CHEMISTRY
AN ASIAN JOURNAL
ACES
FULL PAPER

DOI: 10.1002/asia.201301268

Dinuclear Zinc Hydride Supported by an Anionic Bis(N-Heterocyclic Carbene) Ligand

Arnab Rit, Thomas P. Spaniol, and Jun Okuda*[a]

Abstract: Methylene-linked bis(*N,N'*-di-*tert*-butylimidazol-2-ylidene) **1** reacted with diethylzinc to give dinuclear zinc ethyl compound **2**, which contains a formally anionic bis(carbene) ligand as a result of deprotonation of the methylene bridge. The reaction of **2** with $PhSiH_3$ gave the phenylsilyl compound **3**. The zinc hydride **4** was obtained by the reaction of **2** with $LiAlH_4$ or Ph_3SiOH followed by treatment with $PhSiH_3$. X-ray diffraction studies show that compounds **2**, **3**, and **4** all have a similar dimeric structure with D_{2h} symmetry. The reaction of hydride **4** with carbon dioxide and *N,N'*-diisopropylcarbodiimide gave formato (**5**) and formamidinato (**7**) derivatives as a result of the insertion of the heterocumulene into both Zn–H bonds. Reaction with Ph_2CO gave the diphenylmethoxy compound **6**. Hydride **4** shows catalytic activity in the hydrosilylation of 1,1-diphenylethylene and methanolysis of silanes.

Keywords: carbon dioxide · homogeneous catalysis · hydrides · N-heterocyclic carbenes · zinc

Introduction

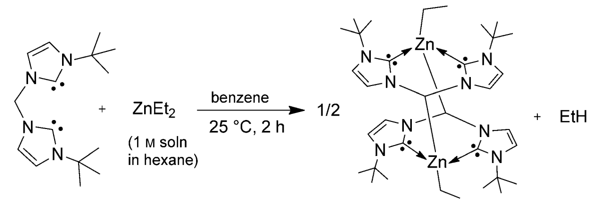
Zinc hydrides are used as reducing agents in organic synthesis,[1] as models for zinc-containing enzymes,[2] and as molecular precursors in materials science.[3] As a result of the low thermal stability of polymeric $(ZnH_2)_n$,[4] more stable zinc hydride derivatives of general formula RZnH were studied and stabilized through chelation with monoanionic ligands[5] or as Lewis base adducts, such as pyridine [(R)ZnH(pyridine)] (R = Et, Ph).[6] Most of these compounds contain bridging hydrido ligands.[7] Well-defined zinc compounds featuring a terminal hydride ligand remain still rare,[2,8] especially those containing both alkyl and hydrido ligands.[8e]

The extensive use of N-heterocyclic carbenes (NHCs)[9] over the last two decades in homogeneous catalysis is based on their ability to act as strong two-σ-electron donors. NHCs are well-established ligands for transition metals, but used to a lesser extent for the Group 12 metal zinc.[10] We have recently reported on molecular zinc dihydrides with the composition $[\{ZnH_2(L)\}_2]$ (L = 1,3-bis(2,4,6-trimethylphenyl/2,6-diisopropylphenyl)imidazol-2-ylidene) as adducts with bulky NHC ligands.[11] Because the monodentate NHC ligands are labile, we resorted to the use of a chelating methylene-linked bis(*N,N'*-di-*tert*-butyl-imidazol-2-ylidene) ligand.[12] Herein, we report the synthesis and reactivity of a zinc hydride stabilized by a new type of monoanionic bis-NHC chelating ligand, methylidyne-3,3'-bis(*N-tert*-butylimidazol-2-ylidene).

Results and Discussion

Dimeric Ethyl Compound 2

The bis-NHC ligand **1** was synthesized by following a literature report[12] and purified by crystallization from a saturated solution in pentane at −35 °C. Treating a solution of **1** in benzene with a 1 M solution of $ZnEt_2$ in hexane at ambient temperature gave the dimeric mono(ethyl) compound **2** in 88 % yield (Scheme 1).[10f] Compound **2** contains a monoanionic bis(NHC) ligand of L_2X type (L = neutral and X = anionic ligand), which is formed by the unusual deprotonation of the methylene proton of the ligand backbone by an ethyl moiety under elimination of ethane. Clean formation of **2** through activation of an sp^3-C–H bond is remarkable because reactions of similar types of ligand with other metal alkyl reagents give either no activation or a mixture of products from which the activated products cannot be isolated in a pure form.[13] Compound **2** is moderately soluble in tetrahydrofuran (THF), but not in aliphatic and aromatic hydro-



1 **2**

Scheme 1. Synthesis of compound **2**.

---

[a] Dr. A. Rit, Dr. T. P. Spaniol, Prof. Dr. J. Okuda
Institut für Anorganische Chemie
RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
Fax: (+49) 241-80-92644
E-mail: jun.okuda@ac.rwth-aachen.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201301268.

carbons. It was characterized by NMR spectroscopy and single-crystal X-ray diffraction.

The ^1H NMR spectrum of **2** contains only one set of signals for both the NHC ligand and the ethyl group; this is consistent with C_i symmetry in solution. In the ^1H NMR spectrum, deprotonation of the methylene group was evident from the integration ratio of the signal at $\delta = 5.82$ ppm relative to other resonances of the ligand and the ethyl group. Ethane was detected by in situ ^1H NMR spectroscopy. Coordination of the NHC ligand to the zinc center was confirmed by a signal at $\delta = 186.4$ ppm in the $^{13}C\{^1H\}$ NMR spectrum; a value characteristic for a zinc(II)-bonded carbene.[10a–d]

Single crystals of the composition $\mathbf{2}\cdot 2\,C_4H_8O$ were obtained from a solution in THF/pentane at −35 °C. The molecular structure consists of a centrosymmetric dimer with a core containing zinc atoms and methylidyne bridges of the NHC ligands (Figure 1). As expected, the Zn−C_{NHC} bond lengths[10b–d,11] (Zn1−C1 2.121(2) Å, Zn1−C8 2.130(3) Å) are slightly longer than the bonds between zinc and the formally anionic ligands (Zn1−C15* 2.108(2) Å, Zn1−C16 2.052(3) Å). The zinc center coordinated by two NHC donors, one methylidyne carbon and one ethyl group, is in a distorted tetrahedral coordination environment. The dihedral angle between two NHC rings of the same ligand is 130.3(1)° with a bite angle of ligand **1** (C1-Zn1-C8) of 91.59(9)°. The Zn⋅⋅⋅Zn distance of 3.8367(6) Å excludes a bonding interaction between the zinc centers.

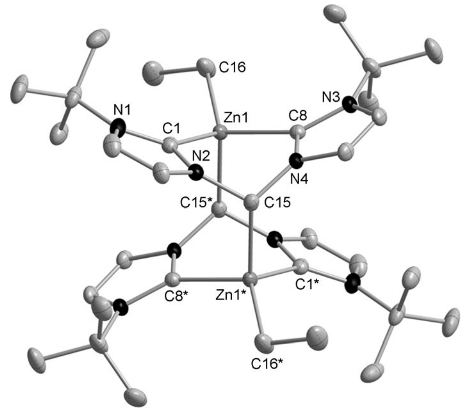
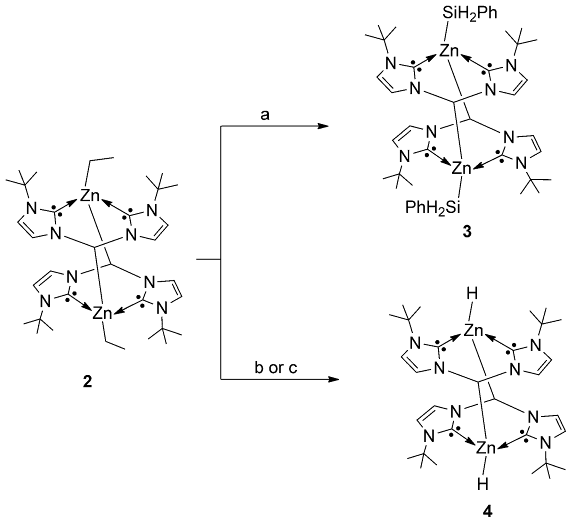


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms and cocrystallized solvent molecules of THF are omitted for clarity. Atoms labeled with an asterisk are related by a symmetry operation (2−x, −y, 1−z).

Phenylsilyl Compound 3

Metal alkyl complexes are reported to react with $PhSiH_3$ to give hydride complexes.[14] When compound **2** was treated with $PhSiH_3$, phenylsilyl compound **3** instead of a hydride species was obtained (Scheme 2). Compound **3** was isolated as crystals in 39 % yield. An in situ ^1H NMR spectroscopy experiment showed the formation of ethane, probably as a result of the deprotonation of $PhSiH_3$ by zinc ethyl in **2**. Compound **3** is highly soluble in THF and aromatic solvents, but insoluble in aliphatic hydrocarbons. It was characterized by multinuclear NMR spectroscopy along with single-crystal X-ray diffraction.



Scheme 2. Synthesis of compounds **3** and **4**: a) $PhSiH_3$, C_6H_6, 60 °C, 4 days; b) $LiAlH_4$, THF, 8 h, 25 °C; c) i) Ph_3SiOH, THF, 25 °C, 12 h; ii) $PhSiH_3$, THF, 25 °C, 2 h.

The ^1H NMR spectrum of **3** shows only one set of signals for the NHC ligand and for the SiH_2Ph group in a ratio of 1:1. The silyl groups give rise to a signal at $\delta = 4.0$ ppm (^1J(Si,H) = 139 Hz) in the ^1H NMR spectrum and a resonance at $\delta = -57.34$ ppm in the $^{29}Si\{^1H\}$ NMR spectrum in $[D_8]$THF.[15] The zinc-bound carbene signal was observed at $\delta = 183.6$ ppm in the $^{13}C\{^1H\}$ NMR spectrum. Molecular dihydrogen (1 bar) did not react with **3**, even at 50 °C for 3 days.

Colorless crystals of the composition $\mathbf{3}\cdot 2\,C_4H_8O$ suitable for X-ray diffraction study were obtained from a solution in THF/Et_2O at −35 °C. The molecular structure consists of a centrosymmetric dimer similar to **2** and with zinc coordinated tetrahedrally by two NHC donors, one methylidyne carbon atom and one SiH_2Ph moiety (Figure 2). The Zn1−Si1 bond length of 2.4522(14) is comparable to that found in related zinc silyl compounds.[15] The Zn⋅⋅⋅Zn distance (3.692(2) Å) is slightly shorter than that in **2**.

Hydride Compound 4

The reaction of **2** with molecular dihydrogen (1 bar, 60 °C, 2 days) gave only unreacted starting material. When compound **2** was treated with one equivalent of $LiAlH_4$ at 25 °C for 8 h in THF, hydride **4** was obtained (Scheme 2). This compound was isolated as colorless crystals in 52 % yield after recrystallization from a solution in THF/pentane at −35 °C. Compound **4** can also be synthesized by first reacting **2** with Ph_3SiOH to yield $[\{Zn(OSiPh_3)(\mathbf{1}-H)\}_2]$ (not isolated) under ethane elimination, which readily reacts with $PhSiH_3$ to give **4** in 71 % yield through Zn−$OSiPh_3$/Si−H

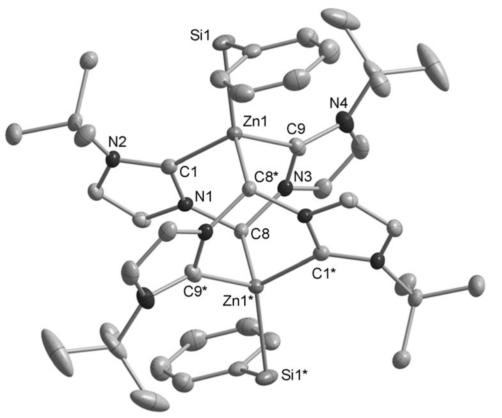


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Atoms labeled with an asterisk are related by a symmetry operation (2−*x*, −*y*, 1−*z*).

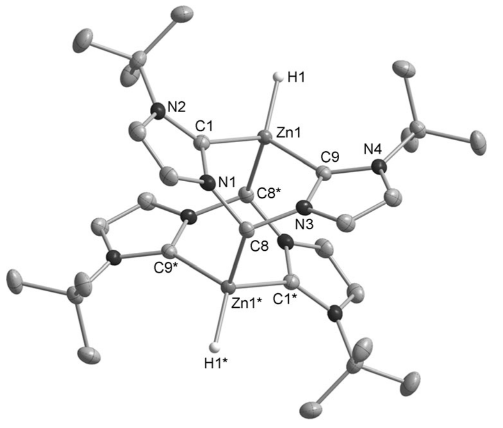


Figure 3. Molecular structures of **4**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms, except that of the hydride coordinated with zinc, are omitted for clarity. Atoms labeled with an asterisk are related by a symmetry operation (1/2−*x*, 1/2−*y*, −*z*).

bond metathesis. The reaction of **2** with other alcohols, such as methanol and Me_3SiOH, gave complicated product mixtures. Compound **4** is soluble in THF, but moderately soluble in aromatic solvents, and is stable in solution at 25 °C for days and can be stored for months at −35 °C.

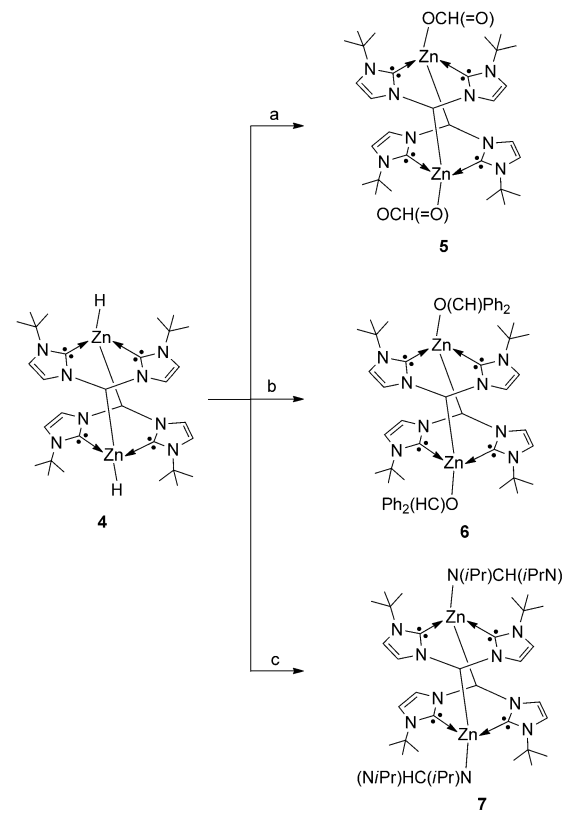
The hydride in **4** is characterized by an intense ν_{Zn-H} vibrational absorption in the IR spectrum at $\tilde{\nu} = 1548\ cm^{-1}$. This absorption shifts to a lower frequency of $\tilde{\nu} = 1117\ cm^{-1}$ for the corresponding deuteride isotopomer ($\nu_{Zn-H}/\nu_{Zn-D} = 1.385$). The ^1H NMR spectrum in [D$_8$]THF shows a broad singlet at $\delta = 4.14$ ppm for the Zn−H resonance and a doublet ($^3J(H,H) = 1.25$ Hz) at $\delta = 5.48$ ppm for the methylidyne bridge proton because of the coupling with the hydrido fragment, as evidenced by ^1H–^1H COSY NMR spectroscopy experiments (see the Supporting Information). In the $^{13}C\{^1H\}$ NMR spectra, the zinc-bonded carbene signal is detected at $\delta = 187.5$ ppm.[10a–d]

Treating a solution of **4** in [D$_8$]THF with D_2 (1 bar) did not result in any H−D exchange, even at 60 °C over several days. This type of inertness has also been observed for the zinc dihydride [{ZnH$_2$(L)}$_2$] (L = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IPr).[11]

Crystals suitable for X-ray diffraction were obtained from a solution in benzene/THF/pentane at 25 °C. The molecular structure reveals that **4** is related to that of **2** and **3**. The zinc centers are tetrahedrally coordinated by two NHCs, one alkyl donor and one terminal hydrido ligand (Figure 3). The only reported compound that contains a terminal hydride next to an alkyl moiety is [(Tptm = tris(2-pyridylthio)methyl).[8e] The Zn−H bond length of 1.61(3) Å is 0.1 Å longer than those found in the four-coordinate compound [(κ^3-Tptm)ZnH].[8e] The Zn−C_{NHC} bond lengths (Zn1−C1 2.105(2) Å, Zn1−C9 2.095(2) Å) are in the range of those found for **2** and **3**.

Reactions of 4 with CO_2, Ph_2CO, and $(iPrN)_2C$

Zinc catalysts are of potential interest for applications in the copolymerization of CO_2 with epoxides[16] and ring-opening polymerization of lactide[17] to give polyesters. Zinc formates are important intermediates in the Cu/ZnO-catalyzed synthesis of methanol.[18] Compound **4** reacts readily with CO_2 ($p(CO_2) = 0.5$ bar) at 25 °C to give formate species **5** (Scheme 3) by double insertion into the Zn−H bonds with



Scheme 3. Synthesis of compounds **5**, **6**, and **7**: a) CO_2 (0.5 bar), THF, 25 °C, 12 h; b) Ph_2CO, THF, 25 °C, 2 h; c) $C(NiPr)_2$, THF, 25 °C, 2 h.

retention of the dimeric structure. Compound **5** is insoluble in common organic solvents, such as THF and aromatic hydrocarbons, but soluble in CH_2Cl_2 and dimethylsulfoxide (DMSO).

The formate unit in **5** is characterized by a singlet at $\delta=8.68$ ppm in ^{1}H NMR spectrum (CD_2Cl_2) and by a signal at $\delta=167.9$ ppm in the $^{13}C\{^1H\}$ NMR spectrum; these chemical shifts are in the range of those reported for $[\{Zn(O_2CH)_2(IMes)\}_2]$[11] and other related compounds.[19b] The IR spectrum of **5** shows two strong absorptions at $\tilde{\nu}=1621$ (ν_{asy}(C=O)) and 1319 cm^{-1} (ν_{sy}(C=O)). The large separation between these two absorptions ($\Delta\nu=302$ cm^{-1}) indicates κ^1 coordination of the formate unit,[19] which is in agreement with the solid-state structure determination.

Colorless single crystals suitable for X-ray diffraction were obtained from a solution in CH_2Cl_2/Et_2O at 25 °C. The molecular structure shows that **5** is a dimer with two formate groups in κ^1-coordination mode (Figure 4). The Zn1–O1 bond length (2.0204(17) Å) is similar to that reported for the compound $[(\kappa^3\text{-Tptm})Zn(O_2CH)]$, with a terminal zinc formate unit.[8e] The C–O bond lengths within the formate units (C1–O1 1.263(3) and C1–O2 1.220(3) Å) indicate partial delocalization of the double bond. The O1-C1-O2 bond angle of 128.5(2)° is in line with the sp^2 character of the formate carbon atom.

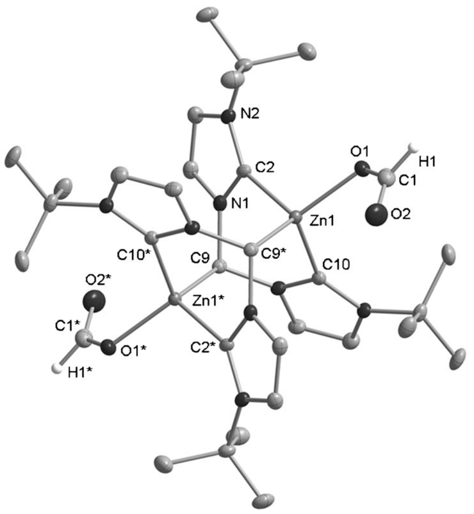


Figure 4. Molecular structure of **5**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms, except for those of the formate moieties and cocrystallized solvent molecules of CH_2Cl_2, are omitted for clarity. Atoms labeled with an asterisk are related by a symmetry operation (1−*x*, −*y*, 1−*z*).

When zinc hydride **4** was treated with benzophenone and $(iPrN)_2C$ at ambient temperature, insertion of CO or CN into both zinc hydride bonds resulted in the quantitative formation of bis(alkoxy) and bis(formamidinato) compounds **6** and **7**, respectively. As with CO_2, no insertion into the Zn–C(methylidyne bridge) was observed; this is in line with the observation that dialkyl zinc only reacts with $(iPrN)_2C$ at elevated temperature to give an insertion product.[20] Both compounds **6** and **7** were isolated as colorless crystals that were highly soluble in common polar organic solvents.

In situ ^{1}H NMR spectroscopic monitoring of both reactions shows that the hydrido ligands in **4** have reacted within 1 h. The alkoxy unit in **6** was confirmed by the presence of signals at $\delta=6.17$ and 83.0 ppm in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra, respectively. The formamidinato unit in **7** is characterized by one singlet at $\delta=6.74$ ppm (^{1}H NMR spectrum) and by a signal at $\delta=161.4$ ppm ($^{13}C\{^1H\}$ NMR spectrum). These chemical shifts are similar to those reported for $[Zn\{CH(iPrN)_2\}(Mesnacnac)]$ (Mesnacnac = $[HC\{C(Me)N(2,4,6\text{-}Me_3C_6H_2)\}_2]$).[19b] Two sets of signals were observed for the *i*Pr groups in **7**, which indicated the κ^1 coordination of the formamidinato units in solution.

The molecular structure of **7** is shown in Figure 5. The dimeric structure contains a crystallographic inversion center within the Zn_2C_2 core. The Zn1–N5 bond length of 2.0181(16) Å is in the range of other reported zinc formamidinato compounds.[19b] The N–C bond lengths of the formamidinato group were found to be 1.343(3) and 1.293(3) Å. The non-coordinated N–*i*Pr fragments are directed away from the central core to avoid steric crowding with the bulky N–*t*Bu groups of the NHC ligands. The N5-C16-N6 bond angle (128.12(19)°) is similar to the observed O-C-O bond angle (128.5(2)°) of the formate compound **5**.

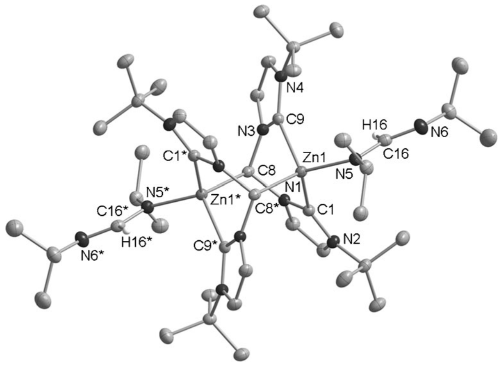
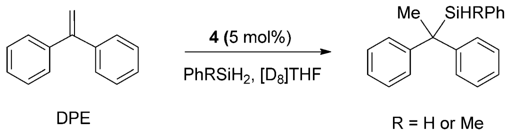


Figure 5. Molecular structure of **7**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms, except for those of the formamidinato moieties and cocrystallized solvent molecules of THF, are omitted for clarity. Atoms labeled with an asterisk are related by a symmetry operation (2−*x*, −*y*, −*z*).

Hydrosilylation of DPE and Methanolysis of Silanes

Zinc hydride compounds have recently attracted attention as an economical alternative to commonly used precious-metal catalysts for catalytic silane coupling with protic solvents, for example, alcohol or water, to give alkoxy or hydroxy silanes, respectively.[21] They are also reported to be active in the catalytic hydrosilylation of aldehydes, ketones, and CO_2.[21a] The latter transformation allows the conversion of cheap, abundant CO_2 into renewable C_1-feedstock chemicals, such as ethyl formate and *N,N*-dimethylformamide.

Zinc hydride compounds have never been used in the catalytic hydrosilylation of alkenes; an important reaction in organic chemistry used to produce silicon-containing compounds.[22] Therefore, we have tested **4** in the catalytic hydrosilylation of 1,1-diphenylethylene (DPE) and have monitored the conversion by ^{1}H NMR spectroscopy. Preliminary studies revealed that **4** is moderately active and only one regioisomer (Markovnikov or 1,2-addition product) was selectively obtained (Scheme 4). Hydrosilylation with $PhSiH_3$ requires a higher reaction temperature than that required for $PhMeSiH_2$ when a stoichiometric amount of silane is used. The tertiary silane $PhMe_2SiH$ did not give any hydrosilylation product (Table 1). When a slight excess of $PhSiH_3$ with respect to DPE ($PhSiH_3/DPE = 1.6:1$) was used, the reaction rate was enhanced compared with that of the stoichiometric reaction and 89% conversion was achieved within 3 h at 25 °C.



Scheme 4. Hydrosilylation of DPE catalyzed by **4**.

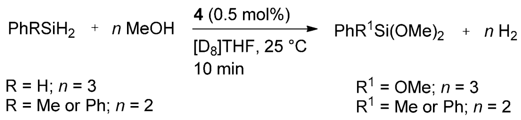
Table 1. Hydrosilylation of DPE catalyzed by **4**.

Silanes	T [°C]	t [h]	Conversion[a] [%]
$PhSiH_3$	25	18	53
	25[b]	3	89[c]
	60	15	80[c]
$PhMeSiH_2$	25	12	88[c]
$PhMe_2SiH$	60(80)	6(4)	–

[a] Conversion to $[Ph_2C(Me)(SiRR_1Ph)]$; determined by in situ ^{1}H NMR spectroscopy. [b] $DPE/PhSiH_3 = 1:1.6$ was used. [c] Remainder is $Ph_2C(Me)H$.

Apart from the hydrosilylation of DPE, the catalytic activity of **4** in the methanolysis of silanes to give poly(methoxy)silanes and dihydrogen was investigated. This reaction not only gives access to Si–O bond containing compounds for various applications in organosilicon[23] and related materials chemistry,[24] but is also reported to be a potent method for on-demand dihydrogen generation from liquid storage materials.[21a]

^{1}H NMR spectroscopic analysis revealed that all employed silanes ($PhRSiH_2$, R = H, Me, and Ph) were selectively converted with a requisite amount of methanol into the corresponding substituted methyl siloxanes with a low catalyst loading (0.5 mol%, 25 °C) within 10 min (Scheme 5). No traces of partially substituted products were obtained and crude reaction products contained only completely substituted methyl siloxanes, as determined by in situ ^{1}H NMR spectroscopy. When one equivalent of methanol was used under the same reaction conditions, $PhMeSiH_2$ gave the mono- and disubstituted products $PhMeSiH(OMe)$ and $PhMeSi(OMe)_2$, respectively, in a ratio of 93:7 within 10 min. These results indicate the higher activity of **4** compared with a related zinc hydride catalyst.[21b]



Scheme 5. Catalytic methanolysis of silanes by using compound **4**.

Conclusion

Dimeric zinc ethyl compound **2**, supported by an anionic chelating bis-NHC ligand, was formed by the reaction of the bis-NHC **1** with $ZnEt_2$. The reaction of **2** with $PhSiH_3$ gave phenylsilyl compound **3** under ethane elimination. The zinc hydride **4** was synthesized by reaction of **2** with $LiAlH_4$ or with Ph_3SiOH followed by reaction with $PhSiH_3$. X-ray crystallography showed that compounds **2**, **3**, and **4** had similar dimeric structures. The hydride **4** reacted with CO_2 and $(i\text{PrN})_2C$ at ambient temperature to give formato (**5**) and formamidinato (**7**) compounds, respectively. The formation of compound **5** is of interest because of the relevance of such species as intermediates in the Cu/ZnO-catalyzed synthesis of methanol. Reaction with Ph_2CO at ambient temperature led to CO insertion into both Zn–H bonds to give diphenylmethoxy compound **6**.

Compound **4** showed moderate activity in the hydrosilylation reaction of DPE to selectively give Markovnikov addition products. Compound **4** exhibited excellent activity in the methanolysis of silanes to readily and selectively yield completely substituted poly(methoxy)silanes and dihydrogen.

Experimental Section

General Considerations

All manipulations were performed under an argon atmosphere by using standard Schlenk or glove box techniques. Glassware was dried at 130 °C in an oven overnight. The solvents used for the synthesis and NMR spectroscopy experiments were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR spectroscopy measurements were performed on a Bruker Avance II 400 MHz spectrometer at 23 °C. The chemical shifts (δ, in ppm) of the ^{1}H NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. IR spectra were measured by using an AVATAR 380 FTIR spectrometer. Abbreviations reported for the IR spectra are as follows: w (weak), m (medium), and s (strong). Carbene **1** was prepared according to literature procedures[12] and $PhSiD_3$ was prepared by $LiAlD_4$ reduction of $PhSiCl_3$.[25] All other chemicals were used as received without further purification. Elemental analyses were performed in the Microanalytical Laboratory of this department.

*Synthesis of **2***

A 1 M solution of Et_2Zn in hexane (0.2 mL, 0.2 mmol) was slowly added to a solution of **1** (0.052 g, 0.2 mmol) in benzene (2 mL). The reaction mixture was stirred for 2 h at 25 °C. Pentane (5 mL) was added and the precipitate was isolated by centrifugation, washed with pentane, and dried under dynamic vacuum to give **2** (0.062 g, 0.088 mmol, 88 %). Crystals suitable for crystallography were obtained by slow diffusion of pentane into a saturated solution of the compound in THF at −35 °C. ^1H NMR (400.1 MHz, $[D_8]$THF): $\delta = 6.90$ (d, $^3J(H,H) = 1.51$ Hz, 4 H; Im-H), 6.77 (d, $^3J(H,H) = 1.51$ Hz, 4 H; Im-H), 5.82 (s, 2 H; CH), 1.93 (t, $^3J(H,H) = 8.03$ Hz, 6 H; CH_2CH_3), 1.51 (s, 36 H; $C(CH_3)_3$), 0.51 ppm (q, $^3J(H,H) = 8.03$ Hz, 4 H; CH_2CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$THF): $\delta = 186.4$ (carbene-C), 119.0 (Im-C), 114.3 (Im-C), 80.1 (CH), 56.8 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 16.4 (CH_2CH_3), 7.4 ppm (CH_2CH_3); elemental analysis calcd (%) for $C_{34}H_{56}N_8Zn_2$ (707.63 g mol^{-1}): C 57.71, H 7.98, N 15.84, Zn, 18.48; found: C 55.68, H 8.35, N 14.94, Zn 18.65.

*Synthesis of **3***

A solution of $PhSiH_3$ (0.018 g, 0.168 mmol) in benzene (0.5 mL) was added to a suspension of **2** (0.03 g, 0.042 mmol) in benzene (0.5 mL). The reaction mixture was heated to 60 °C overnight. All solids dissolved to give a clear solution. The reaction mixture was stirred for 4 days at this temperature. During this time a crystalline solid precipitated. After the reaction time, the reaction mixture was evaporated to dryness, dissolved in benzene, and filtered over Celite. The filtrate was concentrated and hexane was added. The obtained precipitate was washed with hexane and dried in dynamic vacuum. Pure product was obtained after recrystallization (0.014 g, 0.0162 mmol, 39 %). Single crystals suitable for X-ray structure determination were obtained from THF/Et_2O at −35 °C. ^1H NMR (400.1 MHz, $[D_8]$THF): $\delta = 7.67$–7.70 (m, 4 H, *o*Ph), 7.14–7.17 (m, 4 H, *m*Ph), 7.06 (tt, $^3J(H,H) = 7.4$ Hz, $^4J(H,H) = 1.3$ Hz, 2 H; *p*Ph), 6.86 (d, $^3J(H,H) = 1.76$ Hz, 4 H; Im-H), 6.69 (d, $^3J(H,H) = 1.76$ Hz, 4 H; Im-H), 5.51 (s, 2 H; CH), 4.00 ($^1J(Si,H) = 139$ Hz, 4 H; SiH_2Ph), 1.34 ppm (s, 36 H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$THF): $\delta = 183.6$ (carbene-C), 147.6 (*i*Ph), 137.2 (*o*Ph), 127.5 (*m*Ph), 126.1 (*p*Ph), 119.5 (Im-C), 115.5 (Im-C), 79.5 (CH), 57.6 ($C(CH_3)_3$), 32.1 ppm ($C(CH_3)_3$); $^{29}Si\{^1H\}$ NMR (99.4 MHz, $[D_8]$THF): $\delta = -57.34$ ppm; elemental analysis calcd (%) for $C_{42}H_{60}N_8Si_2Zn_2$ (863.92 g mol^{-1}): C 58.39, H 7.00, N 12.97; found: C 56.96, H 7.53, N 12.27.

*Synthesis of **4***

Method A: Compound **2** (0.057 g, 0.08 mmol) and Ph_3SiOH (0.046 g, 0.164 mmol) were mixed in THF (3 mL) and stirred for 12 h at 25 °C. After the reaction time, $PhSiH_3$ (22 μL, 0.176 mmol) in THF (1 mL) was added to the reaction mixture and stirred for 2 h at 25 °C. The reaction mixture was filtered, evaporated to dryness, washed first with cold Et_2O (1 mL) and then with hexane/Et_2O, and dried in vacuo to give a white solid (0.037 g, 0.057 mmol, 71 %).

Method B: A solution of $LiAlH_4$ (0.005 g, 0.132 mmol) in THF (3 mL) was added to a suspension of compound **2** (0.092 g, 0.13 mmol) in THF (1 mL) over 5 min. The reaction mixture was stirred for 8 h at 25 °C. The solution was filtered over Celite to give a clear, light-yellow filtrate. The solution was concentrated to half of its volume and pentane was diffused to precipitate a white solid. The solid was isolated and dried in vacuo (0.044 g, 0.068 mmol, 52 %). Crystals suitable for X-ray structure determination were obtained from a solution in benzene/THF/pentane at 25 °C. ^1H NMR (400.1 MHz, $[D_8]$THF): $\delta = 6.88$ (d, $^3J(H,H) = 1.8$ Hz, 4 H; Im-H), 6.81 (d, $^3J(H,H) = 1.8$ Hz, 4 H; Im-H), 5.48 (d, $^3J(H,H) = 1.3$ Hz, coupling with hydride, 2 H; CH), 4.14 (s, 2 H; Zn-H), 1.41 ppm (s, 36 H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$THF): $\delta = 187.5$ (carbene-C), 119.5 (Im-C), 114.4 (Im-C), 80.4 (CH), 57.6 ($C(CH_3)_3$), 31.6 ppm ($C(CH_3)_3$); IR (KBr): $\tilde{\nu} = 3121$ (w), 3079 (w), 2974 (s), 2936 (w), 2907 (w), 2870 (w), 1548 (s, ν_{Zn-H}), 1478 (w), 1466 (w), 1407 (w), 1391 (m), 1367 (s), 1315 (w), 1283 (m), 1249 (m), 1229 (m), 1209 (s), 1147 (w), 1114 (s), 1081 (w), 1021 (w), 995 (w), 826 (w), 790 (w), 755 (m), 703 (s), 670 (m), 593 (s), 516 (s), 481 cm^{-1} (m); elemental analysis calcd (%) for $C_{30}H_{48}N_8Zn_2$ (651.52 g mol^{-1}): C 55.30, H 7.43, N 17.20; found: C 55.72, H 7.84, N 16.26.

*Synthesis of $[D_2]$**4***

This compound was prepared from compound **2** (0.021 g, 0.03 mmol) and Ph_3SiOH (0.017 g, 0.06 mmol) by using $PhSiD_3$ (0.007 g, 0.066 mmol) instead of $PhSiH_3$ in 82 % yield (0.016 g, 0.0245 mmol). IR (KBr): $\tilde{\nu} = 3122$ (m), 3082 (w), 2968 (s), 2933 (w), 2872 (w), 1479 (w), 1470 (w), 1411 (m), 1391 (m), 1370 (s), 1314 (w), 1291 (m), 1247 (m), 1228 (m), 1209 (s), 1147 (w), 1117 (s, ν_{Zn-D}), 1089 (w), 1021 (w), 997 (w), 826 (w), 798 (w), 749 (m), 720 (s), 712 (s), 674 (m), 585 (s), 522 (s), 503 (w), 462 cm^{-1} (w).

*Synthesis of **5***

A solution of **4** (0.026 g, 0.04 mmol) in THF (2 mL) was pressurized with 0.5 bar of CO_2 at room temperature for 10 min, resulting in the precipitation of a white solid. After standing overnight, the precipitate was filtered, washed with THF and pentane, and dried under reduced pressure (0.025 g, 0.034 mmol, 85 %). Colorless crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2/Et_2O at 25 °C. ^1H NMR (400.1 MHz, CD_2Cl_2, 298 K): $\delta = 8.68$ (s, 2 H; OCHO), 7.03 (d, $^3J(H,H) = 1.76$ Hz, 4 H; Im-H), 6.85 (d, $^3J(H,H) = 1.76$ Hz, 4 H; Im-H), 6.07 (s, 2 H; CH), 1.33 ppm (s, 36 H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): $\delta = 180.4$ (carbene-C), 167.9 (OCHO), 120.2 (Im-C), 115.7 (Im-C), 77.6 (CH), 57.4 ($C(CH_3)_3$), 31.1 ppm ($C(CH_3)_3$); IR (KBr): $\tilde{\nu} = 3152$ (w), 3121 (m), 3084 (w), 2975 (s), 2933 (w), 2875 (w), 2784 (m), 2699 (w), 1621 (s, ν_{asy}(C=O)), 1478 (w), 1470 (w), 1412 (w), 1394 (m), 1371 (s), 1319 (s, ν_{sy}(C=O)), 1289 (m), 1248 (m), 1232 (m), 1209 (s), 1151 (w), 1115 (s), 1082 (w), 825 (w), 756 (s), 742 (s), 719 (s), 678 (m), 585 (m), 505 cm^{-1} (m); elemental analysis calcd (%) for $C_{32}H_{48}N_8Zn_2O_4$ (739.544 g mol^{-1}): C 51.97, H 6.54, N 15.16; found: C 52.25, H 6.62, N 14.46.

*Synthesis of **6***

$Ph_2C(=O)$ (0.012 g, 0.066 mmol) in THF (1 mL) was slowly added to a solution of **4** (0.020 g, 0.031 mmol) in THF (2 mL). After stirring the reaction mixture for 2 h at 25 °C, all volatile compounds were removed under dynamic vacuum. The remaining residue was washed with hexane and dried in dynamic vacuum to yield a white solid (0.025 g, 0.0246 mmol, 79 %). ^1H NMR (400.1 MHz, $[D_8]$THF, 298 K): $\delta = 7.60$–7.62 (m, 8 H; *o*Ph), 7.14–7.17 (m, 8 H; *m*Ph), 7.01 (tt, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 1.3$ Hz, 4 H; *p*Ph), 6.79 (d, $^3J(H,H) = 1.8$ Hz, 4 H; Im-H), 6.42 (d, $^3J(H,H) = 1.5$ Hz, 4 H; Im-H), 6.17 (s, 2 H; $OCHPh_2$), 5.01 (s, 2 H; CH), 1.35 ppm (s, 36 H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$THF): $\delta = 183.0$ (carbene-C), 155.6 (*i*Ph), 128.6 (*o*Ph), 128.0 (*p*Ph), 125.5 (*m*Ph), 119.2 (Im-C), 115.1 (Im-C), 83.0 ($OCHPh_2$), 78.2 (CH), 57.5 ($C(CH_3)_3$), 31.7 ppm ($C(CH_3)_3$); elemental analysis calcd (%) for $C_{56}H_{68}N_8Zn_2O_2$ (1015.944 g mol^{-1}): C 66.20, H 6.75, N 11.03; found: C 65.45, H 7.02, N 10.27.

*Synthesis of **7***

N,N'-Diisopropylcarbodiimide (0.024 g, 0.092 mmol) in THF (1 mL) was slowly added to a solution of **4** (0.028 g, 0.043 mmol) in THF (3 mL). After stirring the reaction mixture for 2 h at 25 °C, all volatile compounds were removed under dynamic vacuum. The remaining residue was washed with cold pentane and dried in vacuo to give a white solid (0.030 g, 0.0335 mmol, 78 %). Crystals suitable for X-ray diffraction were obtained from THF/Et_2O at −35 °C. ^1H NMR (400.1 MHz, $[D_8]$THF, 298 K): $\delta = 7.01$ (d, $^3J(H,H) = 1.8$ Hz, 4 H; Im-H), 6.98 (d, $^3J(H,H) = 1.5$ Hz, 4 H; Im-H), 6.74 (s, 2 H; $(i\text{PrN})_2CH$), 5.65 (s, 2 H; CH), 4.15 (sept, $^3J(H,H) = 6.3$ Hz, 2 H; $CH(CH_3)_2$), 2.59 (sept, $^3J(H,H) = 6.3$ Hz, 2 H; $CH(CH_3)_2$), 1.43 (d, $^3J(H,H) = 6.3$ Hz, 12 H; $CH(CH_3)_2$), 1.36 (s, 36 H; $C(CH_3)_3$), 0.85 ppm (d, $^3J(H,H) = 6.3$ Hz, 12 H; $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$THF): $\delta = 184.4$ (carbene-C), 161.4 ($(i\text{PrN})_2CH$), 121.0 (Im-C), 114.3 (Im-C), 80.1 (CH), 57.9 ($C(CH_3)_3$), 57.7 ($CH(CH_3)_2$), 48.1 ($CH(CH_3)_2$), 31.8 ($C(CH_3)_3$), 27.7 ($CH(CH_3)_2$), 25.0 ppm ($CH(CH_3)_2$); elemental analysis calcd (%) for $C_{44}H_{76}N_{12}Zn_2$ (903.928 g mol^{-1}): C 58.46, H 8.48, N 18.60; found: C 57.98, H 9.37, N 18.38.

*Catalytic Hydrosilylation of DPE with Silanes by Using **4***

$PhSiH_3$ (6.5 mg, 0.06 mmol), $PhMeSiH_2$ (7.3 mg, 0.061 mmol), or $PhMe_2SiH$ (8.2 mg, 0.06 mmol) and DPE (11 mg, 0.06 mmol) were added in this order to a solution of **4** (2 mg, 3 μmol, 5.0 mol %) in $[D_8]$THF

(0.6 mL). The conversion was monitored by in situ ^{1}H NMR spectroscopy.

*Catalytic Methanolysis of Silanes with **4***

$PhMeSiH_2$ (41 μL, 0.3 mmol) and methanol (25 μL, 0.615 mmol) were added in this order by means of a microliter syringe to a solution of **4** (1 mg, 3 μmol, 0.5 mol%) in [D$_8$]THF (0.6 mL), resulting in the rapid evolution of hydrogen gas and in the formation of the cross-dehydrocoupled product. The reaction mixture was monitored by ^{1}H NMR spectroscopy, which showed complete conversion to $PhMeSi(OMe)_2$ within 10 min. In an analogous fashion, the reaction of $PhSiH_3$ (37 μL, 0.3 mmol) with methanol (43 μL, 1.05 mmol) or Ph_2SiH_2 (56 μL, 0.3 mmol) with methanol (25 μL, 0.615 mmol) gave hydrogen and $PhSi(OMe)_3$ or $Ph_2Si(OMe)_2$, respectively, within 10 min.

Crystallography

X-ray crystallography data were collected on a Bruker CCD area-detector diffractometer with $Mo_{K\alpha}$ radiation (monolayer optics, $\lambda = 0.71073$ Å) by using ω scans.[26a] The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed by using SAINT; absorption corrections were applied with SADABS.[26b] The structures were solved by direct methods and refined against F^2 by using all reflections with SHELXL-97, as implemented in the WinGX program system.[26c–e] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included with idealized geometries. Only the hydrogen atoms of the CH unit between the imidazolidine rings (H15 in **2**, H8 in **3** and **4**, H9 in **5**, and H8 in **7**), the formate (H1 in **5**) and the formamidinate (H16 in **7**), as well as the hydride (H1 in **4**) were refined in their position. Crystallographic and refinement data for compounds **2**, **3**, **4**, **5**, and **7** is given in Table 2.

CCDC 930532 (**2**), 930533 (**3**), 930534 (**4**), 930535 (**5**), and 930536 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We gratefully acknowledge financial support from the Cluster of Excellence RWTH Aachen "Tailor-Made Fuels from Biomass" and the Deutsche Forschungsgemeinschaft through the International Research Training Group "Selectivity in Chemo- and Biocatalysis".

[1] a) Y. Gao, H. Urabe, F. Sato, *J. Org. Chem.* **1994**, *59*, 5521–5523; b) Y. Gao, K. Harada, T. Hata, H. Urabe, F. Sato, *J. Org. Chem.* **1995**, *60*, 290–291; c) M. Uchiyama, F. Furumoto, M. Saiko, Y. Kondo, T. Sakamato, *J. Am. Chem. Soc.* **1997**, *119*, 11425–11433.

[2] M. Rombach, H. Brombacher, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **2002**, 153–159.

[3] W. Marciniak, K. Merz, M. Moreno, M. Driess, *Organometallics* **2006**, *25*, 4931–4933.

[4] a) A. E. Finholt, A. C. Bond, Jr., H. I. Schlesinger, *J. Am. Chem. Soc.* **1947**, *69*, 1199–1203; b) J. J. Watkins, E. C. Ashby, *Inorg. Chem.* **1974**, *13*, 2350–2354; c) E. C. Ashby, J. J. Watkins, D. Greig, D. F. Shriver, *Inorg. Synth.* **1977**, *17*, 6–8.

[5] For selected references, see: a) N. A. Bell, A. L. Kassyk, *J. Organomet. Chem.* **1988**, *345*, 245–251; b) A. Looney, R. Han, I. B. Gorrell, M. Cornebise, K. Yoon, G. Parkin, A. L. Rheingold, *Organometallics* **1995**, *14*, 274–288; c) H. Hao, C. Cui, H. W. Roesky, G. Bai, H.-G. Schmidt, M. Noltemeyer, *Chem. Commun.* **2001**, 1118–1119.

[6] A. J. De Koning, J. Boersma, G. J. M. Van Der Kerk, *J. Organomet. Chem.* **1978**, *155*, C5–C7.

[7] a) M. P. Coles, S. M. El-Hamruni, J. D. Smith, P. B. Hitchcock, *Angew. Chem.* **2008**, *120*, 10301–10304; *Angew. Chem. Int. Ed.* **2008**, *47*, 10147–10150; b) S. Schulz, T. Eisenmann, D. Schuchmann, M. Bolte, M. Kirchener, R. Boese, J. Spielmann, S. Harder, *Z. Naturforsch. B* **2009**, *64*, 1397–1400; c) Z. Zhu, J. C. Fettinger, M. M. Olmstead, P. P. Power, *Organometallics* **2009**, *28*, 2091–2095; d) Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P.

Table 2. Crystallographic and refinement data for compounds **2**, **3**, **4**, **5**, and **7**.

	2	**3**	**4**	**5**	**7**
formula	$C_{34}H_{56}N_8Zn_2{\cdot}2(C_4H_8O)$	$C_{42}H_{60}N_8Si_2Zn_2{\cdot}2(C_4H_8O)$	$C_{30}H_{48}N_8Zn_2$	$C_{32}H_{48}N_8O_4Zn_2{\cdot}2(CH_2Cl_2)$	$C_{44}H_{76}N_{12}Zn_2{\cdot}4(C_4H_8O)$
M_r [g mol^{-1}]	851.52	1008.11	651.50	909.38	1192.32
crystal size [mm]	0.29 × 0.08 × 0.08	0.19 × 0.19 × 0.07	0.20 × 0.15 × 0.11	0.30 × 0.20 × 0.08	0.25 × 0.18 × 0.18
crystal color and habit	colorless rod	colorless plate	colorless prism	colorless block	colorless plate
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/c$
a [Å]	11.3917(13)	9.504(7)	22.4773(19)	10.8353(9)	10.7577(8)
b [Å]	10.3514(11)	12.026(9)	7.8926(7)	10.1314(8)	17.8897(14)
c [Å]	18.589(2)	12.774(10)	18.4466(16)	18.5847(15)	16.8086(13)
α [°]	90.00	64.330(12)	90.00	90.00	90.00
β [°]	96.3733(19)	86.365(14)	95.5660(16)	91.9958(13)	99.6643(12)
γ [°]	90.00	81.984(13)	90.00	90.00	90.00
V [Å^3]	2178.4(4)	1303.1(17)	3257.1(5)	2038.9(3)	3188.9(4)
Z	2	1	4	2	2
ρ_{calcd} [g cm^{-3}]	1.299	1.285	1.329	1.481	1.242
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.145	1.012	1.505	1.485	0.805
$F(000)$	912	536	1376	944	1288
θ range [°]	2.26–26.50	1.77–28.59	1.82–29.56	2.19–28.51	1.68–26.46
hkl indices	±14, ±12, ±23	±12, ±16, ±17	−31 to +29, ±10, ±25	±14, ±13, ±24	±13, ±22, ±21
reflns collected	25696	18186	21770	27745	37312
reflns observed [$I > 2\sigma(I)$]	3719	5254	3680	4371	5485
independent reflns (R_{int})	4494 (0.0685)	6530 (0.0620)	4290 (0.0492)	5162 (0.0509)	6574 (0.0467)
data/restraints/parameters	4494/0/264	6530/0/303	4290/0/193	5162/0/247	6574/0/368
R_1, wR_2 [$I > 2\,\sigma(I)$]	0.0385, 0.0856	0.0493, 0.1062	0.0429, 0.1062	0.0390, 0.1037	0.0351, 0.0793
R_1, wR_2 (all data)	0.0502, 0.929	0.0629, 0.1135	0.0510, 1116	0.0486, 0.1109	0.0480, 0.0861
goodness of fit on F^2	1.062	1.043	1.083	1.040	1.077
$\Delta\rho_{max, min}$ [e Å^{-3}]	0.456, −0.390	0.754, −0.853	2.532, −0.310	0.548, −0.985	0.488, −0.355

Power, *Angew. Chem.* **2006**, *118*, 5939–5942; *Angew. Chem. Int. Ed.* **2006**, *45*, 5807–5810; e) I. L. Fedushkin, O. V. Eremenko, A. A. Skatova, A. V. Piskunov, G. K. Fukin, S. Y. Ketkov, E. Irran, H. Schumann, *Organometallics* **2009**, *28*, 3863–3868.

[8] a) R. Han, I. B. Gorrell, A. G. Looney, G. J. Parkin, *J. Chem. Soc. Chem. Commun.* **1991**, 717–719; b) W. Kläui, U. Schilde, M. Schmidt, *Inorg. Chem.* **1997**, *36*, 1598–1601; c) C. Bergquist, L. Koutcher, A. L. Vaught, G. Parkin, *Inorg. Chem.* **1999**, *38*, 422–423; d) D. Mukherjee, A. Ellern, A. D. Sadow, *J. Am. Chem. Soc.* **2010**, *132*, 7582–7583; e) W. Sattler, G. Parkin, *J. Am. Chem. Soc.* **2011**, *133*, 9708–9711.

[9] For reviews on NHCs, see: a) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; b) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992–9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849.

[10] a) A. J. Arduengo III, H. V. R. Dias, F. Davidson, R. L. Harlow, *J. Organomet. Chem.* **1993**, *462*, 13–18; b) T. R. Jensen, L. E. Breyfogle, M. A. Hillmyer, W. B. Tolman, *Chem. Commun.* **2004**, 2504–2505; c) T. R. Jensen, C. P. Schaller, M. A. Hillmyer, W. B. Tolman, *J. Organomet. Chem.* **2005**, *690*, 5881–5891; d) D. Wang, K. Wurst, M. R. Buchmeiser, *J. Organomet. Chem.* **2004**, *689*, 2123–2130; e) For review on group 12 metal NHC complexes see: S. Budagumpi, S. Endud, *Organometallics* **2013**, *32*, 1537–1562; f) the reaction of **1** with $ZnMe_2$ first gave a neutral adduct, which underwent transformation to give a compound analogous to **2**, S. Dagorne, C. Fliedel, private communication.

[11] A. Rit, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem.* **2013**, *125*, 4762–4765; *Angew. Chem. Int. Ed.* **2013**, *52*, 4664–4667.

[12] a) K. D. Wells, M. J. Ferguson, R. McDonald, M. Cowie, *Organometallics* **2008**, *27*, 691–703; b) R. E. Douthwaite, D. Haüssinger, M. L. H. Green, P. J. Silcock, *Organometallics* **1999**, *18*, 4584–4590; c) S. Sauerbrey, P. K. Majhi, J. Daniels, G. Schnakenburg, G. M. Brändle, K. Scherer, R. Streubel, *Inorg. Chem.* **2011**, *50*, 793–799.

[13] K. A. Kreisel, G. P. A. Yap, K. H. Theopold, *Organometallics* **2006**, *25*, 4670–4679.

[14] For selected examples, see: a) S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem.* **2011**, *123*, 4242–4246; *Angew. Chem. Int. Ed.* **2011**, *50*, 4156–4160; b) A. Venugopal, W. Fegler, T. P. Spaniol, L. Maron, J. Okuda, *J. Am. Chem. Soc.* **2011**, *133*, 17574–17577; c) J. Zhou, J. Chu, Y. Zhang, G. Yang, X. Leng, Y. Chen, *Angew. Chem.* **2013**, *125*, 4337–4340; *Angew. Chem. Int. Ed.* **2013**, *52*, 4243–4246; d) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, *Angew. Chem.* **2012**, *124*, 2140–2142; *Angew. Chem. Int. Ed.* **2012**, *51*, 2098–2100.

[15] N. Wiberg, W. Niedermayer, H.-W. Lerner, M. Bolte, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1043–1047.

[16] a) M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019; b) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *Angew. Chem.* **2002**, *114*, 2711–2714; *Angew. Chem. Int. Ed.* **2002**, *41*, 2599–2602; c) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924; d) M. Kröger, C. Folli, O. Walter, M. Döring, *Adv. Synth. Catal.* **2006**, *348*, 1908–1918; e) M. Cheng, N. A. Darling, E. B. Lobkovsky, G. W. Coates, *Chem. Commun.* **2000**, 2007–2008; f) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749.

[17] a) M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 11583–11584; b) M. H. Chisholm, J. C. Huffman, K. Phomphrai, *J. Chem. Soc. Dalton Trans.* **2001**, 222–224; c) L. R. Rieth, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 15239–15248; d) for a review see: J. Wu, T.-L. Yu, C.-T. Chen, C.-C. Lin, *Coord. Chem. Rev.* **2006**, *250*, 602–626.

[18] a) G. C. Chinchen, P. J. Denny, D. G. Parker, M. S. Spencer, D. A. Whan, *Appl. Catal.* **1987**, *30*, 333–338; b) G. C. Chinchen, K. Mansfield, M. S. Spencer, *CHEMTECH* **1990**, *20*, 692–699; e) K. C. Waugh, *Catal. Today* **1992**, *15*, 51–75; c) M. S. Spencer, *Top. Catal.* **1999**, *8*, 259–266; d) M. Kurtz, J. Strunk, O. Hinrichsen, M. Muhler, K. Fink, B. Meyer, C. Wöll, *Angew. Chem.* **2005**, *117*, 2850–2854; *Angew. Chem. Int. Ed.* **2005**, *44*, 2790–2794.

[19] a) X.-M. Chen, Y.-X. Tong, T. C. W. Mak, *Inorg. Chem.* **1994**, *33*, 4586–4588; b) S. Schulz, T. Eisenmann, S. Schmidt, D. Bläser, U. Westphal, R. Boese, *Chem. Commun.* **2010**, *46*, 7226–7228.

[20] a) M. Münch, U. Flörke, M. Bolte, S. Schulz, D. Gudat, *Angew. Chem.* **2008**, *120*, 1535–1537; *Angew. Chem. Int. Ed.* **2008**, *47*, 1512–1514; b) S. Schulz, M. Münch, U. Flörke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2221–2225; c) S. Schmidt, S. Gondzik, S. Schulz, D. Bläser, R. Boese, *Organometallics* **2009**, *28*, 4371–4376.

[21] a) W. Sattler, G. Parkin, *J. Am. Chem. Soc.* **2012**, *134*, 17462–17465; b) D. Mukherjee, R. R. Thompson, A. Ellern, A. D. Sadow, *ACS Catal.* **2011**, *1*, 698–702.

[22] I. Ojima, Z. Li, J. Zhu, *The Chemistry of Organosilicon Compounds*, *Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 1687.

[23] a) T. W. Greene, P. G. Wuts, *Protective Groups in Organic Synthesis*, *2nd ed.*, Wiley, New York, **1991**; b) F. Luo, C. Pan, J. Cheng, *Curr. Org. Chem.* **2011**, *15*, 2816–2829.

[24] a) B. G. Trewyn, I. I. Slowing, S. Giri, H.-T. Chen, V. S.-Y. Lin, *Acc. Chem. Res.* **2007**, *40*, 846–853; b) S. Huh, J. W. Wiench, B. G. Trewyn, S. Song, M. Prusi, V. S.-Y. Lin, *Chem. Commun.* **2003**, 2364–2365.

[25] J. P. Banovetz, H. Suzuki, R. M. Waymouth, *Organometallics* **1993**, *12*, 4700–4703.

[26] a) Bruker, SAINT-Plus, Bruker AXS Inc., Madison, WI, USA, **1999**; b) Bruker, SADABS, Bruker AXS Inc. Madison, WI, USA, **2004**; c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350; d) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122; e) L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: September 17, 2013