Carbene Complexes

Substitution Effects on the Formation of T-Shaped Palladium Carbene and Thioketone Complexes from Li/Cl Carbenoids

Sebastian Molitor, Kai-Stephan Feichtner, Claudia Kupper, and Viktoria H. Gessner^{*[a]}

temperatures.

Abstract: The preparation of palladium thioketone and T-shaped carbene complexes by treatment of thiophosphoryl substituted Li/Cl carbenoids with a Pd⁰ precursor is reported. Depending on the steric demand, the anion-stabilizing ability of the silyl moiety (by negative hyperconjugation effects) and the remaining negative charge at the carbenic carbon atom, isolation of a three-coordinate, T-shaped palladium carbene complex is possible. In contrast, insufficient charge stabilization results in the transfer of the sulfur of the thio-

Introduction

Since the pioneering work by E.O. Fischer and R.R. Schrock, transition-metal complexes with a metal carbon double bond have found wide-ranging applications in stoichiometric as well as catalytic transformations.^[1] Depending on the substituents at the carbenic carbon atom and the involved reactivity they are often classified into Fischer-type carbene and Schrock-type alkylidene complexes. In this context, carbene complexes formed from geminal dilithiated bis(thiophosphoryl) or bis(iminophosphoryl) methanes have gained special interest as they seem to contradict this general classification pattern.^[2] Here, the metal carbon bond is formally formed by a four-electron donation from the ligand to the metal, leaving a highly nucleophilic carbon atom bound to anion stabilizing substituents.^[3,4] This type of carbene complex was first introduced by R.G. Cavell and co-workers, who succeeded in the isolation of titanium and zirconium complexes.^[4c] The carbon center was reported to be multiply bound to the metal (structure **A** in Figure 1) and to the two phosphorus substituents. This was based on short M-C and P-C distances found in the crystal structures thus suggesting strong delocalization of the electron density. This leads to the description of the electronic structure by resonance forms with ylidic character such as form B. In the following years, a variety of different carbene complexes based on dilithio methandiides were prepared incorporating early and late transition metals as well as lanthanides and acti-

 [a] S. Molitor, K.-S. Feichtner, C. Kupper, Dr. V. H. Gessner Institut für Anorganische Chemie Julius-Maximilians-Universität Würzburg Am Hubland, 97074 Würzburg (Germany) E-mail: vgessner@uni-wuerzburg.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304927.

phosphoryl moiety and thus in the formation of a thioketone

complex. While the thicketones are stable compounds the

carbene complexes are revealed to be highly reactive and

decompose under elimination of Pd metal. Computational

studies revealed that both complexes are formed by a substi-

tution mechanism. While the ketone turned out to be the

thermodynamically favored product, the carbene is kinetical-

ly favored and thus preferentially formed at low reaction

Figure 1. Resonance structure of carbene complexes based on methandiides.

nides.^[5] However, due to the restricted access and the extreme sensitivity of dilithio methandiides, these studies have been limited to bis(phosphonium)-substituted systems.^[6] Such phosphorus(V) moieties are well known for their excellent anion stabilizing ability. This allows for the facile dilithiation as well as for the stabilization of the carbene complexes, particularly by stabilization of the high charge accumulation at the carbenic carbon via resonance form **C**.

An alternative approach to this class of carbene complexes has been presented by P. Le Floch, N. Mézailles and co-workers in 2007.^[7] They employed lithium chloride carbenoid **1** to access palladium complex **2**, which had earlier been prepared from the corresponding dilithio methandiide (Figure 2).^[8] To



Figure 2. Reactivity of carbenoids 1 and 3 towards [Pd(PPh₃)₄].

Chem. Eur. J. 2014, 20, 1–12

Wiley Online Library

These are not the final page numbers! 77



extend the applicability of this approach also on carbenoids with other substituents than P^{V} moieties we have recently reported on the silyl derivative 3.^[9] This carbenoid, however, selectively reacted with [Pd(PPh₃)₄] under formation of the palladium thioketone 4. In this case, no formation of a carbene complex was observed. The differences in the reactivity of both Li/Cl carbenoids were attributed to the dramatic loss of stabilization of the negative charge by replacing the thiophosphoryl substituent with the trimethylsilyl group. The remaining negative charge at the central carbon atom was thus assumed as the driving force for the rearrangement to the thermodynamically favored thioketone complex 4. These results prompted us to attempt a modification of our initial ligand system to allow for further stabilization of the negative charge. Silyl groups are known for their anion-stabilizing ability by negative hyperconjugation into low-lying σ^* -SiR orbitals.^[10] Thus, we envisioned that these interactions might be improved by the introduction of phenyl substituents instead of the trimethylsilyl group in 3. Here, we show that indeed variation of the substitution pattern at the silicon allows the isolation of the desired carbene complex. Thereby, the carbene complex turned out to be a rare example of a T-shaped Pd complex that decomposes under elimination of palladium metal. DFT calculations confirm the increasing stability of the carbene complex with the introduction of phenyl substituents as well as low energy pathways to both complexes observed.

Results and Discussion

Thioketone versus carbene formation

Preliminary investigations suggested that the lack of stabilization of the negative charge at the carbenic carbon atom is responsible for the selective formation of the palladium thioketone complex 4. As phenyl substituents are known to be more suitable to stabilize anions by negative hyperconjugation we first aimed at the introduction of phenyl groups. The required chlorinated precursors were synthesized as outlined in Scheme 1. The silvl compounds 5b-d were prepared by an analogous procedure as reported for the trimethylsilyl-substituted compound 5a. Lithiation of diphenylmethylphosphine sulfide (or dicyclohexylmethylphosphine sulfide in the case of 5e) with butyllithium and treatment with the corresponding chlorosilane at low temperatures afforded the α -silylated phosphine sulfides in moderate to good yields as colorless solids. Chlorination was subsequently achieved by deprotonation of the acidic methylene moiety and treatment with hexachloro-

S ∥ R _P ∕P∕ R _P Me	1) <i>n</i> BuLi 2) R ₂ R'SiCl	$R_{P} \xrightarrow{P} SiR_{2}R'$	1) <i>n</i> BuLi 2) C ₂ Cl ₆ ►	SiR ₂ R ['] R _P CI
	5a: R 5b: R	R _P = Ph, R = R' = M∉ R _P = Ph, R = Me, R'	∍; 76 % = Ph; 68 %	6a : 95 % 6b : 78 %
5c : R _P = Ph, R = Ph, R' = Me; 67 %				6c: 63 % 6d: 55 %
	50: R	α _P = Pn, κ = κ' = Pn Δ = Cv. R = R' = Ph	1, 00 % 1: 63 %	6e: 51 %

Scheme 1. Synthesis of the chlorinated precursors 6.

Chem. Eur. J. 2014, 20, 1 – 12 www.chemeurj.org

2

ethane. All compounds were fully characterized by multinuclear NMR spectroscopy in solution and elemental analysis. The molecular structures of silanes **5b**, **c** and **e** were additionally determined by single-crystal X-ray diffraction analysis. Figure 3 exemplarily depicts the molecular structure of the MePh₂Si-substituted compound **5c** (for crystallographic details and the molecular structure of **5b** and **5e**, see the Supporting Information).^[11] All bond lengths and angles are in the expected region, except for the P–C–Si angles, which are in all compounds larger (118.9(1)–127.1(1)°) than the ideal tetrahedral angle of 109.47°.



Figure 3. Molecular structure of silane 5 c. Selected bond lengths [Å] and angles [°] for 5 b, c and e. 5 b: P–C13 1.8030(19), P–S 1.9561(8), P–C7 1.8133(19), P–C1 1.812(2), Si–C14 1.854(2), Si–C15 1.857(2), Si–C16 1.874(2), Si–C13 1.896(2); P-C13-Si 121.06(10); 5 c: P–S 1.9587(6), C21–Si 1.8826(16), C15–Si 1.8700(16), C14–Si 1.8590(17), C13–Si 1.8902(15), C13–P 1.8045(15), C7–P 1.8185(15), C1–P 1.8241(17); P-C13-Si 118.87(8); 5 e: C1–P1 1.851(2), C7–P1 1.850(2), C13–P1 1.827(2), C13–Si 1.898(2), C14–Si 1.889(2), C20–Si 1.881(2), C26–Si 1.8887(19), P1–S1 1.9698(7), P1-C13-Si 127.07(11).

The chlorinated silanes were then converted to the corresponding Li/Cl carbenoids 7b-d by metallation with methyllithium. In none of the cases was the carbenoid stable at ambient temperature.^[12,13] NMR spectroscopy of the carbenoids in C₆D₆ at room temperature showed the decomposition and formation of multiple products, amongst others, Ph₂P(S)Cl. Only the SiPh₃-substituted carbenoid 7d selectively decomposes under dimerization by sulfur transfer.^[11] However, trapping reactions confirmed the selective formation of the carbenoids 7 so that in situ transformations are possible. To investigate the influence of the phenyl substituents on the formation of the thioketone complex, we at first treated the cooled THF solution of dimethylphenyl-substituted carbenoid 7b with a solution of tetrakis(triphenylphosphine)palladium(0), [Pd(PPh₃)₄], at room temperature (Scheme 2). NMR spectroscopic studies of the reaction mixture revealed the high-yielding formation of the thicketone complex 8b, which could be isolated as yellow solid in 64% yield after removal of lithium chloride and triphenyl phosphine. Compound 8b is characterized by a set of three doublets of doublets in the ³¹P{¹H} NMR spectrum, with two signals in the expected region for coordinated triphenylphosphine ligands (δ = 20.6 and 24.4 ppm). The signal for the free phosphine moiety appears at $\delta = 9.51$ ppm, upfield-shifted compared to the thiophosphoryl moiety in the precursor molecules **5b** and **6b** (δ = 38.3 and 45.9 ppm). The coupling con-

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

N These are not the final page numbers!

0



Scheme 2. Formation of the thioketone and carbene complexes 8 and 9 from the corresponding carbenoids 7.

stants of ${}^{2}J_{PP}$ =29.1 and ${}^{3}J_{PP}$ =23.9 and 25.6 Hz are in agreement with the formulation of the thioketone complex. The 29 Si NMR spectroscopic signal appeared as doublet of doublets at $\delta = -11.0 \text{ ppm} ({}^{2}J_{SiP}$ =36.9, ${}^{3}J_{SiP}$ =5.87 Hz). Due to the synthetic method complex **8b** is obtained as racemic mixture. The stereogenic carbon atom results in diastereotopic phenyl and methyl substituents at the adjacent phosphorous and silicon atom, respectively, and thus in the corresponding splitting in the 11 H and 13 C[¹H] NMR spectra.

Interestingly, when the reaction was repeated with a solution of [Pd(PPh₃)₄] cooled to -78 °C, the ³¹P NMR spectrum of the reaction mixture revealed the formation of a second species in small quantities of approximately 8%. This compound is characterized by only two doublets in the ³¹P NMR spectrum, one in the range for coordinated PPh₃ (δ = 22.6 ppm), the second downfield-shifted at δ = 46.4 ppm. This suggested that the introduction of the phenyl substituent also enabled the stabilization of a second palladium complex with only a single coordinating PPh₃ ligand and—most importantly—an intact thiophosphoryl moiety. The coupling constant of ³J_{PP} = 14.8 Hz is close to that reported for the symmetric carbene complex **2** (³J_{PP} = 14.6 Hz), thus indicating the formation of a T-shaped carbene complex **9** (Scheme 2).

Repeating this experiment with the diphenylmethyl and the triphenyl silyl-substituted derivatives 6c and 6d confirmed this tendency observed with 6b. In all cases, the corresponding thioketone complex was formed as the major product. However, with increasing number of phenyl substituents an increasing formation of the palladium carbene complex 9 was observed (entries 3, 5, and 8 in Table 1). This is especially true for reactions performed at low reaction temperatures (entry 6, 7, and 8) and thus accounts for a kinetic preference of the formation of 9. In the case of the reaction of the triphenylsilyl-substituted carbenoid **7 d** with $[Pd(PPh_3)_4]$ at $-78^{\circ}C$ both complexes are formed in an almost equimolar ratio (entry 8). Here, the Pd complexes could be separated by extraction of **9d** with diethyl ether from the highly insoluble thioketone complex 8d. It is noteworthy, that no interconversion between the carbene and the thioketone complex was observed even in the presence of excessive triphenyl phosphine and at high temperatures (up to 100 °C). The ratio between both compounds remained constant even after prolonged storage at room temperature, thus suggesting that both complexes are formed by different, irreversible reaction pathways (vide infra). Also using [Pd(PPh₃)₂]

Table 1. Ratio of thicketone 8 and carbene complex 9 depending on the reaction temperature and the substitution pattern of the carbenoid 7.							
Entry	PR_2	Silyl group	7 [°C] ^[i]	Thioketone 8 [%] ^[ii]	Carbene 9 [%] ⁱⁱ		
1	PPh ₂	SiMe₃	RT	100 (79)	0		
2	PPh_2	SiMe₂Ph	RT	97 (64)	3		
3			−78 °C	92	8		
4	PPh_2	SiMePh ₂	RT	88 (56)	12		
5			−78 °C	75	25		
6	PPh₂	SiPh₃	RT	80 (62)	20		
7			$-40^\circ C$	60	40		
8			−78 °C	48 (41)	52 (15)		

[a] Temperature of the THF solution of $[Pd(PPh_3)_4]$. [b] Ratio of thioketone and carbene complex in the crude reaction product determined by ¹H and ³¹P NMR spectroscopy; isolated yields in brackets. Isolation of the carbene complex was only accomplished with **9 d**.

100 (53)

-78°C

9

PCy₂

SiPh

as a Pd⁰ precursor resulted in the same product mixtures as observed for the tetracoordinated congener.^[14]

To examine the influence of the phosphine moiety on the sulfur transfer we additionally prepared the bis(cyclohexyl)phosphine sulfide 6e. Here, we expected the sulfur transfer to be less favorable due to the more electron-rich phosphorous, which should hamper the reduction to the free phosphine unit. However, treatment of the corresponding carbenoid with [Pd(PPh₃)₄] at low reaction temperatures selectively delivered the thioketone complex even in combination with the SiPh₃ moiety (entry 9, Table 1). This is evidenced by three doublets of doublets in the ³¹P{¹H} NMR spectrum at $\delta = 18.33$ (PCy₂), 22.1, and 23.0 ppm. This observation clearly suggests that the stabilization of the negative charge at the carbenic carbon atom is the crucial factor for the carbene formation. Despite preventing the reduction to the free phosphine, the cyclohexyl ligands reduce the ability of the thiophosphoryl moiety for negative hyperconjugation into low-lying σ^* -PR orbitals. Hence, thioketone complex 8e and not the carbene complex is selectively formed.

All thioketone complexes were characterized by multinuclear NMR spectroscopic studies. Elemental analyses gave consistently low values for C, which we attributed to carbide formation as H and S values were consistent with the proposed formulation and all spectroscopic data indicated that the samples are pure. The molecular structure of thioketone 8b and 8d were determined by single-crystal X-ray diffraction and 8d additionally characterized by high-resolution mass spectrometry (HRMS) showing a mass of m/z = 1119.21 with the simulated peak profile. The molecular structures of thioketone complexes 8b and 8d are depicted in Figure 4 (for crystallographic details, see the Supporting Information). In both complexes, the central structural motif is formed by a Pd-C-S ring, in which the palladium adopts a strongly distorted square-planar coordination with angles between 45.94(8) and 109.90(8) $^{\circ}$ and 45.97(8) and 110.41(8)°, respectively. Due to the short bite of the C-S linkage also the coordination sphere around carbon considerably deviates from the ideal tetrahedral arrangement. The Pd-C (2.169(3) (8b), 2.177(3) (8d)) as well as the C-Si and C-P distances are in the typical range of single bonds. On the

Chem. Eur. J. 2014 , 20, 1 – 12	www.chemeurj.org	

These are not the final page numbers! **77**



Figure 4. Molecular structure of the thioketone complex **8b** (top) and **8d** (bottom). Two CH₂Cl₂ solvent molecules in **8b** and hydrogen atoms of the phenyl substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: **8b**: C13–S 1.748(3), C13–P1 1.832(3), C13–Si 1.885(3), C13–Pd 2.169(3), P2–Pd 2.3634(8), P3–Pd 2.3183(9), Pd–S 2.2985(8); P1-C13-Si 115.05(15), S-C13-Pd 70.93(10), P1-C13-Pd 112.50(14), Si-C13-Pd 113.49(14), C13-Pd-S 45.94(8), S-Pd-P2 98.12(3), P3-Pd-P2 106.04(3), C13–Pd-P3 109.90(8); **8d**: C13–S 1.750(3), C13–P1 1.832(3), C13–Si 1.890(3), C13–Pd 2.177(3), P2–Pd 2.3451(8), P3–Pd 2.3716(8), Pd–S 2.2953(8); P1-C13-Si 118.48(16), S-C13-Pd 70.59(10), P1-C13-Pd 112.77(14), Si-C13-Pd 113.39(14), C13-S-Pd 63.43(9), C13-Pd-P2 110.41(8), C13-Pd-S 45.97(8), S-Pd-P3 98.32(3), P2-Pd-P3 105.58(3).

contrary, the C–S bond of 1.748(3) Å in **8b** and 1.750(3) in **8d** is shorter than a typical C–S single bond, which indicated some π -character. Both, the short C–S bond and the flattened carbon coordination sphere (torsion angle (Si-C-P-S) of 146.9(2)° in **8b** and 147.8(2) in **8d**), are indicative for a π -character of the C–S bond, so that **8b** and **8d** can also be viewed as a side-on coordination complex of the Pd⁰ species to the C=S double bond.^[15,16] It is interesting to note, that the bulkier phenyl substituent of the Me₂PhSi unit in complex **8b** points towards the sterically more demanding triphenyl phosphine substituents.

The Ph₃Si-substituted thioketone complex **8d** proved to be stable towards air and moisture. Storage under ambient conditions for months showed no decomposition for example, by oxidation of the phosphine moiety. This enhanced stability compared with the corresponding thioketone complexes incorporating methylsilyl or PCy₂ units can easily be explained from the plot of the van-der-Waals radii, which confirms an efficient shielding by the phenyl groups (Figure 5). Comparison of the bonding parameters of **8d** with **8b** shows, that the most pronounced difference of both structures involves the Pd–P distances as well as the P–C–Si angle. While the Pd–P bonds are only slightly elongated in **8d**, the P–C–Si angle decreases from 123.1(2) to 118.5(2)° by introduction of the phenyl substitu-



A European Journal Full Paper

Figure 5. Left: plot of the Van-der-Waals-radii of **8d** (left). Right: projection of the central unit of the thioketone complexes **8d** ($R=SiPh_3$) and its SiPhMe₂-derivative **8b** (bright gray).

ents. Both tendencies are in line with the increased steric bulk in 8 d.

The carbene complex could only be isolated from the 1:1 mixture in the case of the SiPh₃-substituted system. Compound 9d is characterized by two doublets in the ³¹P{¹H} NMR spectrum at $\delta = 23.7$ and 46.1 ppm (${}^{3}J_{PP} = 16.4$ Hz). The ${}^{1}H$ NMR spectra as well as HRMS (ESI) (m/z: 857.1212) confirm the bonding of only a single phosphine ligand at palladium. In the carbene complex 9d no diastereotopic splitting of the signals of the Ph groups at phosphorus are evident in the ¹H and ¹³C{¹H} NMR spectra. This is in line with a three-coordinate carbon atom as expected for the carbene complex. Unfortunately, all crystallization attempts failed and resulted in the decomposition (see below) of the highly sensitive complex 9d. In general, three-coordinate palladium complexes are often proposed as intermediates in palladium-catalyzed cross-couplings.^[17] For example, mechanistic studies by Hartwig and coworkers have shown that key intermediates of carbon-nitrogen bond-formation reactions catalyzed by palladium complexes with bulky triarylphosphine ligands bear only one phosphine ligand.^[18] Yet, only few isolated and structurally characterized examples of such three-coordinate palladium complexes are known.[19]

The possible isolation of the T-shaped carbene complex **9** can be referred to the bulkiness of the ligand and the thus involved steric protection. This is confirmed by computational studies which also confirm the geometry of the complex (see below). As can be seen from a space-filling model of the energy-optimized structure of **9d** the open side at the palladium center is efficiently shielded by the phenyl substituents of the silyl moiety (Figure 6). To evaluate an electronic contribu-



Figure 6. Energy-optimized structure and space-filling model of 9 d.

Chem. Eur. J. **2014**, 20, 1 – 12

www.chemeurj.org

FF These are not the final page numbers!



Full Paper

tion to the stability we investigated the electronic structure of 9d. Natural population analysis revealed a high negative charge ($q_c = -1.39$) at the carbonic carbon atom and a Wiberg bond index of only 0.54 for the Pd–C bond (cf. WBI(S–Pd) = 0.45, WBI(C–P) = 1.19). Additionally, natural bond orbital (NBO) analysis indicates only a single bond with no π -interaction between the sp²-hybridized carbon atom and the metal center. The remaining lone pair at the carbon atom is stabilized by negative hyperconjugation effects into $\sigma^*(P-C_{Ph})$ and $\sigma^*(Si C_{\mbox{\tiny Ph}})$ orbitals. These interactions are equally strong as the interaction with unoccupied orbitals at the palladium atom (second-order perturbation theory). Despite the three-coordinate palladium center, complex 9 is better described as an alkyl than as an carbene complex with palladium in the formal oxidation state +2 (resonance structure 9A). Overall, steric ef-



fects play a crucial role in the stabilization of 9d. However, electronic stabilization of the charges is not less important.

XRD analysis of decomposition products of carbene complex 9d revealed amongst others the formation of ylide 10 (Scheme 3) and palladium phosphine complexes. Compound



Scheme 3. Formation of ylide 10 by elimination of Pd metal from carbene complex 9d.

10 is formally formed by elimination of palladium metal from the carbene complex 9d under additional C-P bond formation. The molecular structure of ylide 10 is shown in Figure 7. Ylide 10 crystallizes in the monoclinic space group $P2_1/c$. The P-C bond lengths of the central carbon atom C13 (1.741(3) and 1.769(3) Å) are shorter than typical P-C single bonds, such as those found in 5b and 5c (1.803(2) and 1.8045(15) Å). This accounts for the additional electrostatic interactions within the S-P-C-P framework. Because P1 interacts with both negatively charged centers (S and C13), the P-C distance to the thiophosphoryl moiety is longer than the one to the triphenylphospine unit. Accordingly, the P-S bond in 10 is slightly lengthened compared to 5b and 5c. Scheme 3 depicts the most important resonance structure of ylide 10.

Computational studies

To better understand the observed reactivity we performed detailed computational studies on both, the observed thioketone complexes as well as the carbene analogues. Calculations were



Figure 7. Molecular structure of the ylide 10. Hydrogen atoms of the phenyl substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-P1 1.834(3), C7-P1 1.839(3), C13-P2 1.741(3), C13-P1 1.769(3), C13-Si 1.859(3), C14-P2 1.829(3), C20-P2 1.811(3), C26-P2 1.825(3), C32-Si1 1.904(3), C38-Si 1.896(3), C44-Si 1.895(3), P1-S 1.9782(12); P2-C13-P1 118.18(15), P2-C13-Si 118.98(15), P1-C13-Si 121.32(15).

performed using the B3LYP functional^[20] together with the 6-31g (H), 6-311g(d) (C,P,S,Si), and LanL2TZ(f) basis set^[21] for Pd with the corresponding effective core potential (for further functionals and basis sets tested, see the Supporting Information). At first, energy optimizations were performed on the real systems with the SiMe₃ and the SiPh₃ substituent to evaluate the thermodynamics of the products. Besides thicketone 8d and carbene complex 9d three further isomers were considered (the SiPh₃-substituted systems are depicted in Figure 8). These include: 1) the *cis*-isomer 9d' with the PPh₃ ligand *cis* to the carbene ligand, 2) the dimeric species 9d₂, and 3) the bis-(triphenylphosphine)-substituted derivative 9d-PPh₃. The calculations revealed that thioketone 8d is the thermodynamically most stable compound favored by 16.3 kJ mol⁻¹ over the carbene complex 9d. Isomer 9d' with the triphenyl phosphine ligand in cis-position to the carbene ligand was found to be



Figure 8. Possible isomers of complex 9d and their relative energies compared to thioketone 8d (values in brackets correspond to the energies of the SiMe₂-substituted systems 8a and 9a).

Chem. Eur. J. 2014, 20, 1-12 www.chemeurj.org These are not the final page numbers! 77

5

44.4 kJ mol⁻¹ higher in energy, thus being clearly disfavored compared to the trans-isomer 9d. This is in line with the small ³J_{PP} coupling constants found for all carbene complexes **9** b–d, which are comparable to the one reported for the known carbene complex 2. The Pd carbene complex 9d-PPh₃ proved to be no minimum on the energy surface. Optimization always resulted in the loss of one phosphine ligand due to spatial overload. The same holds true for a dimeric structure $9d_{2}$, which also turned out to be instable. A different picture is obtained for the sterically less demanding trimethylsilyl systems 8a and 9a (Figure 8, energies are given in parentheses). Here, the bis(triphenylphosphine)-substituted derivative 9a-PPh₃ is revealed to be a minimum on the potential-energy surface; however, it is clearly disfavored compared to the thioketone ($\Delta E =$ 141.5 kJ mol⁻¹). A clear preference of the thioketone **8a** is also observed in comparison to the carbene complexes 9a and 9a', which are disfavored by 74.6 and 93.0 kJ mol⁻¹, respectively. Overall, thermodynamics favors the formation of the thioketone complex, both in the case of the SiMe₃ and the SiPh₃ systems. However, this preference is by far less pronounced for the bulkier SiPh₃ systems. The calculations are well in line with the experimental observations and thus explain the increasing formation of the carbene complex with decreasing preference of the thioketone. The stabilization is probably due to a combination of electronic and steric effects.

Next, we turned our attention towards possible mechanistic pathways delivering both the thioketone and the carbene complex. For computational cost we first chose a model system with PPh₃ replaced by PH₃ ligands. After our preliminary investigations on the trimethylsilyl-substituted carbenoid, we suggested a kind of rearrangement leading directly from the carbene complex **9a-PPh₃** to thioketone **8a**.^[9] The latter would be formed selectively due to thermodynamic reasons. However, calculations show that there is no low-energy pathway leading directly from the carbene to the thioketone complex. DFT calculations revealed a reaction barrier of 123.3 kJ mol⁻¹, which is too high to explain the formation of the thioketone also at low reaction temperature (Figure 9). This is especially true for the SiPh₃-substituted system, for which the corresponding carbene complex 9d-PPh₃ was found to be instable due to spatial overload (Figure 7). The absence of a low-energy pathway from the carbene to the thioketone and the irreversibility of this mechanism are in accordance with the experimentally observed absence of an interconversion between the carbene and thioketone complex at room



Figure 9. Direct rearrangement of carbene complex $9a-PH_3$ to thioketone 8a.

www.chemeurj.org

Chem. Eur. J. **2014**, 20, 1–12

6

temperature. It is also noteworthy, that neither the carbene nor the thioketone complex is accessible from the dimeric product **11** of the carbenoid decomposition. Treatment of **11**



with [Pd(PPh₃)₄] at -78 °C or room temperature always resulted in the formation of complex product mixtures.

As there is no pathway leading directly from the carbene to the thioketone a different mechanism has to be active. Considering possible reactive sides (Figure 10) of the starting Li/Cl



Figure 10. Possible reaction pathways of the reaction of Li/Cl carbenoids with a Pd^0 species.

carbenoid three different mechanisms for the reaction of the carbenoid with the Pd⁰ species have to be taken into account: 1) substitution reaction by nucleophilic attack of the carbenoid carbon at the Pd species; 2) oxidative addition of the Pd species into the carbon chlorine bond; 3) elimination of lithium chloride under formation of a free carbene intermediate, which subsequently binds to the palladium precursor. These pathways were studied by computational methods using a monomeric carbenoid as model system. The coordination sphere of the lithium atom was completed by dimethyl ether ligands. Due to computational costs, the trimethylsilyl compound together with PH₃ as model for PPh₃ was used. The calculations show that the elimination mechanism possesses the highest reaction barrier ($\Delta E^{\pm} = 129.2 \text{ kJmol}^{-1}$), thus excluding the viability of the reaction at low reaction temperatures. The same holds true for the oxidative addition with a barrier of 103.4 kJ mol⁻¹ (see the Supporting Information). To experimentally exclude the viability of an oxidative addition into the C-Cl bond under mild reaction conditions we treated the chlorinated compound 6d with [Pd(PPh₃)₄] in THF. NMR spectroscopic monitoring revealed no reaction even after 24 h at room temperature. This leaves-in accordance with the studies by Le Foch and co-workers on complex 2-the substitution process as the most feasible pathway.

The substitution mechanism including the Gibbs free energy of all intermediates and transition states relative to the monomeric carbenoid and [Pd(PPh₃)₃] is shown in Scheme 4.^[22] The first step involves the nucleophilic attack of the carbenoid carbon at the Pd⁰ species (**TS-1**) in an S_N2-type fashion. The reaction barrier amounts to only $\Delta E^{\pm} = 49.0$ kJ mol⁻¹, which is in line with the viability of the reaction at low reaction temperatures. The formed intermediate **Int-1** next undergoes elimination of lithium chloride via **TS-2** to form the carbene inter-

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

N These are not the final page numbers!



one phosphine ligand to form Int-2-PPh₃. Such two coordinat-

ed Pd complexes are well known in

chemistry and also isolable de-

pending on the coordinating li-

gands.^[23] Int-2-PPh₃ subsequent-

ly delivers the carbene complex

via TS-3B with a barrier of only

7.6 kJ mol $^{-1}$ or the thioketone

via **TS-3A** ($\Delta G^{\pm} = 62.7 \text{ kJ mol}^{-1}$).

The difference of 55.1 kJ mol⁻¹

between both reaction barriers

(TS-3A vs. TS-3B) slightly decreases when replacing the

SiMe₃ substituent with its phenyl

analogue ($\Delta G^{\pm} = 42.2 \text{ kJ mol}^{-1}$).

Overall, the calculations reflect

well the experimental observa-

palladium

mediate Int-2, which is 85 kJ mol⁻¹ more stable than the starting reagents. This carbene complex Int-2 turned out to be the crucial species determining the outcome of the reaction. In the next step Int-2 can either react to the carbene complex (path B, Scheme 4) by coordination of the thiophosphoryl unit—and elimination of a further PH₃ ligand—or it can form and its possible isolation in the experiment. Concerning the formation of the thioketone versus the carbene complex the calculations predict a considerable kinetic preference of the carbene formation. This corroborates with the experimental observations of the preferred carbene formation at lower reaction temperatures. In the first step carbene complex Int-2 loses

intermediates



Scheme 4. Nucleophilic substitution mechanism for thioketone and carbene formation [B3LYP/6-311g(d)/ LanL2TZ(f)].

the thioketone complex (path A) by transfer of the sulfur to the carbene carbon atom. An alternative concerted mechanism to the thioketone by transfer of the thiophosphoryl sulfur to the carbenoid carbon and simultaneous LiCl elimination from Int-1 revealed a considerably higher barrier (123 mol⁻¹) than the stepwise pathway via the carbene Int-2.

As substituent effects have proven to crucially influence the reaction outcome, we investigated both pathways-paths A and B-employing the real SiMe₃ and SiPh₃-substituted systems as well as PPh₃ as the co-ligand. An energy profile for both systems is depicted in Figure 11. From a thermodynamical point of view, one clearly recognizes the increasing stability of the carbene complex when replacing the SiMe₃ (red) by the SiPh₃ substituent (black). While in the former case an energy difference of 74.6 kJ mol⁻¹ was observed, only а preference of 16.3 kJ mol⁻¹ was found for the SiPh₃-substituted thioketone. This confirms the increased stability of the carbene complex

TS-3A SiMe SiPh 31.5 23.3 carbene complex 9 TS-3B Int-2 21.1 Int-2-PPh 4.9 -2.7 -10.7 -24 6 -82.6 -99.0 -12 ∆G [kJ mol⁻¹] reaction coordinate thioketone complex 8

Figure 11. Comparison of the formation of carbene complex 9 and thioketone 8 with the SiMe₃ and the SiPh₃ substituents (B3LYP//6-31g(d)/6-311g(d)/LanL2TZ(f)); energies are given relative to the respective intermediate carbene species Int-2.

These are not the final page numbers! **77**

www.chemeurj.org

Chem. Eur. J. 2014, 20, 1-12

7

Conclusion

We reported on the impact of stabilization effects in silyl-substituted Li/Cl carbenoids on their reactivity towards Pd⁰ complexes. An insufficient stabilization of the negative charge at the carbenic carbon atom results in the transfer of the sulfur

tions.



from the thiophosphoryl moiety to the carbenic carbon atom and thus in the formation of a thioketone complex. However, with increasing anion-stabilizing ability (via negative hyperconjugation effects) and steric demand of the silyl and phosphoryl moiety, the isolation of a three-coordinate, T-shaped palladium carbene complex is possible. This formation was also found to be temperature-dependent. While the thioketones are stable compounds the carbene complexes revealed to be reactive and decompose under elimination of Pd metal and formation of a new C-P bond. DFT studies-in line with the experimental observations-show that the thioketone formation is thermodynamically favored, while the carbene complex is the kinetic product of the reaction. Mechanistic studies showed that there is no direct pathway leading from the carbene to the thioketone complex. Instead, both complexes are formed by a substitution mechanism. Both, thermodynamics and kinetics are crucially influenced by the nature of the silyl moiety.

Overall, these studies show that the substitution pattern of carbenoids can crucially influence not only the stability of the carbenoid but also its reactivity and the reaction outcome. Careful selection of the substituents and their electronic effects on the carbenic carbon atom should thus allow for a control of their reactivity and hence allow for novel applications. We are currently investigating the reactivity of the carbenoids towards other transition metals.

Experimental Section

General

All experiments were carried out under a dry, oxygen-free argon atmosphere by using standard Schlenk techniques. Involved solvents were purified and dried by distillation over sodium, molten potassium and sodium/potassium alloy, respectively, and were stored over activated 4 Å molecular sieves. C₆D₆ and CD₂Cl₂ was degassed by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves. H₂O is distilled water. Organolithium reagents were titrated against diphenylacetic acid prior use. $^1H,\ ^{13}C\{^1H\},\ ^{29}Si\{^1H\},$ and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance AV 500 or a Bruker Avance AV 400 spectrometers at 22 °C. All values of the chemical shift are in ppm regarding the δ -scale. ¹H and ¹³C{¹H} NMR spectra were referenced to external tetramethylsilane by the residual solvent peak (¹H NMR spectra) or the solvent itself (13C NMR spectra). $^{31}\mbox{P}\{^1\mbox{H}\}$ NMR spectra were referenced to external 85% H₃PO₄, ²⁹Si{¹H} NMR to TMS. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singulet, d=doublet, t=triplet, m=multiplet, br=broad signal. Signal assignment was supported by DEPT and HMQC experiments. Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. High-resolution mass spectra (ESI) were recorded on an ESI MicrOTOF Focus spectrometer from Bruker Daltonics. Ph₂MePS, Cy₂MePS, and [Pd(PPh₃)₂]^[14] were synthesized according literature procedures. Compounds 5a, 5c, 5d, and their chlorinated analogues have been reported previously. All other reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification. For ¹H and ³¹P{¹H} NMR spectra of all complexes, see the Supporting Information.

General procedure for the precursors 5

Diphenylmethylphosphine sulfide (or dicyclohexylmethylphosphine sulfide) was dissolved in THF and cooled to -78 °C. At this temperature 1.2 equivalents of *n*BuLi (1.65 \times in hexane) were added and the resultant yellow mixture stirred for 3 h at low temperature. In a second Schlenk flask, 1.2 equiv of the corresponding chlorosilane were dissolved in 30 mL diethyl ether and cooled to -78 °C. The lithiated phosphine sulfide was added dropwise by a cannula transfer and slowly warmed to ambient temperature after completion of the addition. After stirring for 3 h, hydrochloric acid (2 \times) was added and the mixture extracted with diethyl ether. Drying over sodium sulfate and removal of the solvent afforded a yellowish solid, which was either washed with a mixture of diethyl ether/ pentane (v/v = 1:2) or purified by flash chromatography.

Compound **5***b*: Yield: 68%; ¹H NMR (500.1 MHz, CDCl₃): δ = 0.32 (s, 6H; SiCH₃), 2.23 (d, ²J_{PH} = 17.2 Hz, 2H; PCH₂Si), 7.27–7.32 (m, 3H; CH_{SIPh}), 7.34–7.47 (m, 8H; CH_{Ph}), 7.80–7.86 ppm (m, 6 CH_{Ph,ortho}); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ = -1.45 (d, ³J_{PC} = 1.5 Hz; SiCH₃), 21.1 (d, ¹J_{PC} = 46.6 Hz; SiCH₂P), 127.8 (CH_{SiPh,ortho}), 128.3 (d, ²J_{PC} = 12.1 Hz; CH_{ortho}), 129.2 (CH_{SiPh,para}), 130.6 (d, ³J_{PC} = 10.6 Hz; CH_{meta}), 130.9 (d, ⁴J_{PC} = 3.0 Hz; CH_{para}), 133.4 (CH_{SiPh,meta}), 135.6 (d, ¹J_{PC} = 80.5 Hz; C_{ipso}), 138.5 ppm (d, ³J_{PC} = 6.3 Hz; C_{SiPh,ipso}); ²⁹Si{¹H</sup> NMR (99.4 MHz, CDCl₃): δ = -4.30 ppm (d, ²J_{PSi} = 3.9 Hz); ³¹P{¹H} NMR (202.5 MHz, CDCl₃): δ = 38.3 ppm; elemental analysis calcd (%) for C₁₆H₂₁PSSi: C 68.81, H 6.32, S 8.75; found: C 68.84, H 6.53, S 8.82; M.p. 88.6°C; GCMS (El): t_R = 16.299; m/z (%): 366 (18) [M⁺], 351 (56) [M⁺-Me], 289 (50) [M⁺-Ph], 135 (100) [SiMe₂Ph⁺].

Compound **5***e*: Yield: 63%; ¹H NMR (500.1 MHz, CDCl₃): δ =0.90–1.10 (m, 6H; CH_{2rCy}), 1.27–1.31 (m, 4H; CH_{2rCy}), 1.50–1.58 (m, 4H; CH_{2rCy}), 1.68–1.75 (m, 4H; CH_{2rCy}), 1.81–1.90 (m, 4H; CH_{2rCy}+CH_{rCy}), 2.09 (d, ²J_{PH}=14.8 Hz, 2H; PCH₂Si), 7.36–7.44 (m, 9H; CH_{para,meta}), 7.67–7.70 ppm (m, 6H; CH_{ortho}); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ =12.2 (d, ¹J_{PC}=38.7 Hz; PCH₂Si), 25.7 (d, ⁴J_{PC}=1.58 Hz; PCH) (CH₂CH₂)₂CH₂), 26.3–26.6 (5×CH₂), 39.6 (d, ¹J_{PC}=48.1 Hz; PCH), 127.8 (CH_{SiPh,meta}), 129.7 (CH_{SiPh,para}), 134.2 (d, ³J_{PC}=2.39 Hz; CH_{SiPh,ipso}), 136.2 ppm (CH_{SiPh,ortho}); ²⁹Si{¹H} NMR (292.5 MHz, CDCl₃): δ = -14.8 ppm (d, ²J_{PS}=5.66 Hz); ³¹P{¹H} NMR (202.5 MHz, C₆C₆): δ = 57.1 ppm; elemental analysis calcd (%) for C₃₁H₃₉PSS: C 74.06, H 7.82, S 6.38; found: C 74.48, H 7.92, S 6.09.

Preparation of 6 b

8

Phosphine sulfide (1.36 mmol, 500 mg) was dissolved in THF (10 mL) and cooled to -78 °C. *n*-Butyllithium (1.0 mL, 1.60 mmol; 1.55 m in hexane) was added and the yellow solution was stirred for 3 h at temperatures below -30°C. In a second Schlenk flask, hexachloroethane (379 mg, 1.60 mmol) was dissolved in diethyl ether and cooled to -78 °C. The lithiated phosphine sulfide was slowly added by cannula transfer and after complete addition warmed to room temperature. The yellow mixture was stirred for 4 h at room temperature and then quenched by addition of 20 mL water. Extraction with diethyl ether (3×60 mL), drying over sodium sulfate, and removal of the solvent afforded a yellow solid. The solid was purified by flash chromatography on silica gel (pentane/ diethyl ether = 2:1) giving the product (racemic mixture) as colorless crystalline solid (425 mg, 1.06 mmol, 78%). ¹H NMR (500.1 MHz, CDCl₃): $\delta = 0.406 + 0.408$ (s, 3 H each; SiCH₃), 4.31 (d, $^{2}J_{PH} = 11.4$ Hz, 1 H; PCH₂Si), 7.22–7.25 (m, 2 H; CH_{SiPh,meta}), 7.31–7.44 (m, 6H; CH_{PPh}), 7.45–7.47 (m, 2H; CH_{SiPh,ortho}), 7.48–7.52 (m, 1H; CH_{SiPh,para}), 7.71–7.77 (m, 2H; CH_{PPh,ortho}), 7.99–8.04 ppm (m, $2 CH_{PPh,ortho}$; ¹³C{¹H} NMR (125.8 MHz, CDCl₃): $\delta = -2.37 + -0.65$ $(SiCH_3)$, 44.5 (d, ${}^{1}J_{CP} = 37.1$ Hz; SiCHCIP), 127.8 (CH_{SiPh,meta}), 129.1 (d, $^{2}J_{PC} = 12.4 \text{ Hz}; CH_{meta}), 129.5 (d, {}^{2}J_{CP} = 12.3 \text{ Hz}; CH_{meta}), 130.6$

Chem. Eur. J. 2014, 20, 1–12

www.chemeurj.org

Preparation of 6 e

Analogous procedure as for **6b**. Yield: 51%; $R_{\rm F}$ =0.72; ¹H NMR (300.1 MHz, CDCl₃): δ =0.55-0.78 (m, 2H; CH₂,PCy), 0.89-1.03 (m, 2H; CH₂,PCy), 1.16-1.32 (m, 3H; CH₂, PCy), 1.48-1.92 (m, 13H; CH₂,PCy), 2.14-18 (m, 1H; CHPCy), 2.26-2.39 (m, 1H; CHPCy), 4.57 (d, 2JHP=12.6 Hz, 1H; CHCl), 7.34-7.43 (m, 9H; CH_{PPh,meta/para}), 7.79-7.81 (m, 6H; CH_{PPh,ottho}); ¹³C{¹H} NMR: (75.5 MHz, CDCl₃): δ = 24.8-29 (m; CH₂, PCy), 35.5 (d, ¹J_{PC}=46.1 Hz; PCH), 37.5 (d, ¹J_{PC}= 45.5 Hz; PCH), 39.2 (d, ¹J_{PC}=28.0 Hz; PCCl), 127.7 (CH_{PPh,meta}), 129.9 (CH_{PPh,para}), 132.8 (d, ³J_{PC}=1.38 Hz; C_{PPh,ipso}), 136.8 ppm (CH_{PPh,ottho}); ²⁹Si{¹H} NMR: (59.6 MHz, CDCl₃): δ =-13.5; ³¹P{¹H} NMR: (121.4 MHz, CDCl₃): δ =64.3 ppm.

Preparation of the palladium complexes 8b and 9b

The chlorinated phosphine sulfide 6b (80 mg, 0.20 mmol) was dissolved in THF (6 mL) and cooled to -78 °C. Methyllithium (0.15 mL, 0.20 mmol; 1.31 m in diethyl ether) was added by syringe, upon which the reaction mixture instantly turned yellow. The mixture was stirred for 2 h at temperatures below -50 °C to prevent decomposition of the in situ formed carbenoid. The mixture was then added by a cannula transfer to a solution of [Pd(PPh₃)₄] (218 mg, 0.19 mmol) in THF (8 mL), upon which the color changed from yellow to orange. After stirring overnight the solvent was removed in vacuo and the orange solid taken up in dichloromethane. The mixture was filtered from the lithium chloride and again taken to dryness. The remaining solid was washed three times with diethyl ether/hexane (10 mL, v/v = 1:2) to remove the triphenylphosphine giving the product as bright yellow solid (115 mg, 0.12 mmol; 64%). Single crystals of 8b were grown by slow concentration of a solution of **9b** in dichloromethane.

Compound **8b**: ¹H NMR (500.1 MHz, CD₂Cl₂): $\delta = -0.19 + 0.03$ (s, 6H; SiCH₃), 6.74–6.78 (m, 6H; CH_{ortho,PPh3}), 7.06–7.32 (m, 37H; CH_{Ph}), 7.60–7.64 ppm (m, 2H; CH_{ortho,PPh2}); ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = 0.64$ (d, ${}^{3}J_{PC} = 4.40$ Hz; SiCH₃), 0.64 (d, ${}^{3}J_{PC} = 6.87$ Hz; SiCH₃), 127.1 (CH_{SiPh,meta}), 127.5 (d, ${}^{2}J_{PC}$ = 6.15 Hz; CH_{PPh2,meta}), 127.8 $(CH_{SiPh,para})$, 127.9 (d, ² J_{PC} = 7.19 Hz; $CH_{PPh2,meta}$), 128.1 (d, ² J_{PC} = 6.22 Hz; $CH_{PPh3,meta}$), 128.2 (d, $^{2}J_{CP} = 5.90$ Hz; $CH_{PPh3,meta}$), 128.5 + 128.9 (CH_{PPh2,para}), 129.6 (d, ${}^{4}J_{PC} =$ 1.77 Hz; CH_{PPh3,para}), 130.1 (d, ${}^{4}J_{PC} =$ 1.78 Hz; $CH_{PPh3,para}$), 134.5 (d, ${}^{2}J_{PC} = 13.2$ Hz; $CH_{PPh3,ortho}$),134.7 (d, $^{1}J_{PC} = 31.5, \ ^{3}J_{PC} = 1.0 \text{ Hz}; C_{PPh3,ipso}$), 134.9 (d, $^{3}J_{PC} = 13.5 \text{ Hz}; CH_{PPh2,ortho}$), 135.28 (d, ${}^{3}J_{PC} = 2.35$ Hz; $C_{SiPh,ipso}$), 135.3 (CH_{SiPh,ortho}), 135.5 (dd, ${}^{2}J_{PC} =$ 13.8 Hz; ${}^{4}J_{PC} = 3.0$ Hz; CH_{PPh3,ortho}), 135.5 (C_{PPh3,ipso}), 136.9 (d, ${}^{2}J_{PC} =$ 19.7 Hz; CH_{PPh2,ortho}), 141.2 ppm (d, ¹J_{PC} = 20.8 Hz; SiCPPh₂); PPh_{2,ipso} hidden ²⁹Si{¹H} NMR (79.5 MHz, CD₂Cl₂): $\delta = -11.0$ ppm (dd, ²J_{PSi}= 36.9, ${}^{3}J_{Psi} = 5.87 \text{ Hz}$; ${}^{31}P{}^{1}H$ NMR (162.0 MHz, C₆D₆): $\delta = 9.51$ (dd, ${}^{3}J_{PP} = 23.9$, ${}^{3}J_{PP} = 25.6$ Hz; PPh₂), 20.6 (dd, ${}^{2}J_{PP} = 29.1$, ${}^{3}J_{PP} = 25.7$ Hz; PPh_3), 24.4 ppm (dd, ${}^2J_{PP} = 29.1$, ${}^3J_{PP} = 23.9$ Hz; PPh_3); elemental analysis calcd (%) for $C_{57}H_{51}P_3SSiPd$: C 68.77, H 5.16, S 3.22; found: C 66.91, H 5.14, S 2.99.

Compound **9b**: This compound was not isolated. ³¹P{¹H} NMR (162.0 MHz, C₆D₆): δ =22.6 (d, ³J_{PP}=14.8 Hz; *P*Ph₃), 46.4 ppm (d, ²J_{PP}=29.1, ³J_{PP}=14.8 Hz; *P*(S)Ph₂).

Preparation of the 8c and 9c

Analogous procedure as for **8b** and **9b**. Separation of both complexes by washing with diethyl ether. Purification by washing with toluene/hexane (v/v = 1:4) to remove the remaining triphenylphosphine.

Compound **8***c*: yield: 56%; ¹H NMR (400.1 MHz, C_6D_6): $\delta = 0.35$ (d, $^{3}J_{PH} = 1.92$ Hz, 3 H; SiCH₃), 6.85–7.08 (m, 30 H; CH_{PPh,meta,para}), 7.09– 7.14 (m, 6H; CH_{PPh3,ortho}), 7.32–7.38 (m, 6H; CH_{PPh3,ortho}), 7.58–7.64 (m 2 H; CH_{PPh,ortho}), 7.78–7.83 (m, 2 H; CH_{PPh,ortho}), 7.89 (dd, ${}^{3}J_{HH} =$ 7.43 Hz, ${}^{4}J_{HH} = 1.43$ Hz, 2 H; CH_{siPh,ortho}), 7.93 (dd, ${}^{3}J_{HH} = 7.60$, ${}^{4}J_{HH} = 1.40$ Hz, 2 H; CH_{siPh,ortho}). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): $\delta = -3.16$ (d, ³J_{PC} = 8.72 Hz; SiCH₃), 127.2 (CH_{siPh,meta}), 127.48 (d, ${}^{3}J_{PC} = 7.4$ Hz; CH_{PPh2,meta}), 127.50 (CH_{siPh,meta}), 127.6 (d, ${}^{3}J_{PC} = 7.40$ Hz; CH_{PPh2,meta}), 128.1 (d, ${}^{3}J_{PC} = 9.63$ Hz; CH_{PPh3,meta}), 128.1 (CH_{SiPh,para}), 128.2 (d, ${}^{2}J_{PC} = 9.29$ Hz; $CH_{PPh3,meta}$), 128.5 ($CH_{SiPh,para}$), 129.5 (d, ${}^{4}J_{PC} = 1.87 \text{ Hz}$; $CH_{PPh3,para}$), 130.0 (d, ${}^{4}J_{PC} = 1.93$ Hz; CH_{PPh3,para}), 134.2 (d, ${}^{2}J_{PC} = 19.1$ Hz; CH $_{PPh2,ortho}$), 134.4 (d, $^{2}J_{PC} = 16.2$ Hz; CH $_{PPh3,ortho}$),134.7 (dd, $^{1}J_{PC} = 31.3$ Hz, ${}^{4}J_{PC} = 0.90 \text{ Hz}; C_{PPh3,ipso}$), 134.8 (d, ${}^{2}J_{PC} = 22.0 \text{ Hz}; CH_{PPh2,ortho}$), 135.1 (CH_{SiPh,ortho}), 135.4 (d, ${}^{1}J_{PC} = 31.6$, ${}^{4}J_{PC} = 2.29$ Hz; C_{PPh3,ipso}), 135.6 (dd, ${}^{2}J_{PC} = 13.8$, ${}^{4}J_{CP} = 2.77$ Hz; CH_{PPh3,ortho}), 136.2 (CH_{SiPh,ortho}), 135.3 (dd, 1) ${}^{1}J_{PC} = 31.9$, ${}^{3}J_{PC} = 2.3$ Hz; C_{ipso}, PPh₃), 137.3 (d, ${}^{2}J_{PC} = 21.7$ Hz; CH_{PPh2.ortho}), 141.1 ppm (m; SiCPPh₂); ²⁹Si{¹H} NMR (99.4 MHz, CDCl₃): $\delta = -16.0$ (br); ³¹P{¹H} NMR (162.0 MHz, C₆D₆): $\delta = 10.0$ (dd, ³J_{PP} = 28.8, ³J_{PP} = 25.2 Hz; PPh₂), 20.3 (vt, ^{2/3}J_{PP} = 29.3; PPh₃), 24.4 ppm (dd, $^{2}J_{PP} = 29.4, \ ^{3}J_{PP} = 25.1 \text{ Hz}; PPh_{3}$).

Compound **9***c*: This compound was not isolated; ${}^{31}P{}^{1}H$ NMR (162.0 MHz, CD₂Cl₂): δ = 23.0 (d, ${}^{3}J_{pp}$ = 15.0 Hz; *PPh*₃), 45.8 ppm (d, ${}^{3}J_{pp}$ = 15.0 Hz; SPPh₂).

Preparation of 8d and 9d

Analogous procedure as for **8b** and **9b**. Separation of both complexes by washing with diethyl ether. The solution of the more soluble carbene complex was transferred to a second Schlenk tube and taken to dryness. The thioketone complex was further washed with diethyl ether and the carbene complex with pentane to remove the remaining triphenylphosphine.

Compound 8d: Orange solid, 62% from the reaction at room temperature (entry 6, Table 1); ¹H NMR (500.1 MHz, CD_2CI_2): $\delta = 6.53-$ 6.57 (m, 6H; $CH_{PPh3,meta}$), 6.77–6.81 (m, 6H; $CH_{PPh3,meta}$), 6.95–7.05 (m, 6H; CH_{PPh3,para}), 6.92–6.97 (m, 6H; CH_{PPh3,ortho}), 7.06–7.10 (m, 6H; CH_{PPh3,ortho}), 7.15 (vt, ³J_{HH}=7.70 Hz, 6H; CH_{SiPh,meta}), 7.23–7.36 (m, 8H; CH_{PPh2}), 7.31 (t, ³J_{HH} = 7.41 Hz, 3 H; CH_{SiPh,para}), 7.55 (dd, ³J_{HH} = 8.10 Hz, ⁴J_{HH} = 1.35 Hz, 6H; CH_{SiPh,ortho}), 7.55–7.60 ppm (m, 2H; CH_{PPh,ortho}); $^{13}C{^{1}H}$ NMR (125.8 MHz, CDCl₃): $\delta = 127.45$ (CH_{SiPh,meta}), 127.46 (d, ${}^{3}J_{PC} = 7.65 \text{ Hz}; CH_{PPh2,meta}$), 127.5 (d, ${}^{3}J_{PC} = 8.05 \text{ Hz}; CH_{PPh2,meta}$), 118.0 $(CH_{PPh2,para})$, 128.3 (d, ${}^{3}J_{PC} = 9.25 \text{ Hz}$; $CH_{PPh3,meta}$), 128.9 ($CH_{SiPh,para}$), 129.6 (d, ${}^{4}J_{PC} = 1.83 \text{ Hz}$; $CH_{PPh3,para}$), 130.0 (d, ${}^{4}J_{PC} = 1.84 \text{ Hz}$; $CH_{PPh3,para}$), 134.50 (dd, ${}^{1}J_{PC} = 34.0$, ${}^{4}J_{PC} = 2.49$ Hz; $CH_{PPh3,ipso}$), 134.50 (dd, ${}^{1}J_{PC} = 31.6$, ${}^{4}J_{PC} = 0.85$ Hz; CH_{PPh3,ipso}), 134.51 (d, ${}^{3}J_{PC} = 12.6$ Hz; $CH_{PPh3,ortho}$), 134.53 (d, ${}^{2}J_{PC} = 22.7$ Hz; $CH_{PPh2,ortho}$), 135.3 (dd, ${}^{2}J_{PC} =$ 13.4, ${}^{5}J_{PC} = 1.72$ Hz; CH_{PPh3,ortho}), 137.2 (d, ${}^{2}J_{PC} = 23.0$ Hz; CH_{PPh2,ortho}), 137.8–138.0 (m; CH_{SIPh,ipso}), 137.9 (d, ${}^{4}J_{PC} = 1.56$ Hz; CH_{SIPh,ortho}), 139.9 ppm (ddd, ${}^{1}J_{PC} = 22.4$, ${}^{2}J_{PC} = 15.7$, ${}^{2}J_{CP} = 5.18$ Hz; CS), PPh_{2,ipso} hidden; ²⁹Si{¹H} NMR (99.4 MHz, CDCl₃): $\delta = -20.7$ (dd, ²J_{SiP} = 38.7, ${}^{3}J_{siP} = 7.66 \text{ Hz}$; ${}^{31}P{}^{1}H$ NMR (162.0 MHz, $C_{6}D_{6}$): $\delta = -0.25 \text{ (vt, } {}^{3}J_{PP} =$ 20.4 Hz; PPh₂), 22.2 (dd, ²J_{PP}=27.8, ³J_{PP}=19.9 Hz; PPh₃), 24.7 (dd, $^{2}J_{PP} = 27.7$, $^{3}J_{PP} = 21.3$ Hz; PPh₃); elemental analysis calcd (%) for $C_{67}H_{55}P_3SSiPd$: C 71.87, H 4.95, S 2.86; found: C 61.30, H 5.18, S 2.59; HRMS (ESI): elemental analysis calcd (%) for C₆₇H₅₆P₃SSiPd: 1119.2135; found: 1119.2141.

Chem. Eur. J. **2014**, 20, 1–12

www.chemeurj.org

9

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

These are not the final page numbers! **77**



CHEMISTRY A European Journal Full Paper

Compound **9d**: Yellow solid, 15% yield from the reaction at −78 °C (entry 8, Table 1); ¹H NMR (400.1 MHz, C₆D₆): δ =6.71–6.76 (m, 6H; CH_{SiPh,meta}), 6.82–7.04 (m, 18H; CH_{Ph}), 7.82–7.84 (m, 6H; CH_{SiPh,ortho}), 7.91–7.97 (m, 6H; CH_{PdPPh,ortho}), 8.25–8.30 ppm (m, 4H; CH_{Pph,ortho}); ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): δ =126.9 (CH_{SiPh,meta}), 127.1 (d, ³J_{PC}=12.1 Hz; CH_{PPh,meta}), 127.7 (d, ³J_{CP}=12.1 Hz; CH_{PdPPh,ortho}), 128.2 (CH_{SiPh,para}), 129.3 (d, ⁴J_{PC}=2.9 Hz; CH_{PPh,para}), 129.8 (dd, ¹J_{PC}=88.5, ⁴J_{PC}=3.0 Hz; CH_{PdPPh,ipso}), 131.5 (d, ³J_{PC}=2.9 Hz; CH_{PdPPh,para}), 133.2 (d, ²J_{PC}=10.2 Hz; CH_{PdPPh,ortho}), 135.6 (d, ²J_{PC}=12.1 Hz; CH_{PdPPh,ortho}), 137.5 (CH_{SiPh,ortho}), 139.0 ppm (m, CH_{SiPh,ipso}), CH_{PPh,ipso} and PCSi hidder; ²⁹Si{¹H} NMR: (99.4 MHz, CD₂Cl₂): δ =−16.3 (br); ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂): δ =23.7 (d, ³J_{PP}=16.4 Hz; PPh₃), 46.1 ppm (d, ³J_{PP}=16.4 Hz; SPPh₂); HRMS (ESI): elemental analysis calcd (%) for C₄₉H₄₁P₂SSiPd: 857.1219; found: 857.1212.

Preparation of 8 e

Analogous procedure as for 8b. Purification by washing with pentane. Orange solid; yield: 53%; ¹H NMR: (500.1 MHz, C_6D_6): $\delta =$ 0.45-0.55 (m, 1H; PCy), 0.65-0.75 (m, 1H; PCy), 0.95-1.85 (m, 14H; PCy), 2.05-2.15 (m, 1H; PCy), 2.25-2.6 (m, 5H; PCy), 6.78-6.83 (m, 6H; PPh_{3,para}), 6.9–7.1 (m, 28H; CH_{arom}), 7.12–7.18 (m, 2H; CH_{arom}), 7.18–7.22 (m, 3H; CH_{siPh}), 8.05 ppm (m, ²J_{PH}=8.1 Hz, 6H; CH_{PPh,ipso}); ¹³C{¹H} NMR: (125.8 MHz, C₆D₆): $\delta = 25.9$ (s; PCHCH₂CH₂CH), 23.3 (d, ${}^{3}J_{PC} = 14.6 \text{ Hz}; PCHCH_{2}CH_{2}), 27.4 (d, {}^{4}J_{PC} = 2.3 \text{ Hz}; PCHCH_{2}CH_{2}CH),$ 28.2 (2d, ³J_{PC}=13.4/6.0 Hz; PCHCH₂CH₂), 29.3 (d, ²J_{PC}=14.5 Hz; PCHCH₂), 31.1 (d, ²J_{PC} = 10.0 Hz; PCHCH₂), 33.1 (dd, ²J_{PC} = 21.9, ⁴J_{PC} = 2.0 Hz; PCH), 34.2 (d, ²J_{PC}=19.3 Hz; PCHCH₂), 38.2 (m; PCH), 128.5-128.9 (m, 21C; $C_{arom'}$ overlying signals), 129.6 (dd, ${}^{3}J_{CP} = 27.4$, ${}^{5}J_{PC} =$ 1.5 Hz; PPh_{3,meta}), 134.7 (d, ${}^{2}J_{PC} = 12.7$ Hz; PPh_{3,otho}), 135.0 (dd, ${}^{1}J_{CP} =$ 32.0, ${}^{3}J_{PC} = 2.4 \text{ Hz}$; PPh_{3,ipso}), 135.1 (dd, ${}^{2}J_{PC} = 12.3$, ${}^{4}J_{PC} = 1$. Hz; PPh_{3.ortho}), 135.2 (dd, ¹J_{PC} = 30.0 Hz; PPh_{3.ipso}), 138.2 (m; SiPh_{3.ortho}), 139.1 (m; SiPh_{3,ipso}); ²⁹Si{¹H} NMR: (99.3 MHz, C₆D₆): $\delta = 21.39$ (dd, $^{2}J_{PSi} = 33.8$, $^{3}J_{PSi} = 7.8$ Hz); $^{31}P{^{1}H}$ NMR: (202.5 MHz, C₆D₆): $\delta = 18.33$ (dd, ${}^{3}J_{PP} = 20.2$, ${}^{3}J_{PP} = 8.1$ Hz; PCy₂), 22.1 (dd, ${}^{2}J_{PP} = 27.4$, ${}^{3}J_{PP} = 8.2$ Hz; PdPPh₃), 23.0 (dd, ²J_{PP} = 25.4, ³J_{PP} = 20.6 Hz; PPh₃).

X-ray crystallography

The crystal data of all compounds were collected on a Bruker SMART-APEX diffractometer with a CCD area detector and multilayer mirror monochromated $Mo_{k\alpha}$ radiation. Crystals were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were effected at -100 °C. The structures were solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication:

CCDC-976964 (**5** b), -976965 (**5** c), -976966 (**5** e), -976967 (**8** b), -976969 (**8** d), and -976968 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Computational details

All calculations were performed with the Gaussian 03 (Rev. E.01) and the Gaussian 09 (Rev. B.01) software package.^[24] All structures were optimized without any symmetry restrictions. Geometry optimizations were performed using DFT with the B3LYP (Becke 3-parameter-Lee–Yang–Parr)^[20] and the B3PW91 functional.^[25] The 6-311g(d) basis set was used for hydrogen, the 6-311g(d) for all other nonmetal elements. For palladium the LanL2TZ(f)^[21] ECP/basis set of triple-z quality was used augmented with an f polarization func-

tion of exponent 1.472.^[26] Transition states were located either by using the qst3 method or via freezing of the respective coordinates (opt=modred) and subsequent optimization on the obtained imaginary frequency. The vibrational frequency analyses showed no imaginary frequencies for the ground states and a single imaginary frequency for the transition states. NBO analyses were carried out on the optimized systems using the NBO 5.G program,^[27] interfaced to the Gaussian 03 program. More detailed information concerning the calculations, including Cartesian coordinates of the optimized geometries and comparison of different methods, can be found in the Supporting Information.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft(Emmy-Noether program), the Fonds der Chemischen Industrieand the Alexander von Humboldt Foundation. We also thank Rockwood Lithium GmbH for the supply of chemicals.

Keywords: carbene complexes · carbenoids · density functional calculations · lithium · substituent effect

- [1] a) U. Klabunde, E. O. Fischer, J. Am. Chem. Soc. 1967, 89, 7141-7142;
 b) R. R. Schrock, J. Am. Chem. Soc. 1974, 96, 6796-6797.
- [2] D. J. Mindiola, J. Scott, Nat. Chem. 2011, 3, 15-17.
- [3] For reviews, see: a) N. D. Jones, R. G. Cavell, J. Organomet. Chem. 2005, 690, 5485–5496; b) T. Cantat, N. Mézailles, A. Auffrant, P. Le Floch, Dalton Trans. 2008, 1957–1972; c) S. T. Liddle, D. P. Mills, A. Wooles, J. Organomet. Chem. 2010, 695, 29; d) S. Harder, Coord. Chem. Rev. 2011, 255, 1252–1267; e) T. K. Panda, P. W. Roesky, Chem. Soc. Rev. 2009, 38, 2782–2804; f) S. T. Liddle, D. P. Mills, A. J. Wooles, Chem. Soc. Rev. 2011, 40, 216–42176; g) G. R. Giesbrecht, J. C. Gordon, Dalton Trans. 2004, 2387–2393; h) O. T. Summerscales, J. C. Gordon, RSC Adv. 2013, 3, 6682–6692.
- [4] For examples, see: a) R. P. K. Babu, R. McDonald, S. A. Decker, M. Klobukowski, R. G. Cavell, Organometallics 1999, 18, 4226-4229; b) O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake, S. T. Liddle, Angew. Chem. 2011, 123, 2431-2434; Angew. Chem. Int. Ed. 2011, 50, 2383-2386; c) R. G. Cavell, R. P. K. Babu, A. Kasani, R. McDonald, J. Am. Chem. Soc. 1999, 121, 5805-5806; d) T. Cantat, L. Ricard, N. Mézailles, P. Le Floch, Organometallics 2006, 25, 6030-6038; e) V. H. Gessner, F. Meier, D. Uhrich, M. Kaupp, Chem. Eur. J. 2013, 19, 16729-16739.
- [5] For examples, see: a) M. T. Gamer, M. Rastätter, P. W. Roesky, Z. Anorg. Allg. Chem. 2002, 628, 2269-2272; b) M. Gregson, E. Lu, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle Angew. Chem. 2013, 125, 13254-13257; Anaw. Chem. Int. Ed. 2013, 52, 13016-13019; Anaw. Chem. Int. Ed. 2013. 52, 13016-13019; c) R. P. Kamalesh Babu, R. McDonald, R. G. Cavell, Chem. Commun. 2000, 481-482; d) N. D. Jones, G. Lin, R. A. Gossage, R. McDonald, R. G. Cavell, Organometallics 2003, 22, 2832-2841; e) G. Lin, N. D. Jones, R. A. Gossage, R. McDonald, R. G. Cavell, Angew. Chem. 2003, 115, 4188-4191; Angew. Chem. Int. Ed. 2003, 42, 4054-4057; f) T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. Le Floch, N. Mézailles, J. Am. Chem. Soc. 2009, 131, 963-972; g) J.-P. Tourneux, J.-C. Berthet, P. Thuéry, N. Mézailles, P. Le Floch, M. Ephritikhine, Chem. Commun. 2010, 46, 2494-2496; h) H. Heuclin, X. F. Le Goff, N. Mézailles, Chem. Eur. J. 2012, 18, 16136-16144; i) D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake, S. T. Liddle, J. Am. Chem. Soc. 2012, 134, 10047-10054; j) D. P. Mills, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, Organometallics 2009, 28, 6771-6776; k) O. J. Cooper, D. P. Mills, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, Chem. Eur. J. 2013, 19, 7071-7083; I) D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, Organometallics 2013, 32, 1239-1250; m) D. P. Mills, L. Soutar, O. J. Cooper, W. Lewis, A. J. Blake, S. T. Liddle, Or-

Chem. Eur. J. **2014**, 20, 1 – 12

www.chemeurj.org

10

 $\ensuremath{\textcircled{}^{\circ}}$ 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



ganometallics 2013, 32, 1251–1264; n) D. P. Mills, L. Soutar, W. Lewis, A. J. Blake, S. T. Liddle, J. Am. Chem. Soc. 2010, 132, 14379–14381; o) D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake, S. T. Liddle, Nat. Chem. 2011, 3, 454–460.

ChemPubSoc Europe

- [6] For examples of dilithio methandiides, see: a) A. Kasani, R. P. K. Babu, R. McDonald, R. G. Cavell, Angew. Chem. 1999, 111, 1580–1581; Angew. Chem. Int. Ed. 1999, 38, 1483–1484; b) T. Cantat, L. Ricard, P. Le Floch, N. Mézailles, Organometallics 2006, 25, 4965–4976; c) L. Orzechowski, G. Jansen, S. Harder, Angew. Chem. 2009, 121, 3883–3887; Angew. Chem. Int. Ed. 2009, 48, 3825–3829; d) J. Vollhardt, H.-J. Gais, K. L. Lukas, Angew. Chem. 1985, 97, 607–609; Angew. Chem. Int. Ed. Engl. 1985, 24, 610–611; e) G. Linti, A. Rodig, H. Pritzkow, Angew. Chem. 2002, 114, 4685–4687; Angew. Chem. Int. Ed. 2002, 41, 4503–4506; f) P. Schröter, V. H. Gessner, Chem. Eur. J. 2012, 18, 11223–11227; g) H. Heuclin, M. Fustier-Boutignon, S. Y.-F. Ho, X.-F. Le Goff, S. Carenco, C.-W. So, N. Mézailles, Organometallics 2013, 32, 498–508; h) O. J. Cooper, A. J. Wooles, Dr. J. McMaster, Dr. W. Lewis, A. J. Blake, S. T. Liddle, Angew. Chem. 2010, 122, 5702–5705; Angew. Chem. Int. Ed. 2010, 49, 5570–5573.
- [7] a) T. Cantat, X. Jacques, L. Ricard, X. F. Le Goff, N. Mézailles, P. Le Floch, Angew. Chem. 2007, 119, 6051–6054; Angew. Chem. Int. Ed. 2007, 46, 5947–5950.
- [8] T. Cantat, N. Mézailles, Y. Jean, P. Le Floch, Angew. Chem. 2004, 116, 6542–6545; Angew. Chem. Int. Ed. 2004, 43, 6382–6385.
- [9] V. H. Gessner, Organometallics 2011, 30, 4228-4231.
- [10] P. von R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk, N. G. Rondan, J. Am. Chem. Soc. 1984, 106, 6467–6475.
- [11] S. Molitor, V. H. Gessner, Chem. Eur. J. 2013, 19, 11858-11862.
- [12] For reviews on carbenoids, see: a) G. Boche, J. C. W. Lohrenz, Chem. Rev. 2001, 101, 697; b) M. Pasco, N. Gilboa, T. Mejuch, I. Marek, Organometallics 2013, 32, 942; c) G. Köbrich, Angew. Chem. 1972, 84, 557; Angew. Chem. Int. Ed. Engl. 1972, 11, 473; d) V. Capriati, S. Florio, Chem. Eur. J. 2010, 16, 4152.
- [13] Further examples of stabilized carbenoids: a) J. Becker, V. H. Gessner, *Dalton Trans.* 2014, 43, 4320-4325; b) C. Kupper, S. Molitor, V. H. Gessner, *Organometallics, 33,* 347-353; c) H. Heuclin, S. Y.-F. Ho, X. F. Le Goff, C.-W. So, N. Mézailles, J. Am. Chem. Soc. 2013, 135, 87-74; d) A. Salomone, F. M. Perna, A. Falcicchio, S. O. Nilsson Lill, A. Moliterni, R. Michel, S. Florio, D. Stalke, V. Capriati, Chem. Sci. 2014, 5, 528-538; e) J. Barluenga, M. A. Rodriguez, P. J. Campos, J. Am. Chem. Soc. 1988, 110, 5568-5569; f) D. I. Coppi, A. Salomone, F. M. Perna, V. Capriati, Chem. Commun. 2011, 47, 9918-9920; g) R. Mansueto, F. M. Perna, A. Salomone, S. Florio, V. Capriati, Chem. Commun. 2013, 49, 10160-10162; j) E. Niecke, P. Becker, M. Nieger, D. Stalke, W. W. Schoeller, Angew. Chem. 1995, 107, 2012-2015; Angew. Chem. Int. Ed. Engl. 1995, 34, 1849-1852; j) V. Capriati, S. Florio, R. Luisi, F. M. Perna, A. Spina, J. Org. Chem. 2008, 73, 9552-9564.
- [14] D. M. Norton, E. A. Mitchell, N. R. Botros, P. G. Jessop, M. C. Baird, J. Org. Chem. 2009, 74, 6674–6680.
- [15] An analogous complex with a CSPd three-membered ring has been reported by reaction of [Pd(PPh₃)₄] with a thioketone compound: K.-H. Yih, G. H. Lee, Y. Wang, *Inorg. Chem.* **2000**, *39*, 24452451.
- [16] For examples of transition-metal thioketone complexes, see: a) T. Muraoka, T. Nakamura, A. Nakamura, K. Ueno, Organometallics 2010, 29, 6624–6626; b) T. Weisheit, H. Petzold, H. Görls, G. Mloston, W. Weigand, R. Wiedemann, Eur. J. Inorg. Chem. 2009, 3545–3551; c) R. Beck, H. Sun, X. Li, S. Camadanli, H.-F. Klein, Eur. J. Inorg. Chem. 2008, 3253–3257; d) H. Petzold, S. Bräutigam, H. Görls, W. Weigand, M. Celeda, G. Mloston, Chem. Lur. J. 2006, 12, 8090–8095; e) J. R. Bleeke, M. Shokeen, E. S. Wise, N. P. Rath, Organometallics 2006, 25, 2486–2500; f) W. A. Schenk, B. Vedder, M. Klüglein, D. Moigno, W. Kiefer, J. Chem. Soc. Dalton Trans. 2002, 3123–3128; g) J. Wolf, H. Werner, Chem. Ber. 1996, 129, 29–31.
- [17] a) J. F. Hartwig, F. Paul, J. Am. Chem. Soc. **1995**, 117, 5373–5374; b) A. Aranyos, D. W. Old, A. Kiyomori, J. P. Wolfe, J. P. Sadighi, S. L. Buchwald, J. Am. Chem. Soc. **1999**, 121, 4369–4378.
- [18] a) M. S. Driver, J. F. Hartwig, J. Am. Chem. Soc. 1995, 117, 4708–4709;
 b) M. S. Driver, J. F. Hartwig, J. Am. Chem. Soc. 1997, 119, 8232–8245.

- [19] Examples of isolated T-shaped palladium complexes: a) J. P. Stambuli,
 C. D. Incarvito, M. Bühl, J. F. Hartwig, *J. Am. Chem. Soc.* 2004, *126*, 1184–1194; b) J. P. Stambuli, Z. Weng, C. D. Incarvito, J. F. Hartwig, *Angew. Chem.* 2007, *119*, 7818–7821; *Angew. Chem. Int. Ed.* 2007, *46*, 7674–7677.
- [20] a) A. D. J. Becke, J. Chem. Phys. 1993, 98, 5648-5662; b) C. Lee, W. Yang,
 R. Parr, Phys. Rev. B 1988, 37, 785.
- [21] a) P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 270; b) P. J. Hay, W. R.
 Wadt, J. Chem. Phys. 1985, 82, 284; c) P. J. Hay, W. R. Wadt, J. Chem.
 Phys. 1985, 82, 299. L. E. Roy, P. J. Hay, R. L. Martin, J. Chem. Theory
 Comput. 2008, 4, 1029–1031.
- [22] It has recently been shown that [Pd(PPh₃)₃] dissociates in solution to lower coordinate species: M. S. G. Ahlquist, P.-O. Norrby, Angew. Chem. 2011, 123, 11998-12001; Angew. Chem. Int. Ed. 2011, 50, 11794-11797.
- [23] For examples of two-coordinate Pd complexes: a) T. Iwamoto, F. Hirakawa, S. Ishida, Angew. Chem. 2012, 124, 12277-12280; Angew. Chem. Int. Ed. 2012, 51, 12111-12114; b) J. Bauer, H. Braunschweig, A. Damme, K. Gruß, K. Radacki, Chem. Commun. 2011, 47, 12783-12785; c) S. R. Titcomb, S. Caddick, F. G. N. Cloke, D. J. Wilson, D. McKerrecher, Chem. Commun. 2001, 1388-1389; d) K. Arentsen, S. Caddick, F. G. N. Cloke, Tetrahedron 2005, 61, 97109715; e) X. Cai, S. Majumdar, G. C. Fortman, C. S. J. Cazin, A. M. Z. Slawin, C. Lhermitte, R. Prabhakar, M. E. Germain, T. Palluccio, S. P. Nolan, E. V. Rybak-Akimova, M. Temprado, B. Captain, C. D. Hoff, J. Am. Chem. Soc. 2011, 133, 1290-1293.
- [24] a) Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, O. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004; b) Gaussian 09, Revision B.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, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakaj, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, 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, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
- [25] Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. 2008, 120, 215241.
- [26] A. W. Ehlers, M. Bçhme, S. Dapprich, A. Gobbi, A. Hçllwarth, V. Jonas, K. F. Köhler, R. Stegman, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, 208, 111114.
- [27] NBO 5.G, E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2001, http://www.chem.wisc.edu/nbo5.

Received: December 17, 2013 Published online on

Chem. Eur. J. **2014**, 20, 1 – 12

www.chemeurj.org

11

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

These are not the final page numbers! **77**



FULL PAPER

Carbene Complexes

S. Molitor, K.-S. Feichtner, C. Kupper, V. H. Gessner*

Substitution Effects on the Formation of T-Shaped Palladium Carbene and Thioketone Complexes from Li/Cl Carbenoids **Complex chemistry!** The reactivity of Li/Cl carbenoids towards Pd⁰ precursors has been studied. While steric and electronic stabilization allow the isolation of a three-coordinate, T-shaped carbene complex, insufficient charge stabilization

Steric effects

[Pd(PPh₃)₄]

lectronic

effects

results in the transfer of the sulfur and the formation of a thioketone complex (see scheme). DFT studies show that both complexes are formed by a substitution mechanism.

carbe

