FULL PAPER

# Efficient Access to Substituted Silafluorenes by Nickel-Catalyzed Reactions of Biphenylenes with Et<sub>2</sub>SiH<sub>2</sub>

# Jens Michael Breunig, Puneet Gupta, Animesh Das, Samat Tussupbayev, Martin Diefenbach, Michael Bolte, Matthias Wagner, Max C. Holthausen,\* and Hans-Wolfram Lerner\*<sup>[a]</sup>

Abstract: The reaction of biphenylene (1) with  $Et_2SiH_2$  in the presence of [Ni-(PPhMe<sub>2</sub>)<sub>4</sub>] results in the formation of a mixture of 2-diethylhydrosilylbiphenyl [2(Et<sub>2</sub>HSi)] and 9,9,-diethyl-9-silafluorene (3). Silafluorene 3 was isolated in 37.5% and 2(Et<sub>2</sub>HSi) in 36.9% yield. The underlying reaction mechanism was elucidated by DFT calculations. 4-Methyl-9,9-diethyl-9-silafluorene (7) was obtained selectively from the [Ni(PPhMe<sub>2</sub>)<sub>4</sub>]-catalyzed reaction

# of $Et_2SiH_2$ and 1-methylbiphenylene. By contrast, no selectivity could be found in the Ni-catalyzed reaction between $Et_2SiH_2$ and the biphenylene derivative that bears *t*Bu substituents in the 2- and 7-positions. Therefore, two pairs of isomers of *t*Bu-substituted sila-

**Keywords:** C–C activation • density functional calculations • nickel • Si– H activation • silanes fluorenes and of the related diethylhydrosilylbiphenyls were formed in this reaction. However, a subsequent dehydrogenation of the diethylhydrosilylbiphenyls with Wilkinson's catalyst yielded a mixture of 2,7-di-*tert*-butyl-9,9-diethyl-9-silafluorene (**8**) and 3,6-di-*tert*butyl-9,9-diethyl-9-silafluorene (**9**). Silafluorenes **8** and **9** were separated by column chromatography.

## Introduction

Silafluorenes are being increasingly recognized as  $\pi$ -conjugated materials with promising potential for device applications, and important contributions have been made in the areas of electro- and photoluminescence.<sup>[1-5]</sup> With their typically low lying LUMO energy level originating from interference of the exocyclic Si–C  $\sigma^*$  orbital and the  $\pi^*$  orbital of the biphenyl fragment,<sup>[6-9]</sup> this class of compounds can be used as electron-transporting material for emitters in organic light-emitting diodes.<sup>[10]</sup> In this context, the ability to control the electronic nature of these chromophores by variation of the functional groups is critical to optimize and finetune their properties.

We have a long-standing interest in boron-doped aromatics<sup>[11–15]</sup> and have developed inter alia a protocol for the synthesis of 9-borafluorenes by treatment of the corresponding 9-silafluorene derivatives with BBr<sub>3</sub>.<sup>[12,13]</sup> However, conven-

[a] J. M. Breunig, P. Gupta, Dr. A. Das, Dr. S. Tussupbayev, Dr. M. Diefenbach, Dr. M. Bolte, Prof. Dr. M. Wagner, Prof. Dr. M. C. Holthausen, Dr. H.-W. Lerner Institut für Anorganische Chemie Goethe-Universität Frankfurt Max-von-Laue-Strasse 7, 60438 Frankfurt (Germany) Fax: (+49)69-79829260 E-mail: lerner@chemie.uni-frankfurt.de max.holthausen@chemie.uni-frankfurt.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201402599.

ient access to silafluorenes with an asymmetric substitution pattern in the 4-positions is lacking as of yet.

A number of synthetic routes towards 9-silafluorenes have been reported earlier (cf. Scheme 1): Silafluorenes were prepared i) by Pd-catalyzed C–C coupling reactions of diaryl silanes ArAr'SiR<sub>2</sub> carrying a triflate group in the 2position of the aryl substituent Ar, whereby bond formation occurs with the corresponding unsubstituted 2-position of the aryl substituent Ar';<sup>[16,17]</sup> ii) by ring closure via a silylium



Scheme 1. Known preparation routes of 9-silafluorenes. i) [Pd], Et<sub>2</sub>NH, dimethylacetamide, 100 °C, 24 h; ii) Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, 1,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>, RT, 1 h or [Rh], 1,4-dioxane, 135 °C, 15 min; iii) [Ir],  $+R^{3}CCR^{3}$ , Bu<sub>2</sub>O, 110 °C, 24 h; iv) E=Li, Mg;  $+R_{2}SiCl_{2}$ .

Chem. Asian J.	2014, 9,	3163-3173
----------------	----------	-----------

Wiley Online Library

ion formed in the reaction of HSi-functionalized 2-silylbiphenyl derivatives  $2(R_2HSi)$  and the trityl cation<sup>[18]</sup> or by Rh-catalyzed H<sub>2</sub> elimination from  $2(R_2HSi)$  and subsequent C–C coupling;<sup>[19–21]</sup> iii) by Ir-catalyzed [2+2+2] cycloaddition of silicon-bridged 1,6-diynes with alkynes;<sup>[22]</sup> and iv) by metathesis reactions of 2,2'-dimetalated biphenyls and  $R_2SiX_2^{[8,23-26]}$  or triorganyl silanes  $R_3SiX$ .<sup>[27–29]</sup> Furthermore, a Pd-catalyzed reaction starting from 2,2-dihalogenated biphenyls and Et<sub>2</sub>SiH<sub>2</sub> has also been reported.<sup>[30]</sup> However, each of these protocols has specific disadvantages.<sup>[31]</sup>

In search of alternative synthetic concepts we asked ourselves whether it is possible to gain access to 9-silafluorenes via transition metal catalyzed routes from biphenylenes and diethylsilane through C–C and Si–H bond-activation reactions with concomitant dehydrogenation. For biphenylenes bearing bulky substituents in the 1,8- or 2,7-positions, oxidative addition of the metal should occur selectively into the sterically less hindered C–C bond of the four-membered ring of biphenylenes.<sup>[32]</sup> In this way, the selective preparation of 9-silafluorene derivatives with sophisticated substitution patterns should be possible.

As relevant precedent, we noticed a recent report of Matsuda et al. on the Pd-catalyzed hydrosilylation of biphenylenes with triorganyl silanes to give 2-silylbiphenyls.<sup>[33]</sup> Hence, without doubt, such products were formed in C–C and Si–H activation reactions, but unfortunately the use of dialkyl silanes was not considered by these authors. Here we report an efficient approach for the synthesis of substituted 9-silafluorenes based on the nickel-catalyzed reaction of biphenylenes with  $Et_2SiH_2$ .

#### **Results and Discussion**

Following the approach of Matsuda et al., we first investigated the Pd-catalyzed hydrosilylation of biphenylene with  $Et_2SiH_2$ , but after heating the reaction mixture to 110 °C for 24 h we found only 16% conversion of biphenylene (20% after 6 d at 110 °C), and the 2-silylbiphenyl **2**(Et<sub>2</sub>HSi) was formed in a mixture with the desired 9-silafluorene **3** (Scheme 2).<sup>[34]</sup> Isolation of **3** from this reaction mixture would further lower the yield drastically.





Chem. Asian J. 2014, 9, 3163-3173

In our search for alternative, more efficient catalysts, we identified nickel complexes that were reported previously to activate both  $C-C^{[35-42]}$  and Si-H bonds,<sup>[43-45]</sup> and we chose to continue our efforts by employing the well-defined nickel catalyst  $[Ni(PPhMe_2)_4]$ .<sup>[46]</sup> Treatment of **1** with Et<sub>2</sub>SiH<sub>2</sub> and 5 mol%  $[Ni(PPhMe_2)_4]$  in toluene at 110 °C resulted in a fast reaction with concomitant release of H<sub>2</sub>. The <sup>1</sup>H NMR spectrum of the reaction solution revealed complete consumption of biphenylene after 4 h at 110 °C and formation of silylated biphenyl **2**(Et<sub>2</sub>HSi) and silafluorene **3** in a ratio of 40:60 (Scheme 2). We were able to separate the two products by column chromatography and isolated **2**(Et<sub>2</sub>HSi) and **3** in 36.9 and 37.5% yield, respectively. The outcome of this reaction is independent of the solvent (e.g., THF, toluene, benzene, or 1,4-dioxane).

To assess mechanistic aspects of this reaction, we conducted a series of further experiments. Firstly, the  $[Ni(PPhMe_2)_4]$  catalyst was mixed with  $Et_2SiH_2$  in the absence of biphenylene, but no reaction was observed up to 110 °C. Secondly, the  $[Ni(PPhMe_2)_4]$  catalyst was mixed with biphenylene in the absence of  $Et_2SiH_2$ , and biphenylene dimerization to tetraphenylene was observed at 110 °C with no reaction at lower temperatures. In this context we note that Johnson and Beck<sup>[35]</sup> obtained tetraphenylene in a similar reaction at 90 °C by employing the nickel catalyst  $[Ni(cod)_2]/PiPr_3$  (cod = 1,5-cyclooctadiene). In contrast, when the reaction was conducted at room temperature, the dinuclear species **B** and **C** (Scheme 3) were isolated, but no tetraphenylene was



Scheme 3. Ni-catalyzed synthesis of tetraphenylene. i) R = iPr, + biphenylene, toluene, 30 min, 25 °C; ii) R = iPr, 6 h, 25 °C, toluene; iii) R = iPr, 90 °C, toluene.<sup>[35]</sup>

formed under these conditions. On the basis of these findings, it was concluded that tetraphenylene formation at 90 °C occurs via dinuclear intermediates **B** and **C**, while the mononuclear pathway was proposed to be less favorable.<sup>[35]</sup>

We further investigated the possibility of interconversion between the products  $2(Et_2HSi)$  and 3 by dihydrogen elimination/addition in the presence of the  $[Ni(PPhMe_2)_4]$  catalyst. In a reaction of [Ni- $(PPhMe_2)_4$  with 2(Et<sub>2</sub>HSi) carried out at 110°C, no 3 was formed by dehydrogenation even in the presence of a hydrogen scavenger (3,3-dimethyl-1butene). We then examined the reactivity of 3 towards dihydrogen (1 or 130 bar) at 110 °C in the presence of  $[Ni(PPhMe_2)_4]$ , but no 2(Et<sub>2</sub>HSi) was formed. Thus, we conclude that 2-(Et<sub>2</sub>HSi) and 3 are not interconvertible under any reaction conditions relevant to their formation.

To elucidate the mechanistic details underlying the experimental observations, we carried out a computational study on  $[Ni(PMe_3)_4]$  and  $Me_2SiH_2$  as smaller molecular models. For selected pathways we performed additional calculations using the realistic catalyst [Ni- $(PPhMe_2)_4$ ]. The dispersion-corrected BP86-D2 functional was chosen in combination with the def2-TZVP basis set; the performance of this level of density functional theory (DFT) was favorably tested in a careful benchmark study against highlevel coupled-cluster results for a set of model reactions relevant to the present study (see the Supporting Information for details). All relative energies reported in this work are based on Gibbs free energies in kcal mol<sup>-1</sup> at 298.15 K. In the following, we report our results for the Ni(PMe<sub>3</sub>)<sub>4</sub>-catalyzed di-



Scheme 4. Activation of Ni catalyst **A0** and its insertion into the C–C bond of biphenylene. Gibbs free energies  $\Delta G_{298}^{\circ}$  [kcalmol<sup>-1</sup>] are relative to **A0**.

merization of biphenylene and for the reaction between biphenylene and Me<sub>2</sub>SiH<sub>2</sub>.

The computed reaction paths commence with activation of the coordinatively saturated complex [Ni(PMe<sub>3</sub>)<sub>4</sub>] (**A0**) by liberation of PMe<sub>3</sub> to create a vacant coordination site (Scheme 4). Dissociation of the first PMe<sub>3</sub> ligand to give [Ni(PMe<sub>3</sub>)<sub>3</sub>] (**A1**) can readily occur under the reaction conditions ( $\Delta_r G_{298}^\circ = 15 \text{ kcal mol}^{-1}$ ), whereas detachment of a second phosphine ligand would be a substantially more endergonic step ( $\Delta_r G_{298}^\circ = 36 \text{ kcal mol}^{-1}$  relative to **A0**). Energetically favored, in fact, is the activation of one of the strained central C–C bonds in biphenylene by oxidative addition to **A1**, which leads to exergonic formation of metallacycle **B1** with an overall activation barrier of 22 kcal mol<sup>-1</sup> (referenced to **A0**). Subsequent liberation of a second PMe<sub>3</sub> ligand from **B1** leads to the 16-electron complex **B2**  $(\Delta_r G_{298}^{\circ} = 7 \text{ kcal mol}^{-1})$ . We investigated an obvious mononuclear pathway, that is, oxidative addition of another biphenylene molecule to **B2** followed by reductive elimination of tetraphenylene, but we regarded such a process as irrelevant because of its unreasonably high activation barrier (see Supporting Information, Section 5 and Scheme 2S). Instead, we identified a dinuclear route that nicely explains tetraphenylene formation, including all pertinent experimental findings reported by Johnson and Beck<sup>[35]</sup> (Scheme 3).

In our computational evaluation of the dinuclear route we adopted E1, the structural analogue of the experimentally characterized species **B** (Scheme 3), as starting point. We

Chem. Asian J. 2014, 9, 3163-3173

relate its formation to dimerization of two molecules of B2 on release of another phosphine ligand per unit to give E1  $(\Delta_r G_{298}^{\circ} = -9 \text{ kcal mol}^{-1} \text{ for this step})$ . This dimerization occurs asymmetrically, and E1 features, apart from an Ni-Ni  $\sigma$  bond, one formal Ni<sup>III</sup> ion engaged in three Ni-C  $\sigma$  bonds and a formal Ni<sup>I</sup> ion involved in one Ni–C  $\sigma$  bond and  $\eta^2$  coordination with one of the phenyl rings. This formal mixed-valence description is moderately pronounced, as indicated by CM5 charges<sup>[47]</sup> of +0.393 and +0.288 calculated for the Ni<sup>III</sup> and Ni<sup>I</sup> ions, respectively. The two nickel centers in E1 cooperatively promote the first C-C coupling step through transition state  $TS_{E1-E2}$  to yield metallacycle E2, which formally contains two Ni<sup>I</sup> ions, in an exergonic step ( $\Delta_{\rm r} G_{208}^{\circ} = -12 \, \rm kcal \, mol^{-1}$ ). This reductive elimination proceeds with a moderate energy barrier of  $16 \text{ kcal mol}^{-1}$ , which indicates that it is kinetically feasible and irreversible at room temperature (reverse barrier:  $27 \text{ kcal mol}^{-1}$ ).

The second C-C coupling step resulting in E3, in which tetraphenylene is coordinatively bound to two Ni<sup>0</sup> centers, is also exergonic ( $\Delta_{\rm r} G_{298}^{\circ} = -12 \text{ kcal mol}^{-1}$ ). However, it has a significantly higher energy barrier of 26 kcal mol<sup>-1</sup>, which is most probably related to the loss of Ni-Ni interaction via  $TS_{E2-E3}$ . The Ni atoms readily coordinate free phosphine ligands in the next steps to liberate tetraphenylene (E6) with reformation of the initial catalyst A0 in a highly exergonic reaction sequence  $(\Delta_{\rm r} G_{298}^{\circ} = -83 \text{ kcal mol}^{-1})$ . These results are nicely in line with the findings of Johnson and Beck, who reported the first C-C coupling to proceed at room temperature and the second, yielding tetraphenylene, to occur only on heating. With an overall activation barrier of 26 kcalmol<sup>-1</sup>, the dinuclear pathway is clearly more favorable than the mononuclear route (31 kcalmol<sup>-1</sup>, see the Supporting Information). Nevertheless, DFT predicts a rather moderate barrier of 22 kcalmol<sup>-1</sup> for the initial C-C bond activation of biphenylene, in contrast to our experimental results, in which no reaction was observed at room temperature.

We hence investigated the influence that our choice of PMe<sub>3</sub> ligands as molecular model has on the computed reaction paths compared to the PPhMe<sub>2</sub> ligands used in our experiments. In the realistic catalyst model, liberation of one of the phosphine ligands from the  $[Ni(PPhMe_2)_4]$  complex is significantly endergonic by 23 kcalmol<sup>-1</sup>, and the activation barrier for subsequent insertion into the C-C bond of biphenylene is 9 kcalmol<sup>-1</sup> (see Supporting Information, Section 5 and Scheme 3S). The overall activation barrier of this insertion step is 32 kcal mol<sup>-1</sup>, which is clearly efficiently surmountable only at elevated temperatures. The main contribution to the increase in the total barrier to insertion stems from the energy needed for the detachment of PPhMe<sub>2</sub>, and we attribute the stronger binding of PPhMe<sub>2</sub> to additional stabilizing  $\pi$ -stacking interactions among the phenyl rings in the reactant complex  $[Ni(PPhMe_2)_4]$ .

We studied two pathways for the initial phase of the reaction, which commence with oxidative addition of the silane or biphenylene to the nickel catalyst. Initial Si-H bond activation by A1 leads to silvl hydride complex H1 and, after decoordination of another phosphine ligand, to H2 in a substantially endergonic sequence (Scheme 5). Subsequent oxidative addition of biphenylene to H2 via TS<sub>H2-B3</sub> yields B3 with an overall reaction barrier of 36 kcalmol<sup>-1</sup> relative to A0.<sup>[48]</sup> With its high barrier, this process is kinetically not competitive with the alternative route commencing with the oxidative addition of the C-C bond in biphenvlene to form complex B1 in an exergonic step. In view of the expected substantial entropic penalty, we did not investigate pathways involving dinuclear species.<sup>[49]</sup> After loss of PMe<sub>3</sub> from **B1**, B3 is formed by oxidative addition of the silane with only a small activation barrier, so that the initial C-C bond activation barrier of 22 kcalmol<sup>-1</sup> (with respect to A0) represents the overall kinetic bottleneck for this route. Hence, fully in line with our experimental observations detailed above, initial Si-H bond activation is clearly disfavored and biphenylene C-C bond activation is the initial step in the



Scheme 5. Two alternative pathways for the formation of **B3**. Gibbs free energies  $\Delta G_{298}^{\circ}$  [kcalmol<sup>-1</sup>] are relative to **A0**.

Chem. Asian J. 2014, 9, 3163-3173

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 6. Pathways leading to the products 2-dimethylhydrosilylbiphenyl (P1) and 9-silafluorene (P2). Gibbs free energies  $\Delta G_{_{298}}^{\circ}$  [kcalmol<sup>-1</sup>] are relative to A0.

overall course of the reaction, also in the presence of dimethylsilane.

From **B3**, a silyl shift from the Ni ion onto the carbon framework leads to the formation of **B4**, in which one of the phenyl rings has been silylated in *ortho* position (Scheme 6). At this point two pathways branch off: a) a low-barrier hydrogen atom transfer via  $TS_{B4-B5}$  leads to the  $\pi$ -coordinated complex **B5** and coordination of PMe<sub>3</sub> ligands finalizes the reaction sequence leading to product **P1**; b) Si–H bond activation with concomitant H–H bond formation through multicenter transition state<sup>[51]</sup>  $TS_{B4-B6}$  leads to the formation of dihydrogen complex **B6**, which readily eliminates H<sub>2</sub> to give **B7**. The second Si–C bond is formed on reductive elimination of silafluorene **P2**, which involves intermediate  $\pi$ -bonded complex **B8** and ligand substitution by PMe<sub>3</sub>.

As illustrated in Scheme 6, both pathways starting from **B4** have moderately low energy barriers and most of the steps are exergonic. With prohibitively high reverse activation barriers of 34 and 39 kcal mol<sup>-1</sup>, respectively, products **P1** and **P2** are not readily interconvertible under the reaction conditions. Hence, the resulting product mixture is not thermodynamically controlled and, independent of the relative stability of **P1** and **P2**, the product distribution is deter-

mined by the relative barrier heights associated with the two routes leading to P1 and P2 (i.e., TS<sub>B4-B5</sub> and TS<sub>B4-B6</sub>, respectively). With nearly barrierless formation of P1 and a barrier of 2 kcal mol<sup>-1</sup> associated with the formation of P2, the computational results do not quantitatively account for the experimental observation that the two products are formed in approximately equal yield, but this small difference in barrier heights falls within the accuracy limitations of the computational method chosen (2 kcal  $mol^{-1}$ , cf. the benchmark section provided in the Supporting Information). However, only minute barriers occur along reaction paths (a) and (b), and we find that the initial C-C bond activation step via TS<sub>A1-B1</sub> is rate-limiting. Subsequent to formation of B1, oxidative addition of the silane occurs with an effective barrier of only 12 kcal mol<sup>-1</sup> (**B1** $\rightarrow$ TS<sub>B2-B3</sub>, Scheme 5). We find this route to be favored over the first kinetically relevant steps of the oxidative addition of a second biphenylene unit, which occurs with an effective

barrier of 16 kcal mol<sup>-1</sup> (E1 $\rightarrow$ TS<sub>E1-E2</sub>, Scheme 4). Hence, nicely in line with the experimental observations, dimerization of biphenylene to form tetraphenylene does not occur in the presence of dimethylsilane.

The computed reaction mechanism indicates no obvious way to improve silafluorene yields in the product distribution. This can be accomplished, however, by adopting the known dehydrogenation of 2-hydrosilylbiphenyls with Wilkinson's catalyst.<sup>[21]</sup> However, [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] cannot just be added to the reaction mixture, because this catalyst is poisoned by PPhMe<sub>2</sub> and/or Et<sub>2</sub>SiH<sub>2</sub>. Consequently, we conducted a brief aqueous workup and flash column chromatography prior to the conversion of silylbiphenyl **2**(Et<sub>2</sub>HSi) to the silafluorene **3** (yield of **3**: 49 %).

To gain access to silafluorene derivatives, our approach relies on the steric hindrance of one of the two C–C single bonds in the four-membered rings of biphenylenes. Substituents in the 1- and 8-positions of biphenylenes should prevent oxidative addition of the catalyst. Accordingly, we examined the  $[Ni(PPhMe_2)_4]$ -catalyzed reaction of 1-methylbiphenylene (4) and 1,8-dimethylbiphenylene (5) with Et<sub>2</sub>SiH<sub>2</sub> with regard to their reactivity and selectivity (Scheme 7). Whereas 4 reacted nicely with Et<sub>2</sub>SiH<sub>2</sub> in the presence of [Ni-



Scheme 7. Influence of the substitution patterns on the selectivity of sila-fluorene formation. i)  $[Ni(PPhMe_2)_4]$ ,  $C_6D_6$ , 120 °C, 2 h; ii)  $[Ni(PPhMe_2)_4]$ ,  $C_6D_6$ , 120 °C, 2 h; iii) 1)  $[Ni(PPhMe_2)_4]$ , toluene, 110 °C, 5.5 h; 2) H<sub>2</sub>O; 3)  $[Rh(PPh_3)_3CI]$ , toluene, 135 °C, 3 d.

(PPhMe<sub>2</sub>)<sub>4</sub>], biphenylene **5** showed no reactivity at all. Clearly, steric repulsion of the two methyl groups prevents C–C bond activation during fluorene formation. Surprisingly, the steric hindrance introduced by a single methyl group suffices to obtain selectivity in the [Ni(PPhMe<sub>2</sub>)<sub>4</sub>]-catalyzed reaction of **4** with Et<sub>2</sub>SiH<sub>2</sub> (Scheme 7). 4-Methyl-9,9-diethyl-9-silafluorene (**7**) is a colorless liquid, the constitution of which was determined by 2D NMR experiments. Concomitant with the formation of **7** also the two isomeric biphenyl species 2-diethylsilyl-6-methylbiphenyl and 2-diethylsilyl-2'methylbiphenyl were produced in this reaction. Takai et al. showed that treatment of 2-dimethylsilyl-2'-methylbiphenyl with Wilkinson's catalyst gave a silaphenanthrene derivative by C–H activation of the arylmethyl group of the silylated methylbiphenyl.<sup>[21]</sup>

For the nickel-mediated reaction of biphenylene carrying bulky *tert*-butyl groups in the 2- and 7-positions, no selectivity was observed. However, by means of our protocol established before to improve the yield of the parent silafluorene, we converted the product mixture to an isomeric mixture of 2,7-di-*tert*-butyl-9,9-diethyl-9-silafluorene (8) and 3,6-di-*tert*butyl-9,9-diethyl-9-silafluorene (9; Scheme 7).

The isomeric silafluorenes **8** and **9** were separated by column chromatography and crystallized by slow evaporation of CHCl<sub>3</sub> solutions (see Figure 1 and the Supporting Information for more details). Silafluorene **8** crystallizes in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit. Compound **9** crystallizes in the monoclinic space group  $P2_1/n$  with one molecule in the asymmetric unit. X-ray quality crystals of **3** (monoclinic, *Pc*, two mole-



Figure 1. Molecular structures of 3, 8, and 9.

cules in the asymmetric unit) were obtained by storing a concentrated hexane solution at -40 °C (see Figure 1 and the Supporting Information for more details).

By cooling a concentrated diethyl ether solution of [Ni-(PPhMe<sub>2</sub>)<sub>4</sub>] to -78 °C single crystals of the catalyst were obtained (see Supporting Information). [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] crystallized in the triclinic space group  $P\bar{1}$  with one molecule in the asymmetric unit. The structure of [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] exhibits perpendicular edge-to-face (T-shaped) configurations of

Chem. Asian J. 2014, 9, 3163-3173

CHEMISTRY

## **AN ASIAN JOURNAL**

two phenyl rings of the phosphine ligands.<sup>[52,53]</sup> One interaction of the phenyl rings of PPhMe<sub>2</sub> ligands is intramolecular and is located between H12 and the center of gravity of phenyl ring C41–C46 with a distance of 2.582 Å. The second interaction of the phenyl rings of the PPhMe<sub>2</sub> ligands is intermolecular (Figure 2) with a distance of 2.857 Å.

In addition we also investigated the  $[Ni(PPhMe_2)_4]$ -catalyzed reaction of biphenylene with  $R_3SiH$  (Table 1;  $R_3Si =$ 



Figure 2. Packing diagram of  $[Ni(PPhMe_2)_4]$  (triclinic,  $P\overline{1}$ ). H atoms on the methyl groups are omitted for clarity. Dashed lines indicate intraand intermolecular T-shaped CH- $\pi$  interactions.

Table 1. Yields of the reactions of biphenylene with triorganyl silanes in the presence of  $[Ni(PPhMe_2)_4]$ .



Et<sub>3</sub>Si,  $nPr_3Si$ ,  $iPr_3Si$ ,  $tBu_3Si$ , Me<sub>2</sub>PhSi, Ph<sub>3</sub>Si). In these reactions the corresponding 2-silylbiphenyls **2**(R<sub>3</sub>Si) were formed in good yields when the mixtures were heated to 110 °C for 4 h (cf. Table 1).

Surprisingly, the Ni-catalyzed reaction with triisopropylsilane and tri-*tert*-butylsilane resulted only in conversion of biphenylene to tetraphenylene, just as found in the reaction of **1** with  $[Ni(PPhMe_2)_4]$  in the absence of silanes. Apparently, the steric bulk introduced by bulky alkyl groups in these two silanes makes their Si–H bonds inaccessible for oxidative addition to the nickel biphenylene metallacycle **B2**, such that its dimerization and thus tetraphenylene formation becomes favored.

Finally we found that the  $[Ni(PPhMe_2)_4]$ -catalyzed reaction of **4** with Et<sub>3</sub>SiH (Scheme 8) yielded an inseparable mixture of the isomeric 2-triethylsilyl-6-methylbiphenyl (**10**) and 2-triethylsilyl-2'-methylbiphenyl (**11**).



Scheme 8. Reaction of 4 with  $Et_3SiH$  in the presence of  $[Ni(PPhMe_2)_4]$  yielding an isomeric mixture of 10 and 11. i)  $[Ni(PPhMe_2)_4]$ ,  $C_6D_6$ , 120°C, 2 h.

### **Summary and Conclusions**

Convenient access to silafluorenes with sophisticated substitution patterns was established. Reaction of biphenylene with  $Et_2SiH_2$  in the presence of  $[Ni(PPhMe_2)_4]$  resulted in the formation of a mixture of 2(Et<sub>2</sub>HSi) and 3, which were separable by column chromatography in decent yields. Under the same conditions, 7 was obtained selectively by employing 1-methylbiphenylene as reactant. In contrast, no selectivity was found in the Ni-catalyzed reaction between  $Et_2SiH_2$  and the 2,7-tBu<sub>2</sub>-substituted biphenylene derivative, and two tBu-substituted silafluorene isomers 8 and 9 were obtained in a mixture with the related diethylhydrosilylbiphenyls. However, by subsequent dehydrogenation of the diethylhydrosilylbiphenyls with Wilkinson's catalyst, a mixture of isomeric silafluorenes 8 and 9 was obtained and separated by column chromatography. Further, we investigated the [Ni(PPhMe<sub>2</sub>)<sub>4</sub>]-catalyzed reaction of biphenylene with  $R_3SiH$  ( $R_3Si = Et_3Si$ ,  $nPr_3Si$ ,  $iPr_3Si$ ,  $tBu_3Si$ ,  $Me_2PhSi$ ,  $Ph_3Si$ ), and the corresponding 2-silylbiphenyls  $2(R_3Si)$  ( $R_3Si = Et_3Si$ , *n*Pr<sub>3</sub>Si, Me<sub>2</sub>PhSi, Ph<sub>3</sub>Si) were obtained in good yields when the mixtures were heated to 110°C for 4 h. The constitutions of these 2-silylbiphenyls were confirmed by NMR spectroscopy. Surprisingly, no hydrosilylation of biphenylene was observed with the silanes iPr<sub>3</sub>SiH and tBu<sub>3</sub>SiH, and only tetraphenylene was obtained.

The underlying reaction mechanism was elucidated by means of DFT calculations. In keeping with earlier experimental findings, we identified a dinuclear pathway for tetraphenylene formation, which is observed for the reaction of the nickel catalyst with biphenylene in the absence of silanes. This route starts with the activation of the nickel catalyst by detachment of a phosphine ligand and subsequent insertion into the strained C–C bond of biphenylene to give nickel biphenylene intermediate **B2**. This intermediate dimerizes with concomitant detachment of two more phosphine ligands and two C–C coupling steps, cooperatively mediated by the two nickel ions, leading to tetraphenylene formation.

In the presence of silane, oxidative addition of the Si–H bond to the nickel ion in **B2** is kinetically favored over tetraphenylene formation. The resulting hexacoordinate nickel species readily undergoes reductive elimination to form a silylated phenyl ring in intermediate **B4**. Two competing pathways branch off at this point and lead to the formation of the two products observed experimentally with low activation barriers: 2-dimethylhydrosilylbiphenyl (**P1**) is formed by C–H bond formation through reductive elimination,

whereas Si-H bond activation and subsequent elimination of dihydrogen leads to the 9,9-dimethyl-9-silafluorene (**P2**). The two products are formed with high exergonicity and are not interconvertible under the reaction conditions.

## **Experimental Section**

#### Computational Details

Geometry optimizations and Hessian calculations were carried out with Gaussian 09 (Revision D.01)<sup>[54]</sup> by employing the BP86<sup>[55,56]</sup> density functional including Grimme's D2 empirical dispersion correction<sup>[57]</sup> in combination with the def2-TZVP<sup>[58]</sup> basis set obtained from the EMSL basis set exchange library.<sup>[59-61]</sup> To accelerate calculations we made use of the resolution-of-identity<sup>[62-64]</sup> approximation, and automatically generated auxiliary basis sets were employed as provided by the auto<sup>[65,66]</sup> keyword implemented in Gaussian09. This functional was selected after a careful benchmark study (see Supporting Information). All stationary points were characterized as minima or first-order saddle points by eigenvalue analysis of the computed Hessians. The connectivities of transition states and the respective minima implied in the presentation were validated by means of energy minimizations following small geometry displacements along the reaction coordinate obtained from the vibrational frequency analyses of transition-state structures. XYZ coordinates of optimized minima and transition states are provided in the Supporting Information. Unscaled zero-point vibrational energies as well as thermal and entropic correction terms were added to total energies to obtain Gibbs free energies (298 K) by using the standard procedures implemented in the Gaussian program.

#### General Remarks

All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques or in an argon-filled glovebox. NMR spectra were recorded on Bruker DPX-250, Avance 300, Avance 400, or Avance 500 spectrometers. Chemical shifts are referenced to (residual) solvent signals (<sup>1</sup>H, <sup>13</sup>C) or to external 85 % H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) and tetramethyl-silane (<sup>29</sup>Si). [Ni(cod)<sub>2</sub>], PPhMe<sub>2</sub>, Et<sub>3</sub>SiH, *n*Pr<sub>3</sub>SiH, *i*Pr<sub>3</sub>SiH, Ph<sub>3</sub>SiH, Me<sub>2</sub>PhSiH, and Et<sub>2</sub>SiH<sub>2</sub> are commercially available and were used as received. *t*Bu<sub>3</sub>SiH was prepared according to the published procedure.<sup>[67-69]</sup> For syntheses of biphenylene and its derivatives, see the Supporting Information. HPLC was either performed with reversed phase (Reprosil-Pur C18-AQ, 10 µm, 250 × 20 mm) or normal phase (Nucleosil 100 Si, 10 µm, 250 × 20 mm).

#### Synthesis

**Synthesis of [Ni(PPhMe<sub>2</sub>)<sub>4</sub>]:** [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] was prepared by a modified literature procedure.<sup>[46]</sup> [Ni(cod)<sub>2</sub>] (1.05 g, 3.82 mmol) and PPhMe<sub>2</sub> (2.19 g, 15.9 mmol) were mixed in a Schlenk tube, whereupon the mixture turned intensely red and warmed up. Et<sub>2</sub>O (15 mL) was added and the resulting orange solution was stirred for 2 d at room temperature. The solution was concentrated to about 2 mL and cooled to  $-78^{\circ}$ C. Orange X-ray-quality crystals formed. The supernatant was removed by cannula and the orange solid was dried to constant mass in vacuo. Yield: 1.964 g (84%). <sup>1</sup>H NMR (300.0 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =7.41–7.35 (m, 8H, ArH), 7.15–7.04 (m, 12H, ArH), 1.30 ppm (s, 24H, Me); <sup>31</sup>P[<sup>1</sup>H] NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =-9.7 ppm (cf. ref. [70]); <sup>13</sup>C[<sup>1</sup>H] NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =148.0 (m, ArC), 129.9 (m, ArC), 128.0 (m, ArC), 126.8 (s, ArC), 22.2 ppm (m, Me).

**Reaction of biphenylene (1) with Et<sub>2</sub>SiH<sub>2</sub> and [Pd(dba)<sub>2</sub>]/DavePhos**: An NMR tube was charged with **1** (40 mg, 0.26 mmol), Et<sub>2</sub>SiH<sub>2</sub> (35 mg, 0.40 mmol), [Pd(dba)<sub>2</sub>] (dba=*trans,trans*-dibenzylideneacetone, 11 mg, 0.019 mmol), and DavePhos (10 mg, 0.025 mmol). C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the tube was sealed. After heating to 110 °C for 24 h the reaction mixture was investigated by NMR spectroscopy.

**Reaction of Et\_2SiH\_2 with [Ni(PPhMe<sub>2</sub>)<sub>4</sub>]:** An NMR tube was charged with  $Et_2SiH_2$  (20 mg, 0.23 mmol) and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (40 mg, 0.065 mmol).

 $C_6D_6~(0.5\,mL)$  was added and the tube was sealed. After heating to 110°C for 2 h the reaction mixture was investigated by NMR spectroscopy, and only the starting materials  $Et_2SiH_2$  and  $[Ni(PPhMe_2)_4]$  were observable.

**Reaction of biphenylene (1) with [Ni(PPhMe<sub>2</sub>)<sub>4</sub>]:** An NMR tube was charged with **1** (20 mg, 0.13 mmol) and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (80 mg, 0.13 mmol).  $C_6D_6$  (0.5 mL) was added and the tube was scaled. After heating to 110 °C for 2 h the reaction mixture was investigated by NMR spectroscopy.

**Reaction of 2(Et<sub>2</sub>HSi) with [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] and 3,3-dimethyl-1-butene**: An NMR tube was charged with 2(Et<sub>2</sub>HSi) (52 mg, 0.22 mmol), [Ni-(PPhMe<sub>2</sub>)<sub>4</sub>] (6 mg, 0.01 mmol), and 3,3-dimethyl-1-butene (0.14 mL).  $C_6D_6$  (0.5 mL) was added and the tube was sealed. After heating to 110 °C for 13 h the reaction mixture was investigated by NMR spectroscopy.

**Reaction of 3 with [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] in an H<sub>2</sub> atmosphere**: Compound **3** (120 mg, 0.503 mmol) and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (31 mg, 0.051 mmol) were dissolved in toluene (20 mL). This mixture was heated in an autoclave under an H<sub>2</sub> atmosphere (130 bar) to 110 °C for 16 h. An aliquot of this mixture was investigated by NMR spectroscopy.

**Reaction of biphenylene (1) with Et\_2SiH\_2 and [Ni(PPhMe\_2)\_4] in an H\_2 atmosphere: Compound 1 (100 mg, 0.657 mmol), Et\_2SiH\_2 (87 mg, 0.99 mmol), and [Ni(PPhMe\_2)\_4] (20 mg, 0.033 mmol) were dissolved in toluene (20 mL). This mixture was heated to 110 °C for 3 h in an autoclave under an H\_2 atmosphere (130 bar). An aliquot of this mixture was investigated by NMR spectroscopy. The product ratio of 2(Et\_2HSi):3 was still 4:6, but the major product of the reaction was biphenyl.** 

**Reaction of 1 with**  $iPr_3SiH$ : An NMR tube was charged with 1 (50 mg, 0.33 mmol), [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (10 mg, 0.016 mmol), and  $iPr_3SiH$  (62 mg, 0.39 mmol). C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the NMR tube was sealed. After heating to 110 °C for 4 h the reaction mixture was investigated by NMR spectroscopy.

**Reaction of 1 with tBu\_3SiH:** An NMR tube was charged with **1** (40 mg, 0.26 mmol), [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (8 mg, 0.01 mmol), and  $tBu_3SiH$  (80 mg, 0.40 mmol). C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the NMR tube was sealed. After heating to 110 °C for 4 h the reaction mixture was investigated by NMR spectroscopy.

Synthesis of 2-triethylsilylbiphenyl [2(Et<sub>3</sub>Si)]: Compound 1 (50 mg, 0.33 mmol) and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (10 mg, 0.016 mmol) were charged in an NMR tube. Et<sub>3</sub>SiH (115 mg, 0.989 mmol) and  $C_6D_6$  (1.5 mL) were added and the tube was sealed. After 2 h at 110 °C the <sup>1</sup>H NMR spectrum showed quantitative formation of 2(Et<sub>3</sub>Si). The reaction mixture was quenched with water and extracted into ethyl acetate (twice). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered. All volatile substances were removed in vacuo. The crude product was purified by flash column chromatography (silica gel/hexane). Yield: 93%. The NMR data were in accordance with those found in the literature.<sup>[33]</sup> <sup>29</sup>Si INEPT NMR (59.6 MHz,  $C_6D_6$ ):  $\delta$ =3.5 ppm.

Synthesis of 2-tripropylsilylbiphenyl [2(nPr<sub>3</sub>Si)]: An NMR tube was charged with 1 (50 mg, 0.33 mmol), [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (12 mg, 0.020 mmol),  $nPr_3SiH$  (55 mg, 0.35 mmol), and  $C_6D_6$  (1.5 mL). The tube was sealed and kept at 110°C. After 4 h the reaction mixture was quenched with water and the organic compounds in the aqueous layer were extracted into ethyl acetate. The combined organic layers were dried over Na2SO4 and filtered. The solvent was removed in vacuo. Purification by flash column (silica gel/hexane) yielded 2(nPr<sub>3</sub>Si) (92 mg, 90%) as a colorless oil. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 7.56$  (dd, <sup>3</sup>J(H,H) = 7.2 Hz, <sup>4</sup>J(H,H) = 1.6 Hz, 1 H, ArH), 7.40-7.32 (m, 5 H, ArH), 7.31-7.27 (m, 2 H, ArH), 7.21  $(dd, {}^{3}J(H,H) = 7.2 Hz, {}^{4}J(H,H) 1.6 Hz, 1H, ArH), 1.24-1.14 (m, 6H,$ CH<sub>2</sub>), 0.85 (t, <sup>3</sup>*J*(H,H)=7.2 Hz, 9H, CH<sub>3</sub>), 0.47–0.43 ppm (m, 6H, CH<sub>2</sub>); <sup>13</sup>C[<sup>1</sup>H] NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 149.7$ , 144.7, 136.0, 135.8, 129.8, 129.4, 128.4, 127.7, 127.2, 126.2 (ArC), 18.6, 17.6, 16.3 ppm  $(CH_2CH_2CH_3)$ ; <sup>29</sup>Si INEPT NMR (59.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -1.6$  ppm; elemental analysis calcd (%) for C<sub>21</sub>H<sub>30</sub>Si: C 81.22, H 9.74; found: C 81.01, H 9.53.

Synthesis of 2-dimethylphenylsilylbiphenyl [2(Me<sub>2</sub>PhSi)]: Compound 1 (50 mg, 0.33 mmol), Me<sub>2</sub>PhSiH (45 mg, 0.33 mmol), and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>]

(12 mg, 0.020 mmol) were dissolved in C<sub>6</sub>D<sub>6</sub> (1.5 mL). The NMR tube was sealed and the mixture was heated to 110 °C for 4 h. After quenching with water and extraction of the product into ethyl acetate, the crude product was purified by column chromatography (silica gel/hexane) to afford **2**(Me<sub>2</sub>PhSi) (81 mg, 85%). The <sup>1</sup>H and <sup>13</sup>C[<sup>1</sup>H] NMR data were in accordance those reported by Matsuda et al.<sup>[33]</sup> <sup>29</sup>Si HMBC (250.1 MHz, 49.7 MHz, CDCl<sub>3</sub>):  $\delta = -8.0$  ppm.

Synthesis of 2-triphenylsilylbiphenyl [2(Ph<sub>3</sub>Si)]: A sealable NMR tube was charged with 1 (50 mg, 0.33 mmol), Ph<sub>3</sub>SiH (86 mg, 0.33 mmol), and  $[Ni(PPhMe_2)_4]$  (12 mg, 0.020 mmol). After adding C<sub>6</sub>D<sub>6</sub> (1.5 mL), the tube was sealed and kept at 110 °C for 4 h. The reaction mixture was quenched with water and the product in the aqueous layer was extracted into ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. All volatile substances were removed in vacuo. Flash column chromatography (silica gel/hexane) yielded 2(Ph<sub>3</sub>Si) (98 mg, 72%) as a colorless solid. <sup>1</sup>H NMR (400.1 MHz,  $CD_2Cl_2$ ):  $\delta = 7.58$  (ddd,  ${}^{3}J(H,H) = 7.5 \text{ Hz}, {}^{4}J(H,H) = 1.5 \text{ Hz}, {}^{5}J(H,H) = 0.6 \text{ Hz}, 1 \text{ H}, \text{ ArH}), 7.50$  $(dvt, {}^{3}J(H,H) = 7.5 Hz, {}^{4}J(H,H) = 1.4 Hz, 1 H, ArH), 7.44-7.41 (m, 6 H,$ ArH), 7.35-7.23 (m, 11H, ArH), 6.95-6.88 (m, 3H, ArH), 6.83-6.79 ppm (m, 2H, ArH);  ${}^{13}C{}^{1}H$  NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 151.2$ , 143.7, 138.9, 136.5, 135.8, 132.8, 131.1, 130.0, 129.8, 129.4, 128.0, 127.6, 126.9, 126.5 ppm (ArC); <sup>29</sup>Si HMBC (400.1 MHz, 79.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta =$ -15.2 ppm; elemental analysis calcd (%) for C<sub>30</sub>H<sub>24</sub>Si: C 87.33, H 5.86; found: C 85.25, H 5.93.

Synthesis of 2-diethylsilylbiphenyl [2( $Et_2HSi$ )] and 9,9-diethylsilafluorene (3): A Schlenk flask was charged with 1 (1.087 g, 7.142 mmol), Et<sub>2</sub>SiH<sub>2</sub> (1.00 g, 11.3 mmol), and  $[Ni(PPhMe_2)_4]$  (0.22 g, 0.36 mmol). Toluene (60 mL) was added and the resulting yellow solution was heated to reflux for 4 h. Within 10 min after starting heating, the solution turned red. After an additional hour the color of the mixture turned to black with a yellow hue. After quenching of the mixture with water (40 mL), the product in the aqueous layer was extracted into ethyl acetate (3×40 mL). The combined organic phases were dried over MgSO4 and filtered. All volatile substances were removed in vacuo to give the crude product as a yellow oil. Column chromatography (silica gel/hexane) yielded 2-(Et<sub>2</sub>HSi) as a colorless oil ( $R_f = 0.66, 634 \text{ mg}, 36.9\%$ ) and **3** as a colorless solid ( $R_{\rm f}$ =0.57, 639 mg, 37.5%). X-ray-quality crystals of **3** were grown from a concentrated hexane solution at -40 °C. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR of 2(Et<sub>2</sub>HSi) and 3 are in accord with the data reported by Takai et al.<sup>[21] 29</sup>Si INEPT (59.6 MHz,  $C_6D_6$ ):  $\delta = -4.8$  [2(Et<sub>2</sub>HSi)], 5.5 ppm (3). Optimized synthesis of 9,9-diethylsilafluorene (3): Compound 1 (393 mg, 2.58 mmol), [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (80 mg, 0.13 mmol), and Et<sub>2</sub>SiH<sub>2</sub> (0.38 g, 4.3 mmol) in toluene (25 mL) were heated to reflux for 4 h. The color of the solution turned from yellow to black with a yellow hue.  $H_2O$  (20 mL) was added and the two layers were separated. The product in the aqueous layer was extracted into ethyl acetate (3×20 mL). The combined organic layers were dried over MgSO4 and filtered. All volatile substances were removed in vacuo to give crude 3 as a yellow oily residue (681 mg). Flash column chromatography (silica gel/hexane) yielded a colorless oil (458 mg). This oil was dissolved in toluene (30 mL), and [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] (83 mg, 0.09 mmol) and 3,3-dimethyl-1-butene (1.3 mL, 10 mmol) were added. After heating this mixture to reflux for 1 d,  $H_2O$  (20 mL) was added and the two layers were separated. The organic compounds in the aqueous layer were extracted into toluene (2×30 mL). Drying the combined organic layers over MgSO4, removal of all volatile substances in vacuo, and flash column chromatography (silica gel/hexane) yielded 3 (300 mg, 49%).

Synthesis of 4-methyl-9,9-diethyl-9-silafluorene (7): 1-Methylbiphenylene (4; 30 mg, 0.18 mmol), Et<sub>2</sub>SiH<sub>2</sub> (24 mg, 0.27 mmol), and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (5 mg, 0.008 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) were heated to 120 °C for 2 h in a sealed vial. The reaction mixture was quenched with water and the product was extracted into ethyl acetate (three times). Drying over MgSO<sub>4</sub>, filtering, and removing all volatile substances in vacuo gave crude 7 as a yellow oil. Reversed-phase HPLC (MeOH, flow rate: 3 mLmin<sup>-1</sup>, retention time: 33.3 min) yielded 7 as a colorless oil (22 mg, 48%). <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$ =8.07 (d, <sup>3</sup>*J*(H,H)=8 Hz, 1H, H<sup>5</sup>), 7.66 (ddd, <sup>3</sup>*J*(H,H)=7 Hz, <sup>4</sup>*J*(H,H)=1.5 Hz, <sup>5</sup>*J*(H,H)=0.7 Hz, 1H, H<sup>8</sup>), 7.49 (ddd, <sup>3</sup>*J*(H,H)=7 Hz, <sup>4</sup>*J*(H,H)=1.5 Hz, <sup>5</sup>*J*(H,H)=0.6 Hz, 1H,

H<sup>1</sup>), 7.45 (dvt, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.5 Hz, 1 H, H<sup>6</sup>), 7.27 (dvt, <sup>3</sup>*J*-(H,H) = 7 Hz, <sup>4</sup>*J*(H,H) = 1 Hz, 1 H, H<sup>7</sup>), 7.24 (dm, <sup>3</sup>*J*(H,H) = 7.7 Hz, 1 H, H<sup>3</sup>), 7.18 (vt, <sup>3</sup>*J*(H,H) = 7 Hz, 1 H, H<sup>2</sup>), 2.76 (s, 3 H, ArMe), 1.01–0.83 ppm (m, 10 H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>Cl<sup>1</sup>H] NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$ =150.6 (C<sup>5A</sup>), 147.0 (C<sup>4A</sup>), 139.0, 138.9 (C<sup>1A,8A</sup>), 134.4 (C<sup>3</sup>), 134.3 (C<sup>4</sup>), 133.3 (C<sup>8</sup>), 131.0 (C<sup>1</sup>), 130.0 (C<sup>6</sup>), 126.8 (C<sup>2</sup>), 126.4 (C<sup>7</sup>), 125.8 (C<sup>5</sup>), 24.5 (ArMe), 7.7, 4.0 ppm (CH<sub>2</sub>CH<sub>3</sub>); <sup>29</sup>Si HMBC (400.1 MHz, 79.5 MHz, CDCl<sub>3</sub>):  $\delta$ = 4.2 ppm; elemental analysis calcd (%) for C<sub>17</sub>H<sub>20</sub>Si: C 80.89, H 7.99; found: C 80.59, H 8.09.

Synthesis of 2,7-di-tert-butyl-9,9-diethyl-9-silafluorene (8) and 3,6-di-tertbutyl-9,9-diethyl-9-silafluorene (9): 2,7-Di-tert-butylbiphenylene (6; 350 mg, 1.32 mmol), Et<sub>2</sub>SiH<sub>2</sub> (263 mg, 2.98 mmol), and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (53 mg, 0.087 mmol) in toluene (20 mL) were heated to 110 °C for 5.5 h, whereupon the color of the mixture changed from yellow to dark red with a yellow hue. H<sub>2</sub>O (20 mL) was added, the two phases were separated, and the product in the aqueous layer was extracted into ethyl acetate (3×30 mL). The combined organic layers were dried over MgSO4 and filtered. All volatile substances were removed in vacuo. Flash column chromatography yielded a mixture of 8 and 9 (442 mg). A vial was charged with 310 mg of this product mixture, [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] (65 mg, 0.070 mmol), 3,3-dimethyl-1-butene (0.60 mL), and toluene (22 mL). The vial was sealed and the mixture was heated to 135 °C for 3 d, whereupon the color of the mixture changed to black. After aqueous workup (20 mL) and extraction of the  $H_2O$  phase with toluene (3×20 mL), all volatile substances were removed in vacuo to yield the products as a dark red oil. Column chromatography (silica gel/hexane) yielded analytically pure 8 ( $R_{\rm f}$ =0.36, 98 mg, 30%) and crude 9 ( $R_{\rm f}$ =0.44, 82 mg, 25%). Analytically pure 9 was obtained by normal-phase HPLC (n-heptane, flow rate: 3 mLmin<sup>-1</sup>, retention time: 20.5 min). Analytical data of 8: <sup>1</sup>H NMR (300.0 MHz, CDCl<sub>3</sub>):  $\delta = 7.70$  (d,  ${}^{3}J(H,H) = 8.1$  Hz, 2H, ArH), 7.60 (d,  ${}^{4}J(H,H) = 2$  Hz, 2H, ArH), 7.43 (dd,  ${}^{3}J(H,H) = 8.1$  Hz,  ${}^{4}J(H,H) = 2$  Hz, 2H, ArH), 1.36 (s, 18H, *t*Bu), 1.06–1.01 (m, 6H, CH<sub>3</sub>), 0.97–0.89 ppm (m, 4H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta = 149.5$ , 146.0, 137.2, 130.0, 127.2, 120.2 (ArC), 34.8, 31.6 (ArtBu), 7.9, 4.1 ppm (CH<sub>2</sub>CH<sub>3</sub>); <sup>29</sup>Si INEPT (59.6 MHz, CDCl<sub>3</sub>):  $\delta = 4.8$  ppm; elemental analysis calcd (%) for C24H34Si: C 82.22, H 9.77; found: C 82.46, H 9.89. Analytical data of 9: <sup>1</sup>H NMR (500.2 MHz, CDCl<sub>3</sub>):  $\delta = 7.87$  (d, <sup>4</sup>*J*(H,H)=1.6 Hz, 2H, ArH), 7.54 (d,  ${}^{3}J(H,H) = 7.5$  Hz, 2H, ArH), 7.29 (dd,  ${}^{3}J(H,H) = 7.5$  Hz,  ${}^{4}J_{-}$ (H,H)=1.6 Hz, 2H, ArH), 1.40 (s, 18H, tBu), 1.03-1.00 (m, 6H, CH<sub>3</sub>), 0.92–0.87 ppm (m, 4H, CH<sub>2</sub>);  ${}^{13}C{}^{1}H$  NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta =$ 153.1, 148.8, 134.6, 133.1, 124.4, 117.5 (ArC), 35.1, 31.5 (ArtBu), 7.8, 4.0 ppm (CH<sub>2</sub>CH<sub>3</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CDCl<sub>3</sub>):  $\delta = 3.9$  ppm; HRMS (MALDI): m/z calcd for  $C_{24}H_{34}Si^+$ : 350.2430 [ $M^+$ ]; found: 350.2422.

Reaction of 1-methylbiphenylene (4) with triethylsilane: A sealable NMR tube was charged with 4 (30 mg, 0.18 mmol), Et<sub>3</sub>SiH (32 mg, 0.28 mmol), and [Ni(PPhMe<sub>2</sub>)<sub>4</sub>] (5 mg, 0.008 mmol). C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the NMR tube was sealed. After heating to 120 °C for 2 h, the orange-yellow solution was treated with water. The product in the aqueous layer was extracted into ethyl acetate (twice). All volatile substances were removed in vacuo to yield 58 mg of a yellow oil. Reversed-phase HPLC (MeOH, flow rate: 3 mL min<sup>-1</sup>, retention time: 38 min) yielded an mixture of isomeric products 2-triethylsilyl-6-methylbiphenyl (10) and 2triethylsilyl-2'-methylbiphenyl (11) (40 mg, 78%). <sup>1</sup>H NMR (300.0 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.61–7.58 (m, 1 H, ArH, **10** or **11**), 7.43–7.28 (m, 7 H, ArH, **10** and 11), 7.24-7.09 (m, 8H, ArH, 10 and 11), 2.07 (s, 3H, ArMe, 10 or 11), 1.99 (s, 3H, ArMe 10 or 11), 0.83-0.77 (m, 18H, CH<sub>2</sub>CH<sub>3</sub>, 10 and **11**), 0.47–0.34 ppm (m, 12 H,  $CH_2CH_3$  **10** and **11**);  ${}^{13}C{}^{1}H{}$  NMR  $(75.4 \text{ MHz}, \text{ CDCl}_3): \delta = 148.8, 148.7, 143.8, 143.0, 136.2, 135.9, 135.8,$ 135.7, 135.6, 133.3, 130.6, 130.1, 129.9, 129.8, 129.7, 128.3, 127.9, 127.5, 127.1, 126.6, 126.0, 124.9 (ArC, 10 and 11), 21.2, 20.6 (ArMe, 10 and 11), 7.7, 7.6, 4.1, 3.8 ppm (CH<sub>2</sub>CH<sub>3</sub>, 10 and 11); <sup>29</sup>Si INEPT (59.6 MHz, CDCl<sub>3</sub>):  $\delta = 3.6$ , 3.4 ppm (10 and 11); elemental analysis calcd (%) for  $C_{19}H_{26}Si: C 80.78, H 9.28;$  found: C 80.39, H 9.11. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **10** and **11** are similar to those reported for the trimethylsilyl analogues.[71,72]

Single-crystal X-ray diffraction: The data for 3 were measured on a STOE IPDS-II diffractometer equipped with a sealed tube with  $Mo_{K\alpha}$ 

Chem. Asian J. 2014, 9, 3163-3173

An empirical absorption correction with the program radiation. PLATON<sup>[73]</sup> was performed. The data for remaining structures ([Ni-(PPhMe<sub>2</sub>)<sub>4</sub>], 8, and 9) were measured on a STOE IPDS-II diffractometer using a Genix Microfocus X-ray source with mirror optics and Mo<sub>Ka</sub> radiation. The data were corrected for absorption with the frame-scaling procedure contained in the X-AREA package.<sup>[74]</sup> The structures were solved by direct methods by using the program SHELXS and refined against  $F^2$ with full-matrix least-squares techniques by using the program SHELXL.<sup>[75]</sup> The crystal of **3** was a nonmerohedral twin with a fractional contribution of 0.228(5) for the minor domain. The absolute structure could not be determined reliably, Flack x parameter: -0.3(2). In 8, both tert-butyl groups are disordered over two sites with a site occupation factor of 0.582(16) and 0.642(7) for the major occupied site, respectively. The disordered atoms were refined isotropically. CCDC 1006499 (3), 1006496 (5), 1006495 (6), 1006503 (8), 1006502 (9), 1006501(12), 1006497 (13), 1006498 (14) and 1006500 ([Ni(PPhMe\_2)\_4]) contain the supplementation (13), 1006498tary 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.

#### Acknowledgements

This work was supported by the Beilstein-Institut, Frankfurt/Main (Germany), within the research collaboration NanoBiC (projects eNet and  $\pi$ Oligo). Quantum-chemical calculations were performed at the Center for Scientific Computing (CSC) Frankfurt on the Fuchs and LOEWE-CSC high-performance computer clusters.

- [1] a) J. Y. Corey, Adv. Organomet. Chem. 2011, 59, 1–180; b) J. Y. Corey, Adv. Organomet. Chem. 2011, 59, 181–328.
- [2] Y.-Q. Mo, X.-Y. Deng, X. Jiang, Q.-H. Cui, J. Polym. Sci. Part A 2009, 47, 3286–3295.
- [3] J. C. Sanchez, A. G. DiPasquale, A. L. Rheingold, W. C. Trogler, *Chem. Mater.* 2007, 19, 6459–6470.
- [4] J. C. Sanchez, W. C. Trogler, J. Mater. Chem. 2008, 18, 3143-3156.
- [5] E. Wang, C. Li, W. Zhuang, J. Peng, Y. Cao, J. Mater. Chem. 2008, 18, 797–801.
- [6] K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, J. Am. Chem. Soc. 1996, 118, 11974–11975.
- [7] J. H. Hong, P. Boudjouk, I. Stoenescu, Organometallics 1996, 15, 2179–2181.
- [8] Y. Liu, T. C. Stringfellow, D. Ballweg, I. A. Guzei, R. West, J. Am. Chem. Soc. 2002, 124, 49–57.
- [9] A. V. Zabula, A. Y. Rogachev, I. A. Guzei, R. West, *Organometallics* 2013, 32, 3760–3768.
- [10] S. Zhang, R. Chen, J. Yin, F. Liu, H. Jiang, N. Shi, Z. An, C. Ma, B. Liu, W. Huang, Org. Lett. 2010, 12, 3438–3441.
- [11] J. M. Breunig, A. Hübner, M. Bolte, M. Wagner, H.-W. Lerner, Organometallics 2013, 32, 6792–6799.
- [12] A. Hübner, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, Angew. Chem. Int. Ed. 2012, 51, 12514–12518; Angew. Chem. 2012, 124, 12682–12686.
- [13] A. Hübner, Z.-W. Qu, U. Englert, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, J. Am. Chem. Soc. 2011, 133, 4596–4609.
- [14] A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle, M. Wagner, Angew. Chem. Int. Ed. 2009, 48, 4584–4588; Angew. Chem. 2009, 121, 4654–4658.
- [15] C. Reus, S. Weidlich, M. Bolte, H.-W. Lerner, M. Wagner, J. Am. Chem. Soc. 2013, 135, 12892–12907.
- [16] M. Shimizu, K. Mochida, T. Hiyama, Angew. Chem. Int. Ed. 2008, 47, 9760–9764; Angew. Chem. 2008, 120, 9906–9910.
- [17] R. Shintani, H. Otomo, K. Ota, T. Hayashi, J. Am. Chem. Soc. 2012, 134, 7305–7308.
- [18] A. S. Dudnik, N. Chernyak, C. Huang, V. Gevorgyan, Angew. Chem. Int. Ed. 2010, 49, 8729–8732; Angew. Chem. 2010, 122, 8911–8914.

- [19] Y. Kuninobu, K. Yamauchi, N. Tamura, T. Seiki, K. Takai, Angew. Chem. Int. Ed. 2013, 52, 1520–1522; Angew. Chem. 2013, 125, 1560– 1562.
- [20] M. Onoe, K. Baba, Y. Kim, Y. Kita, M. Tobisu, N. Chatani, J. Am. Chem. Soc. 2012, 134, 19477–19488.
- [21] T. Ureshino, T. Yoshida, Y. Kuninobu, K. Takai, J. Am. Chem. Soc. 2010, 132, 14324–14326.
- [22] T. Matsuda, S. Kadowaki, T. Goya, M. Murakami, Org. Lett. 2007, 9, 133–136.
- [23] K. L. Chan, S. E. Watkins, C. S. K. Mak, M. J. McKiernan, C. R. Towns, S. I. Pascu, A. B. Holmes, *Chem. Commun.* 2005, 5766–5768.
- [24] J. Y. Corey, L. S. Chang, J. Organomet. Chem. **1986**, 307, 7–14.
- [25] H. Gilman, R. D. Gorsich, J. Am. Chem. Soc. 1958, 80, 1883–1886.
   [26] J. Song, C. Du, C. Li, Z. Bo, J. Polym. Sci. Part A 2011, 49, 4267–
- 4274.
  [27] J. P. M. van Klink, H. J. R. de Boer, G. Schat, O. S. Akkerman, F. Bickelhaupt, A. L. Spek, *Organometallics* 2002, *21*, 2119–2135.
- [28] P. F. Hudrlik, D. Dai, A. M. Hudrlik, J. Organomet. Chem. 2006, 691, 1257-1264.
- [29] Z. Wang, H. Fang, Z. Xi, Tetrahedron Lett. 2005, 46, 499-501.
- [30] Y. Yabusaki, N. Ohshima, H. Kondo, T. Kusamoto, Y. Yamanoi, H. Nishihara, *Chem. Eur. J.* 2010, 16, 5581–5585.
- [31] Good yields of silafluorenes were reported for route (i) only for bulky groups such as isopropyl. Furthermore, for the synthesis of unsymmetrically substituted silafluorenes the Pd-catalyzed C-C coupling reactions between C(Tf) and C(H) of diaryl silanes ArAr'SiR<sub>2</sub> have poor selectivity when Ar' bears an additional substituent in the 3-position (e.g., OMe or F). The trityl-cation-induced silafluorene synthesis yielding an unsymmetrically 2,7-substituted silafluorene (reaction (ii) in Scheme 1) has so far only been described for one example in the literature. An Rh-catalyzed coupling of the 2'-methyl-2-silylbiphenyl derivative leads to a product mixture. The major product of this reaction is a silaphenanthrene derivative, which is formed by dehydrogenative coupling of the hydrosilyl moiety with the methyl group. Route (iii) is limited to substitution patterns in the 2,3-positions. In the end, the reaction of type (iv) (Scheme 1) runs into selectivity problems if substituents are introduced in inappropriate positions of biphenyls.
- [32] Normally, C-C activation reactions have succeeded on using strained ring systems such as the four-membered rings of biphenylenes.<sup>[76,77]</sup> In contrast, Si-H bond activation reactions are often described in the literature.<sup>[78,79]</sup> As we wanted to perform both reactions simultaneously, the activation of the Si-H and C-C bonds represent competitive reactions.
- [33] T. Matsuda, H. Kirikae, Organometallics 2011, 30, 3923-3925.
- [34] For comparison, the Pd-catalyzed hydrosilylation of biphenylene with trialkyl silanes was completed after 2–3 h under the same reaction conditions.<sup>[33]</sup>
- [35] R. Beck, S. A. Johnson, Chem. Commun. 2011, 47, 9233-9235.
- [36] B. L. Edelbach, R. J. Lachicotte, W. D. Jones, *Organometallics* 1999, 18, 4040–4049.
- [37] B. L. Edelbach, R. J. Lachicotte, W. D. Jones, *Organometallics* 1999, 18, 4660–4668.
- [38] J. J. Eisch, A. M. Piotrowski, K. I. Han, C. Krüger, Y. H. Tsay, Organometallics 1985, 4, 224–231.
- [39] C. Müller, R. J. Lachicotte, W. D. Jones, Organometallics 2002, 21, 1975–1981.
- [40] S. Saito, T. Yoshizawa, S. Ishigami, R. Yamasaki, *Tetrahedron Lett.* 2010, 51, 6028–6030.
- [41] T. Schaub, U. Radius, Chem. Eur. J. 2005, 11, 5024-5030.
- [42] H. Schwager, S. Spyroudis, K. P. C. Vollhardt, J. Organomet. Chem. 1990, 382, 191–200.
- [43] W. Chen, S. Shimada, M. Tanaka, Y. Kobayashi, K. Saigo, J. Am. Chem. Soc. 2004, 126, 8072–8073.
- [44] M. Tanabe, R. Yumoto, K. Osakada, Chem. Commun. 2012, 48, 2125–2127.
- [45] T. Zell, T. Schaub, K. Radacki, U. Radius, *Dalton Trans.* 2011, 40, 1852–1854.

CHEMISTRY

**AN ASIAN JOURNAL** 

- [46] C. A. Tolman, D. W. Reutter, W. C. Seidel, J. Organomet. Chem. 1976, 117, C30-C33.
- [47] A. V. Marenich, S. V. Jerome, C. J. Cramer, D. G. Truhlar, J. Chem. Theory Comput. 2012, 8, 527–541.
- [48] The optimized structures of **H1**, **H2**, and **TS**<sub>**H2**.**B3**</sub> exhibit features in line with the earlier notion of a structural continuum between hydrido silyl and  $\eta^2$ -SiH silane  $\sigma$  complexes;<sup>[49,50]</sup> the Lewis structures in Scheme 5 illustrate the respective limiting case considered most relevant for the individual species based on the Ni–H and Si–H bond lengths found in the optimized geometries.
- [49] R. Beck, S. A. Johnson, Organometallics 2012, 31, 3599-3609.
- [50] V. M. Iluc, G. L. Hillhouse, Tetrahedron 2006, 62, 7577-7582.
- [51] S. S. Yi, E. L. Reichert, M. C. Holthausen, W. Koch, J. C. Weisshaar, *Chem. Eur. J.* 2000, 6, 2232–2245.
- [52] C. A. Hunter, J. K. M. Sanders, J. Am. Chem. Soc. 1990, 112, 5525– 5534.
- [53] F. Meyer-Wegner, H.-W. Lerner, M. Bolte, Acta. Cryst. Sect. C 2010, 66, 0182-0184.
- [54] Gaussian 09 (Revision D.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, J. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brohters, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, 2013.
- [55] J. P. Perdew, Phys. Rev. B 1986, 33, 8822-8824.
- [56] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [57] S. Grimme, J. Comput. Chem. 2006, 27, 1787–1799.

- [58] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297– 3305.
- [59] D. Feller, J. Comput. Chem. 1996, 17, 1571-1586.
- [60] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, J. Chem. Inf. Model. 2007, 47, 1045–1052.
- [61] EMSL basis set exchange. https://bse.pnl.gov/bse/portal.
- [62] R. A. Kendall, H. A. Früchtl, Theor. Chem. Acc. 1997, 97, 158–163.
- [63] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, 240, 283–290.
- [64] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* 1997, 97, 119–124.
- [65] B. I. Dunlap, J. Chem. Phys. 1983, 78, 3140-3142.
- [66] B. I. Dunlap, Theochem-J. Mol. Struct. 2000, 529, 37-40.
- [67] H.-W. Lerner, Coord. Chem. Rev. 2005, 249, 781-798.
- [68] N. Wiberg, Coord. Chem. Rev. 1997, 163, 217–252.
- [69] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Schuster, H. Nöth, I. Krossing, M. Schmidt-Amelunxen, T. Seifert, J. Organomet. Chem. 1997, 542, 1–18.
- [70] V. Miluykov, A. Kataev, O. Sinyashin, P. Lönnecke, E. Hey-Hawkins, Organometallics 2005, 24, 2233–2236.
- [71] A. Nagaki, N. Takabayashi, Y. Tomida, J.-i. Yoshida, Beilstein J. Org. Chem. 2009, 5, 16.
- [72] R. Klein, P. Sedmera, J. Cejka, K. Mach, J. Organomet. Chem. 1992, 436, 143–153.
- [73] A. L. Spek, Acta Crystallogr. Sect. D 2009, 65, 148-155.
- [74] Stoe & Cie, X-AREA. Diffractometer control program system 2002.
- [75] G. M. Sheldrick, Acta. Cryst. Sect. A 2008, 64, 112-122.
- [76] C. Perthuisot, B. L. Edelbach, D. L. Zubris, N. Simhai, C. N. Iverson, C. Müller, T. Satoh, W. D. Jones, *J. Mol. Catal. A* 2002, 189, 157– 168.
- [77] A. Steffen, R. M. Ward, W. D. Jones, T. B. Marder, Coord. Chem. Rev. 2010, 254, 1950–1976.
- [78] J. Y. Corey, Chem. Rev. 2011, 111, 863-1071.
- [79] J. Y. Corey, J. Braddock-Wilking, Chem. Rev. 1999, 99, 175-292.

Received: June 3, 2014 Published online: September 9, 2014