhMeSiH$(NHiPr)	100 (84)
6	Ph_2SiH_2	tBuNH$_2$	Ph_2SiH(NHtBu)	100 (78)
7	$PhMeSiH_2$	tBuNH$_2$	$PhMeSiH$(NHtBu)	100 (90)
8[d]	Ph_2SiH_2	DippNH$_2$	Ph_2SiH(NHDipp)	99 (64)
9	$MesSiH_3$	tBuNH$_2$	$MesSiH_2$(NHtBu)	100 (86)

[a] Reaction conditions: **3** (5 mol %) in benzene or C_6D_6. [b] NMR yields, the values in parentheses refer to the yields of isolated product. [c] **2** (10 mol %), 100 °C, 24 h. [d] Reaction time: 12 h.

The experimental results demonstrated that **2** and **3** are efficient catalysts for reactions of a wide range of amines and silanes, even for bulky secondary amines, thus indicating that the coordination of NHCs to the ytterbium effectively modulates the catalytic activity. To isolate possible intermediates, the reaction of **3** with $PhSiH_3$ was investigated under various reaction conditions. Unfortunately, attempts to isolate the putative (NHC)YbH_2 have been unsuccessful to date. As the reaction of $PhSiH_3$ with $(SiMe_3)_2NH$ catalyzed by **3** is clean and yielded $PhSiH_2N(SiMe_3)_2$ as the sole product when a range amine/silane ratios were used, the influence of the amount of **3** on the reaction rate and conversions was studied by NMR spectroscopy in C_6D_6 at room temperature. The amount of the catalyst has a substantial influence on the reaction rate and conversions. The reaction rate increases linearly with an increase of the amount of catalyst (Figure 2), and the conversions also increased when the amount of the catalyst was increased (see the Supporting Information, Table S1). The use of an excess of $PhSiH_3$ (Si/N ratios from 1:1 to 6:1; see the Supporting Information, Table S2) has a very limited effect on the conversions in 30 minutes, whereas the use of a large excess amount of amine $HN(SiMe_3)_2$ (Si/N ratios 1: ≥ 6, Table S3) significantly suppresses the reaction to give very low or no conversions within 30 minutes.

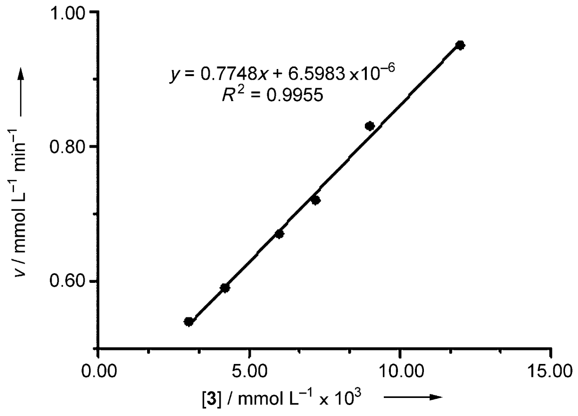


Figure 2. Rate of the formation of silylamine (υ) versus the concentration of the catalyst **3**. This plot shows the first-order dependence of the reaction on the concentration of **3** (C_6D_6, 298 K).

The mechanism of the reaction has yet to be investigated. However, it is possible that the key intermediate for the coupling reaction might be a NHC-stabilized ytterbium hydride formed by σ-bond metathesis of **3** with silanes. The stoichiometric reaction of **3** with $PhSiH_3$ at different concentrations in C_6D_6 was monitored by ^{1}H NMR analysis and the formation of $PhSiH_2N(SiMe_3)_2$ was observed. However, the ^{117}Yb NMR spectra showed no peaks corresponding to a new product in these cases probably because of the instability of the intermediate under the experimental conditions. The reactions shown in Table 2 (entries 1, 2 and 3) were performed with catalyst by **1** in the presence two equivalents of IMes, and similar results were obtained as with **3** as the catalyst. The reaction of $(SiMe_3)_2NH$ with $PhSiH_3$ catalyzed by **1** in the presence of the bidentate donor $Me_2NCH_2CH_2NMe_2$ resulted in a very low conversion (ca. 4 %) in 1 h. These experiments indicate that the NHC plays a key role in the catalytic reactions probably as a result of the strong σ-donor properties of NHC ligands. It is known that homoleptic rare-earth-metal hydrides tend to oligomerize as precipitates in solution.[14] The presence of an NHC on the ytterbium center may prevent rapid oligomerization of the hydride in solution and allow it survive for a long enough time for the subsequent hydrogen elimination reaction with amines to occur, thus significantly improve the catalytic performance. The steric effects of NHCs on the catalytic reactions shown in Table 1 further demonstrated the important role of NHCs in the catalytic reactions.

In summary, we have shown that NHC adducts of a ytterbium amide catalyze cross-dehydrogenative-coupling of amines and silanes to yield various coupling products. The rare-earth-metal NHC silylamide complexes are highly reactive catalysts for the coupling reactions, as indicated by the unprecedented high yielding coupling of several bulky amines with silanes. In addition, the selective formation of a single coupling product can be realized by changing the molar ratios of the two substrates in the case of the primary silane $PhSiH_3$.

The experimental results indicated that NHCs can significantly improve and modulate catalytic performances of rare-earth-metal silylamides. Efforts to characterize the reaction intermediates and to expand the catalytic applications of the rare-earth NHC silylamide adducts are currently in progress.

Experimental Section

Preparation of **3**: A solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (0.91 g, 3.0 mmol) in toluene (30 mL) was added to a solution of Yb[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (1.91 g, 3.0 mmol) in toluene. The resulting solution was stirred for 12 h at room temperature and then concentrated under vacuum. After storage at −40 °C overnight **3** was obtained as reddish black crystals (2.1 g, 88 %). m.p: 248 °C. ^{1}H NMR (C$_6$D$_6$, 400 MHz): $\delta = 0.21$ (s, 36 H, Si*Me*$_3$), 2.01 (s, 12 H, Ar−*Me*), 2.12 (s, 6 H, Ar−*Me*), 6.05 (s, 2 H, NC*H*=C*H*N), 6.81 ppm (s, 4 H, Ar−*H*); ^{13}C NMR (C$_6$D$_6$, 100.64 MHz): $\delta = 5.69$ (SiMe$_3$), 12.28 (Ar−*Me*), 20.88 (Ar−*Me*), 122.0 (N*C*H=*C*HN), 130.2, 134.9, 135.4, 139.7 (aromatic carbons), 205.4 ppm (NCN). Elemental anal. calcd for C$_{33}$H$_{60}$N$_4$Si$_4$Yb: C 49.65, H 7.58, N 7.02; found: C 50.21, H 7.52, N, 6.31.

Further details of the synthesis and characterization of **2** and **3**, catalytic processes, and characterization of the resulting silylamines are given in the Supporting Information.

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[1] a) C. Roth, *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 134; b) Y. Tanabe, M. Murakami, K. Kitaichi, Y. Yoshida, *Tetrahedron Lett.* **1994**, *35*, 8409; c) Y. Tanabe, T. Misaki, M. Kurihara, A. Iida, Y. Nishii, *Chem. Commun.* **2002**, 1628; d) A. Iida, A. Horii, T. Misaki, Y. Tanabe, *Synthesis* **2005**, 2677; e) K. Yan, A. Ellern, A. D. Sadow, *J. Am. Chem. Soc.* **2012**, *134*, 9154; f) D. A. Armitage, *The Silicon-Heteroatom Bond*, Wiley, Chichester, **1991**, pp. 365–484.

[2] a) Y. Blum, R. M. Laine, *Organometallics* **1986**, *5*, 2081; b) C. Biran, Y. D. Blum, R. Glaser, D. S. Tse, K.-A. Youngdahl, R. M. Laine, *J. Mol. Catal.* **1988**, *48*, 183; c) W. D. Wang, R. Eisenberg, *Organometallics* **1991**, *10*, 2222; d) Y. D. Blum, K. B. Schwartz, R. M. Laine, *J. Mater. Sci.* **1989**, *24*, 1707.

[3] a) J. X. Wang, A. K. Dash, J. C. Berthet, M. Ephritikhine, M. S. Eisen, *J. Organomet. Chem.* **2000**, *610*, 49; b) K. Takaki, T. Kamata, Y. Miura, T. Shishido, K. Takehira, *J. Org. Chem.* **1999**, *64*, 3891; c) F. Lunzer, C. Marschner, S. Landgraf, *J. Organomet. Chem.* **1998**, *568*, 253; d) H. Q. Liu, J. F. Harrod, *Organometallics* **1992**, *11*, 822.

[4] J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern, A. D. Sadow, *J. Am. Chem. Soc.* **2011**, *133*, 16782.

[5] For reviews, see: a) P. G. Eller, D. C. Bradley, M. B. Hursthouse, D. W. Meek, *Coord. Chem. Rev.* **1977**, *24*, 1; "Lanthanide Amides": b) R. Anwander, *Top. Curr. Chem.* **1996**, *179*, 33; for the synthesis of Ln[N(SiMe$_3$)$_2$]$_n$ ($n = 2, 3$), see: c) D. C. Bradley, J. S. Ghorta, F. A. Hart, *J. Chem. Soc. Dalton Trans.* **1973**, 1021; d) T. D. Tilley, R. A. Andersen, A. Zalkin, *Inorg. Chem.* **1984**, *23*, 2271; e) G. B. Deacon, G. D. Fallon, C. M. Forsyth, H. Schumann, R. Weimann, *Chem. Ber./Recueil* **1997**, *130*, 409; f) W. J. Evans, M. A. Johnston, R. D. Clark, R. Anwander, J. W. Ziller, *Polyhedron* **2001**, *20*, 2483; g) A. K. Dash, A. Razavi, A. Mortreux, C. W. Lehmann, J. F. Carpentier, *Organometallics* **2002**, *21*, 3238; h) E. Sheng, S. Wang, G. Yang, S. Zhou, L. Cheng, K. Zhang, Z. Huang, *Organometallics* **2003**, *22*, 684; i) K. Dehnicke, A. Greiner, *Angew. Chem.* **2003**, *115*, 1378; *Angew. Chem. Int. Ed.* **2003**, *42*, 1340; j) M. Niemeyer, *Inorg. Chem.* **2006**, *45*, 9085; k) P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, A. V. Protchenko, *J. Organomet. Chem.* **2002**, *647*, 198; l) W. J. Evans, D. K. Drummond, H. Zhang, J. L. Atwood, *Inorg. Chem.* **1988**, *27*, 575.

[6] For recent leading references, see: a) M. R. Bürgstein, H. Berberich, P. W. Roesky, *Chem. Eur. J.* **2001**, *7*, 3078; b) S. Y. Seo, T. J. Marks, *Chem. Eur. J.* **2010**, *16*, 5148; c) K. Komeyama, D. Sasayama, T. Kawabata, K. Takehira, K. Takaki, *Chem. Commun.* **2005**, 634; d) Q. Li, S. Wang, S. Zhou, G. Yang, X. Zhu, Y. Liu, *J. Org. Chem.* **2007**, *72*, 6763; e) Q. Shen, W. Huang, J. Wang, X. Zhou, *Organometallics* **2008**, *27*, 301; f) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673; g) Q. Wang, L. Xiang, H. Song, G. Zi, *Inorg. Chem.* **2008**, *47*, 4319; h) X. Yu, S. Y. Seo, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 7244; i) S. Y. Seo, X. Yu, T. J. Marks, *J. Am. Chem. Soc.* **2009**, *131*, 263; j) S. Y. Seo, T. J. Marks, *Org. Lett.* **2008**, *10*, 317; k) Q. Wu, J. Zhou, Z. Yao, F. Xu, Q. Shen, *J. Org. Chem.* **2010**, *75*, 7498; l) K. Komeyama, D. Sasayama, T. Kawabata, K. Takehira, K. Takaki, *J. Org. Chem.* **2005**, *70*, 10679; m) G. Li, M. Lamberti, M. Mazzeo, D. Pappalardo, G. Roviello, C. Pellecchia, *Organometallics* **2012**, *31*, 1180.

[7] For selected reviews, see: a) P. W. Roesky, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1881; b) Y. Nakayama, H. Yasuda, *J. Organomet. Chem.* **2004**, *689*, 4489; c) K. C. Hultzsch, D. V. Gribkov, F. Hampel, *J. Organomet. Chem.* **2005**, *690*, 4441; d) F. T. Edelmann, *Chem. Soc. Rev.* **2009**, *38*, 2253.

[8] a) G. Gerstberger, C. Palm, R. Anwander, *Chem. Eur. J.* **1999**, *5*, 997; b) R. M. Gauvin, A. Mortreux, *Chem. Commun.* **2005**, 1146; c) Y. Liang, R. Anwander, *Dalton Trans.* **2006**, 1909; d) E. Le Roux, Y. Liang, M. P. Storz, R. Anwander, *J. Am. Chem. Soc.* **2010**, *132*, 16368.

[9] For selected reviews, see: a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; b) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612.

[10] a) P. L. Arnold, I. J. Casely, *Chem. Rev.* **2009**, *109*, 3599; b) P. L. Arnold, S. T. Liddle, *Chem. Commun.* **2006**, 3959; c) H. Yao, J. Zhang, Y. Zhang, H. Sun, Q. Shen, *Organometallics* **2010**, *29*, 5841; d) Z. R. Turner, R. Bellabarba, R. P. Tooze, P. L. Arnold, *J. Am. Chem. Soc.* **2010**, *132*, 4050.

[11] a) W. A. Herrmann, F. C. Munck, G. R. J. Artus, O. Runte, R. Anwander, *Organometallics* **1997**, *16*, 682; b) C. Meermann, G. Gerstberger, M. Spiegler, K. W. Törnroos, R. Anwander, *Eur. J. Inorg. Chem.* **2008**, 2014.

[12] Y. Chen, H. Song, C. Cui, *Angew. Chem.* **2010**, *122*, 9142; *Angew. Chem. Int. Ed.* **2010**, *49*, 8958.

[13] a) H. Schumann, M. Glanz, J. Winterfeld, H. Hemling, N. Kuhn, T. Kratz, *Chem. Ber.* **1994**, *127*, 23690; b) H. Schumann, D. Glanz, D. Winterfeld, H. Hemling, N. Kuhn, T. Kratz, *Angew. Chem.* **1994**, *106*, 1829; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1733.

[14] a) W. L. Korst, J. C. Warf, *Inorg. Chem.* **1966**, *5*, 1719; b) H. Imamura, Y. Maeda, T. Kumai, Y. Sakata, S. Tsuchiya, *Catal. Lett.* **2003**, *88*, 69.

[15] CCDC 890130 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.