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Structure, Bonding, and Reactivity of Room-Temperature-Stable Lithium Chloride Carbenoids

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S Supporting Information



ABSTRACT: Electronic stabilization of the negative charge by a thiophosphinoyl and pyridyl/quinolyl substituent allows for the isolation of two lithium chloride carbenoids at room temperature. Molecular structure analysis by X-ray crystallography and multinuclear NMR spectroscopy reveal no direct lithium-carbon interaction in the solid state and in solution. This leads to remarkable thermal stability but also to a reduced ambiphilic character of the compounds. Thus, properties typically observed for nonstabilized Li/Cl carbenoids are less pronounced. Nevertheless, computational studies still show that despite the charge delocalization within the compound a high negative charge remains at the carbenoid carbon atom. Preliminary reactivity studies confirm this nucleophilic character and show that the carbenoids can still be used as a "carbene" source for the formation of carbene complexes.

INTRODUCTION

Since the pioneering work by Simmons and Smith¹ carbenoids have been frequently used reagents in organic syntheses, above all in cyclopropanation and homologation reactions.² However, in comparison to the related carbenes-which have experienced dramatic research interest over the past decades over a wide range of applications-carbenoids have almost been neglected.³ Despite their potential as carbene precursors and their ambiphilic nature there are only a few examples probing their versatile reactivity and use as ligands for transition-metal carbene complexes.⁴ This limitation is mainly due to the high reactivity of carbenoids and their lack of thermal stability.² This is particularly true for lithium halide carbenoids, which normally undergo salt elimination at very low temperaturesoften below -78 °C-giving way to highly unstable carbene species and often to complex product mixtures. Thus over the past years, progress in more selective and controlled applications of carbenoids has mainly been achieved with the more covalent zinc derivatives.⁶

Nevertheless, it is well known that the reactivity of carbenoids is influenced by several factors beyond the nature of the metal atom: these are for example (i) the nature of the leaving group (determining the electrophilicity), (ii) the substituents at the carbenic carbon atom (electronic and spatial

stabilization), and (iii) ancillary ligands. Indeed in 2007, Le Floch and co-workers succeeded in the isolation of the first room-temperature-stable Li/Cl carbenoid A by employing thiophosphinoyl moieties as stabilizing substituents.^{7,8} Despite its stability this system was found to still possess an ambiphilic character, as evidenced by the formation of a palladium carbene complex or the activation of the B-H bond in BH₃ Lewis base adducts. Our group has focused on the impact of the substitution pattern at the carbenoid carbon atom on the stability and also the reactivity.9 Recently, we have shown that the thermal stability of the carbenoid is considerably reduced when simply replacing one of the thiophosphinoyl groups in A with a silyl moiety (carbenoid **B**). This is also accompanied by a change in the reactivity. As such, no carbene complex formation was observed by treatment of the carbenoid B with [Pd- $(PPh_3)_4$] but the selective formation of a thicketone complex occurs.¹⁰ Also, B-H bond activation gave a totally different product than was found for A.^{11,12}

These observations prompted us to further study the impact of the substitution pattern at the carbenoid carbon on the stability and reactivity. Herein, we report on the preparation of

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Figure 1. Example of Li/Cl carbenoids with different electronic stabilization.

two novel room-temperature-stable carbenoids **3a,b** incorporating N-heteroaromatic substituents (Scheme 1). We demonstrate how the unique electronic structure correlates with the ambiphilic character and the observed reactivity patterns of these systems.



RESULTS AND DISCUSSION

The pyridyl- and quinolyl-substituted carbenoids 3a,b were targeted via the synthetic strategy outlined in Scheme 1. At first the protonated precursors 1a,b were prepared by a one-pot reaction via deprotonation of 2-picoline and 2-methylquinoline, respectively (for details, see the Experimental Section). The following chlorination was accomplished by lithiation and treatment with hexachloroethane, giving 2a,b as racemic mixtures in only moderate yields due to the formation of the bis-chlorinated compound as a byproduct.¹⁶ All compounds were characterized by multinuclear NMR spectroscopy and elemental analysis. Due to the stereogenic central carbon atom in 2 the phenyl substituents at the phosphorus become diastereotopic and appear as separate resonances in the ¹H and $^{13}C{^{1}H}$ NMR spectra. The $^{31}P{^{1}H}$ NMR signals resonate at δ 51.0 (2a) and 50.4 ppm (2b). The molecular structures of 1b and 2a,b were additionally determined by single-crystal X-ray diffraction analysis (see the Supporting Information). 2a crystallizes in the monoclinic space group $P2_1/c$ and **2b** in the orthorhombic space group *Pbca* (Figure 2). In contrast to the molecular structure of 2b, the asymmetric unit of 2a contains two highly disordered molecules, each consisting of both enantiomeric forms of 2a.

Treatment of the chlorinated precursors with 1 equiv of methyllithium at room temperature afforded the selective formation of the carbenoids 3a,b in quantitative yields, as evidenced by monitoring of the reaction progress by ${}^{31}P\{{}^{1}H\}$ NMR spectroscopy (Scheme 1). No competing substitution reaction was observed under these reaction conditions. Isolation gave 3a as a bright yellow solid in quantitative yield and 3b as an orange solid in 93% yield. Both carbenoids proved to be stable at room temperature. At ambient temperature no decomposition was detected in the solid state, even after storage for weeks under an inert atmosphere. A THF solution of carbenoid 3a is stable at temperatures up to 60 °C. In the



Figure 2. Molecular structure of compound **2b**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **2b**: Cl1–Cl 1.785(2), P1–Cl 1.853(2), Cl–C2 1.511(3), N1–C2 1.319(3), S1–P1 1.9503(8), P1–Cl1 1.815(2), P1–Cl7 1.811(2); C2–C1–P1 114.99(15), C2–C1–Cl1 112.01(16), Cl1–C1–P1 106.3(1), C1–P1–S1 115.12(8), N1–C2–C1 114.01(19). For crystallographic data of **2a** and **1b**, see the Supporting Information.

solid state no decomposition was observed up to about 100 °C, as evidenced by differential scanning calorimetry (DSC) measurements (see the Supporting Information). Other than the Li/Cl carbenoid **A** reported by Floch and co-workers in 2007 and its iodine congener,^{7,8} **3a,b** are the only room-temperature-stable carbenoids known so far.

Both carbenoids feature well-resolved NMR spectra, thus indicating no fluxional behavior in solution (C₆D₆). Additionally, they were found to form THF solvates with two coordinating ether molecules (see the Supporting Information for NMR spectra). Carbenoid 3a is characterized by a single resonance in the ³¹P{¹H} NMR spectrum at δ 39.4 ppm and one signal at δ 1.42 ppm in the ⁷Li NMR spectrum. The carbenoid carbon atom was found to resonate at δ 60.1 ppm $(^{1}J_{PC} = 127.8 \text{ Hz})$, which is shifted slightly downfield in comparison to the protonated precursor 2a (δ 58.8 ppm, ${}^{1}J_{PC}$ = 50.1 Hz). Such a downfield shift is typical for carbenoid species. This observation can be explained by the polarization of the C-X bond upon metalation and an increased carbenelike character. However, the carbenoid ¹³C signal in other known Li/Hal carbenoids is generally found to be more strongly deshielded relative to the protonated analogues ($\Delta\delta$ 40-280 ppm).¹³ For example, lithiation of chloroform is accompanied by a downfield shift of $\Delta\delta$ 65.9 ppm. Hence, the only slightly downfield shifted resonance in 3a indicates an only weakly pronounced polarization. Analogous spectroscopic properties were observed for the quinolyl analogue **3b**. Here, the ${}^{13}C{}^{1}H{}$ NMR signal of the carbenoid carbon atom appears as a broad doublet at δ 67.9 ppm (**2b**: δ 59.9 ppm).

Single crystals of both carbenoids were grown from THF solutions. The molecular structures are shown in Figure 3, and selected bond lengths and angles are given in Table 1. The carbenoids crystallize as monomers in the monoclinic space groups $P2_1/n$ (**3a**) and Pn (**3b**), respectively. In both cases, the lithium atom is 4-fold coordinated by the sulfur atom of the thiophosphinoyl moiety and the pyridyl/quinolyl nitrogen as well as two THF solvent molecules. As reported for metalated versions of **1a**, no direct contact between the lithium and the metalated carbon atom is observed.¹⁶ This corroborates the observations made by the NMR studies, thus suggesting that the structure is also maintained in solution (little downfield shift of the ${}^{13}C{}^{1}H$ NMR resonance, no diastereotopic



Figure 3. Molecular structures of carbenoids 3a (top) and 3b (bottom). Ellipsoids are drawn at the 50% probability level. For crystallographic and structure refinement details, see the Supporting Information.

splitting of the Ph₂P signals). In the molecular structures of both carbenoids, the metalated carbon atom features an almost planar geometry with sums of angles around C1 of 358.6(1) (**3a**) and 358.7(1)° (**3b**). This is in line with a change in the hybridization from sp³ to sp², as suggested by the increased ¹*J*_{PC} coupling constants in the ¹³C{¹H} NMR spectrum. The C(1)– Cl bonds amount to 1.760(1) (**3a**) and 1.766(2) Å (**3b**), which are slightly shorter than that found in the starting compounds (e.g. **2a** 1.795(6) Å (average); see the Supporting Information). Hence, the lengthening of the C–Cl bond typically found for nonstabilized Li/Cl carbenoids is not observed in **3**.¹⁴ The

Fable 1. Selected Bond Ler	ngths (Å)	and Angles	(deg)	of 3a,b
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C(1)–P distances of 1.740(1) (3a) and 1.746(2) Å (3b) are shorter than in 2a or 2b (e.g., 2a: 1.854(7) Å (average)), reflecting the electrostatic interactions known for α -metalated P(V) species. In addition, the short C1–C2 distances of 1.409(2) (3a) and 1.401(2) Å (3b) (average C1–C2 distance in 2a: 1.514(5) Å) indicate strong contribution of charge delocalization into the aromatic ring systems. This is also reflected by the distinct perturbations in the C–C and C–N bond lengths in the heterocycles (cf. Table 1).

Overall, the structural parameters as well as the NMR data suggest that both carbenoids possess a considerably decreased carbenoid character. To gain further insight into the electronic properties of **3a,b** we performed DFT calculations including natural bond orbital (NBO) studies at the B3LYP/6-311+ +g(d) level of theory. At first, a model system of **3a,b** was chosen, in which THF was replaced by Me₂O. However, the structure parameters of the energy-optimized structures are in good agreement with the experimental data (e.g., C–Cl in **3b**: calcd 1.780 Å, exptl 1.766 Å). The HOMO of carbenoid **3a** (Figure 4; for **3b** see the Supporting Information) is mainly



Figure 4. (a) Molecular orbitals of 3a (isosurface value of 0.2). (b) Natural population analysis charges and Wiberg bond indices of 3a and 2a.

located at the nitrogen of the pyridyl substituent. On the other hand, HOMO-5 represents the bonding π interaction between C1 and C2, yet polarized toward C1, while the LUMO is its antibonding counterpart. The Wiberg bond indices (WBI)

	3a	3b		3a	3b
Cl-C1	1.760(1)	1.766(2)	C5-C6	1.377(2)	1.419(2)
S-P	1.998(1)	1.997(1)	N-C6	1.344(2)	1.379(2)
P-C1	1.740(1)	1.746(2)	S-Li	2.451(2)	2.466(3)
$P-C_{Ph}$	1.818(1), 1.824(1)	1.819(2), 1.824(2)	Li-O	1.88(1), 1.949(3)	1.951(3), 1.956(3)
C1-C2	1.409(2)	1.401(2)	N-Li	2.041(2)	2.112(3)
N-C2	1.375(2)	1.359(2)	N-Li-S	107.2(1)	107.4(1)
C2-C3	1.428(2)	1.452(2)	C2-C1-P	123.1(1)	124.0(1)
C3-C4	1.367(2)	1.345(2)	C2-C1-Cl	118.1(1)	118.3(1)
C4-C5	1.397(2)	1.431(2)	P-C1-Cl	117.4(1)	116.4(1)

clearly confirm the partial double-bond character of the C1-C2 bond (WBI = 1.33). This value is higher than that calculated for the starting material 2a but lower than the WBI of a "real" double bond (WBI(ethene) = 2.04) or of an undisturbed aromatic system (WBI(benzene) = 1.44). The WBIs also reflect the charge delocalization into the aromatic ring system by more pronounced differences in the bond indices in comparison to 2a. It is interesting to note that the highest WBI in the pyridyl ring corresponds with the shortest C-C bond (C3-C4) found in the crystal structure. The NBO charges still account for a considerable negative charge at the "metalated" carbon atom $(q_{\rm C} = -0.65)$. This charge accumulation is slightly higher than that of the pyridyl nitrogen $(q_N = -0.62)$ and is further stabilized by electrostatic effects with the positively charged phosphorus atom. Although the increase of the negative charge upon metalation is most pronounced at the carbon atom ($\Delta q_{\rm C}$ = -0.31), the calculated charges still reflect the charge delocalization into the heterocycle ($\sum \Delta q = -0.27$).

Overall, the character of compound 3a can be described as an intermediate state between a lithium chloride carbenoid (resonance structure A) and a β -chloro lithium amide (B). A similar electronic structure has been reported by Stalke and coworkers for 2-picolyllithium, also on the basis of experimental charge density studies.¹⁵ DFT studies revealed an analogous electronic structure for 3b with a slightly more pronounced charge delocalization into the aromatic ring system (see the Supporting Information). This electronic situation correlates well with the NMR spectroscopic and crystallographic data as well with the high thermal stability of the carbenoids. To experimentally evaluate the carbenoid character, we next turned our attention to preliminary reactivity studies in order to search for a "hidden" carbene-like reactivity of 3. We challenged both its nucleophilicity and electrophilicity (Scheme 2). Treatment





of **3a** with electrophiles EX (MeI and Me₃SnCl) resulted in simple attack at the metalated carbon atom to form the corresponding products **4a**,**b** as well as the lithium halide in high yields. Despite the localization of the HOMO at the nitrogen of the pyridyl substituent, the substitution reactions exclusively take place at the carbon atom.

The electrophilicity of **3a** was tested by a cyclopropanation reaction with cyclohexene as well as *trans*-stilbene. However, no conversion was observed even upon heating of a solution of the carbenoid in neat cyclohexene (or in THF or toluene solution) at 50 °C for several hours. This is further confirmed by computational studies on the cyclopropanation reaction of **3a** with ethene as the olefin. Here, the calculations predict an activation barrier of 41.0 kcal mol⁻¹ (see the Supporting Information). Nevertheless, the carbene-like reactivity becomes



obvious in the reaction of 3a with the Pd(0) precursor. Treatment of **3a** in diethyl ether with $[Pd(PPh_3)_4]$ gave way to the selective formation of carbene complex 5 with formation of lithium chloride. This transformation was found to be slow but quantitative at room temperature, as evidenced by monitoring the reaction process by ³¹P{¹H} NMR spectroscopy. However, due to the difficult separation of 5 from the formed PPh₃, the complex could be isolated in only 57% yield as a yellow solid. 5 is characterized by two doublets of the same intensity in the ³¹P{¹H} NMR spectrum at 19.1 and 40.6 ppm with a coupling constant of ${}^{3}J_{PP}$ = 46.2 Hz (C₆D₆). The ${}^{13}C{}^{1}H$ NMR shift of the carbenic carbon atom resonates as a doublet of doublets at 39.0 ppm (J_{PC} = 110 and 103 Hz), which is shifted strongly to high field in comparison to signals for "normal" carbene complexes but shifted downfield relative to the bis-(thiophosphinoyl)methanediide-based carbene complex ($\delta_{
m C}$ -18 ppm) previously reported by our group.¹⁶ Yet, the ¹³C NMR shift of 5 still accounts for a highly ionic electronic structure of the metal-carbon bond, C⁻-Pd⁺, with palladium in the +2 oxidation state. All attempts to grow X-ray-quality single crystals of 5 for diffraction analysis failed because of their sensitivity and the difficult separation of 5 from the formed triphenylphosphine. ESI/MS spectrometry, however, revealed the molecular ion at m/z 676.1 with the expected peak profile, and thus corroborating the composition of complex 5 as concluded from NMR studies. The pincer-type N,C,S-bonding mode of the ligand to the palladium center was additionally confirmed by DFT calculations (see the Supporting Information for computational details). Thereby, alternative bidentate coordination modes were revealed to be disfavored by at least $6.2 \text{ kcal mol}^{-1}$. Overall, the formation of the palladium complex 5 confirms the still present carbenoid character of 3 and its use as a potential "carbene" source for the preparation of further carbene complexes.

CONCLUSIONS

In summary, we have reported the preparation of two stable lithium chloride carbenoids. The efficient electronic stabilization by employing pyridyl and quinolyl moieties in combination with a thiophosphinoyl substituent allowed their isolation at room temperature. Spectroscopic data together with computational studies provide a clear picture of the electronic structure and the charge delocalization within these systems. As such, Xray diffraction studies showed no lithium–carbon interaction and NMR spectroscopy gave an only weakly deshielded carbenoid ¹³C NMR signal. Accordingly, the electronic situation in these compounds is best described by an intermediate state between a lithium chloride carbenoid and a β -chloro lithium amide. This is in line with the stability and also reduced ambiphilicity of the carbenoids. However, reactivity studies confirm the nucleophilic character and show that the carbenoids can still be used as a "carbene" source for the formation of carbene complexes. We are currently investigating the transfer of the carbenoids to other transition metals.

EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried over sodium or potassium (or over P_4O_{10} , CH_2Cl_2) and distilled prior to use. H_2O was distilled water. Organolithium reagents were titrated against diphenylacetic acid prior to use. ¹H, ⁷Li, ¹³C, and ³¹P NMR spectra were recorded on Avance-500, Avance-400, and Avance-300 spectrometers at 22 °C if not stated otherwise. All values of the chemical shifts are in ppm regarding the δ scale. All spin–spin coupling constants (*J*) are given in hertz (Hz). To display multiplicities and signal forms correctly, the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Signal assignments were supported by DEPT and HMQC experiments. The numbering scheme for the NMR assignments is given in Chart 1.



Elemental analyses were performed on an Elementar vario MICROcube elemental analyzer and the DSC (differential scanning calorimetry) measurements on a TA Instruments calorimeter (TA DCS Q1000, V8.1, Build 261) with a heating rate of 10 K/min from 25 to 300 °C. Samples were prepared under an argon atmosphere in a glovebox and sealed in a aluminum crucible. All reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium, or Acros Organics and used without further purification. Compound **1a** was prepared according to literature procedures.¹⁷

Preparation of 1b. A 3.52 g portion (24.6 mmol) of 2methylquinoline was dissolved in 40 mL of THF and cooled to -78 °C. At this temperature 12.0 mL (28.0 mmol) of *n*-butyllithium (2.33 M in hexane) was added, giving a deep red solution. After it was stirred for 1 h at low temperature, the reaction mixture was warmed to room temperature and stirred for an additional 3 h. The mixture was then cooled again to -78 °C and slowly added to a cooled solution of 5.97 g (27.0 mmol) of chlorodiphenylphosphine in 40 mL of THF. The suspension was warmed to room temperature and stirred overnight. After addition of 867 mg (27.0 mmol) of elemental sulfur the mixture was stirred for 5 h and 100 mL water was added. The phases were separated, and the aqueous phase was extracted with diethyl ether $(3 \times$ 50 mL). The combined organic layers were dried over sodium sulfate and the solvent removed in vacuo, giving a brown oil, which was purified by flash chromatography with THF/pentane (1/2 v/v; R_f = 0.71), giving the product 1b as a slightly yellow solid (5.01 g, 13.9 mmol; 57%). Single crystals of 1b were grown by slow diffusion of pentane into a THF solution. ¹H NMR (400.1 MHz, CDCl₃): δ 4.31 1H; H-7).¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ 44.5 (d, ¹J_{PC} = 49.0 Hz; C-10), 123.4 (d, ${}^{7}J_{PC}$ = 2.6 Hz; C-4), 126.4 (d, ${}^{3}J_{PC}$ = 1.3 Hz; C-

8), 127.1 (d, ${}^{5}J_{PC} = 2.1$ Hz; C-6), 127.7 (d, ${}^{5}J_{PC} = 1.4$ Hz; C-2), 128.5 (d, ${}^{3}J_{PC} = 12.4$ Hz; C-13), 128.7 (bs; C-5), 129.5 (bs; C-3), 131.6 (d, ${}^{4}J_{PC} = 3.2$ Hz; C-14), 131.7 (d, ${}^{2}J_{PC} = 10.4$ Hz; C-12), 132.4 (d, ${}^{1}J_{PC} = 81.6$ Hz; C-11), 135.9 (bd, ${}^{4}J_{PC} = 1.9$ Hz; C-7), 147.7 (bd, ${}^{4}J_{PC} = 1.7$ Hz; C-1), 153.0 (d, ${}^{2}J_{PC} = 6.9$ Hz; C-9). ${}^{31}P{}^{1}H$ NMR (162.0 MHz, CDCl₃): δ 41.2. Anal. Calcd for C₂₂H₁₈NPS: C, 73.52; H, 5.05; N, 3.90; S, 8.92. Found: C, 73.31; H, 5.02; N, 3.97; S, 9.04.

Preparation of 2a. A 1.3 mL portion (2.01 mmol) of n-BuLi (1.55 M in hexane) was added dropwise to a solution of 565 mg (1.83 mmol) of compound 1a in 20 mL of Et₂O at -78 °C. The resulting orange mixture was warmed to room temperature and stirred for 4 h. In a second Schlenk flask 435 mg (1.84 mmol) of hexachloroethane was dissolved in 20 mL of Et₂O and cooled to -78 °C. The lithiated compound was added via cannula transfer over a period of 15 min, and the solution was slowly warmed to room temperature. After 16 h 50 mL of water was added and the mixture was extracted with diethyl ether $(3 \times 50 \text{ mL})$. The combined organic layers were dried over sodium sulfate and the solvent removed in vacuo, giving a brown oil, which was purified by flash chromatography with Et_2O /pentane (2/1 v/v; $R_f = 0.47$) as eluent, affording the product as a colorless crystalline solid (389 mg, 1.13 mmol, 62%). Crystals suitable for XRD analysis were grown by slow concentration of a solution of 2a in acetone at 5 °C. ¹H NMR (300.1 MHz, C_6D_6): δ 6.15 (d, ² J_{PH} = 3.9 Hz, 1H; H-6), 6.40-6.46 (m, 1H; H-2), 6.85-6.94 (m, 3H; H-10/4), 6.96-7.06 (m, 4H; H-9), 7.75-7.85 (m, 2H; H-3/1), 8.00 (m, 4H; H-8). ¹³C{¹H} NMR (75.5 MHz, C_6D_6): δ 58.8 (d, ${}^1J_{PC}$ = 50.1 Hz: C-6), 123.5 (d, ${}^{5}J_{\rm PC}$ = 2.2 Hz; C-2), 125.9 (d, ${}^{3}J_{\rm PC}$ = 2.6 Hz; C-4), 128.2 (d, ${}^{3}J_{\rm PC}$ = 12.2 Hz; C-9), 128.6 (d, ${}^{3}J_{PC} = 12.4$ Hz; C-9), 130.8 (d, ${}^{1}J_{PC} = 37.5$ Hz; C-7), 131.6 (d, ${}^{4}J_{PC} = 3.0$ Hz; C-10), 131.8 (d, ${}^{4}J_{PC} = 3.0$ Hz; C-10), 131.9 (d, ${}^{1}J_{PC} = 35.9$ Hz; C-7), 132.5 (d, ${}^{2}J_{PC} = 9.9$ Hz; C-8), 132.7 (d, ${}^{2}J_{PC}$ = 9.9 Hz; C-8), 136.1 (d, ${}^{4}J_{PC}$ = 2.0 Hz; C-3), 148.2 (d, ${}^{4}J_{PC}$ = 1.0 Hz; C-1), 154.6 (s; C-5). ${}^{31}P{}^{1}H{}$ NMR (121.5 MHz, C₆D₆): δ 51.0. Anal. Calcd for C₁₈H₁₅NPClS: C, 62.88; H, 4.40; N, 4.07; S, 9.32. Found: C, 62.89; H, 4.07; N, 4.12; S, 9.03.

Preparation of 2b. The procedure was analogous to that for 2a: yield 26%; $R_{\rm f} = 0.55$ (1/1 diethyl ether/pentane). ¹H NMR (400.1 MHz, C_6D_6): δ 6.38 (d, ² $J_{\rm PH} = 3.9$ Hz, 1H; H-10), 6.84–6.93 (m, 3H; H-13/14), 7.12–7.18 (m, 4H; H-13/14/8), 7.31–7.37 (m, 2H; H-3/4), 7.62 (d, ³ $J_{\rm HH} = 8.7$ Hz, 1H; H-Quin), 7.85–7.91 (m, 2H; H-12), 7.97 (d, ³ $J_{\rm HH} = 8.4$ Hz, 1H; H-Quin), 8.14–8.21 (m, 2H; H-12), 8.35 (dd, ³ $J_{\rm HH} = 8.6$ Hz, ⁴ $J_{\rm HH} = 0.9$ Hz, 1H; H-Quin). ¹³C{¹H} NMR (75.5 MHz, C_6D_6): δ 59.9 (d, ¹ $J_{\rm PC} = 49.4$ Hz; C-10), 122.8 (d, $J_{\rm PC} = 1.6$ Hz; C-Quin), 127.0 (d, ³ $J_{\rm PC} = 1.0$ Hz; C-8), 127.9 (d, ⁷ $J_{\rm PC} = 1.1$ Hz; C-4), 128.1 (d, ³ $J_{\rm PC} = 12.3$ Hz; C-13), 128.7 (d, ³ $J_{\rm PC} = 12.4$ Hz; C-13), 129.5 (bs; C-5/3), 130.6 (d, ¹ $J_{\rm PC} = 32.0$ Hz; C-11), 131.6 (d, ⁴ $J_{\rm PC} = 3.0$ Hz; C-14), 131.8 (d, ¹ $J_{\rm PC} = 31.1$ Hz; C-11), 131.9 (d, ⁴ $J_{\rm PC} = 3.0$ Hz; C-14), 132.5 (d, ² $J_{\rm PC} = 1.6$ Hz; C-Quin), 147.2 (d, ⁴ $J_{\rm PC} = 0.9$ Hz; C-12), 136.6 (d, $J_{\rm PC} = 1.6$ Hz; C-Quin), 147.2 (d, ⁴ $J_{\rm PC} = 0.9$ Hz; C-1), 154.7 (s; C-9). C-6 covered by solvent signal. ³¹P{¹H} NMR (162.0 MHz, C_6D_6): δ 50.4. Anal. Calcd for C₂₂H₁₇CINPS: C, 67.09; H, 4.35; N, 3.56; S, 8.14. Found: C, 67.26; H, 4.48; N, 3.57; S, 8.39.

Preparation of 3a. A 300 mg portion (873 μ mol) of compound 2a was dissolved in 1 mL of THF and cooled to -78 °C. A 676 μ Lportion (873 μ mol) of methyllithium (1.29 M in Et₂O) was added dropwise with stirring. The yellow solution was warmed to room temperature over a period of 4 h, during which time a yellow solid precipitated. Subsequently, the mixture was cooled to -78 °C, the solid was allowed to settle, and the supernatant solution was removed via syringe. The product was washed three times with hexane while the mixture was still kept at -78 °C. Finally, after removal of the solvent in vacuo at room temperature, the product was isolated as a yellow solid and stored in the glovebox (429 mg, 873 µmol, >98%). Crystals suitable for XRD analysis were grown by slow concentration of a solution of 3a in THF/pentane. ¹H NMR (500.1 MHz, C_6D_6): δ 1.31 (t, ${}^{3}J_{HH} = 6.6$ Hz, 8H; THF), 3.44 (t, ${}^{3}J_{HH} = 6.6$ Hz, 8H; THF), 6.01 (vt, 1H; H-2), 7.00-7.08 (m, 6H; H-9/10), 7.09-7.13 (m, 1H; H-3),7.49-7.51 (m, 1H; H-1), 7.51-7.54 (m, 1H; H-4), 8.22-8.26 (dd, ${}^{3}J_{\text{HH}} = 12.7, {}^{4}J_{\text{HH}} = 7.3 \text{ Hz}, 4\text{H}; \text{H-8}). {}^{7}\text{Li NMR} (194.4 \text{ MHz}, C_{6}\text{D}_{6}): \delta$ 1.42. ¹³C{¹H} NMR (125.8 MHz, C_6D_6): δ 25.5 (s; THF), 60.1 (d, ¹*J*_{PC} = 127.8 Hz; C-6), 68.1 (s; THF), 106.4 (bs; C-2), 115.4 (d, ${}^{3}J_{PC}$ = 8.0 Hz; C-4), 127.9 (d, ${}^{3}J_{PC}$ = 12.4 Hz; C-9), 130.0 (d, ${}^{4}J_{PC}$ = 2.8 Hz; C-10), 133.3 (d, ${}^{2}J_{PC}$ = 10.3 Hz; C-8), 135.4 (s; C-3), 138.1 (d, ${}^{1}J_{PC}$ = 92.0 Hz; C-7), 146.1 (s; C-1), 163.9 (d, ${}^{2}J_{PC}$ = 14.6 Hz; C-5). ³¹P NMR (162.0 MHz, C₆D₆): δ 39.4. Anal. Calcd for C₂₆H₂₈ClLiNO₂PS: C, 63.22; H, 6.12; N, 2.84; S, 6.49. Found: C, 63.21; H, 6.20; N, 3.05; S, 6.43.

Preparation of 3b. The procedure was analogous to that for 3a: yield 93%. Crystals were grown by diffusion of pentane into a solution of 3b in THF at -40 °C. ¹H NMR (400.1 MHz, C₆D₆): δ 1.28 (m, 8H; THF), 3.46 (m, 8H, THF), 6.79–6.82 (m, 1H, H-Quin), 6.97–7.07 (m, 8H; H-13,14,Quin), 7.10–7.15 (m, 2H; H-3,4), 7.57–7.73 (m, 1H; H-8), 8.25–8.32 (m, 4H; H-12). ⁷Li NMR (194.4 MHz, C₆D₆): δ 1.30. ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ 25.5 (s; THF), 68.2 (s, THF), 67.9 (bd, ¹J_{PC} ≈ 115 Hz; C-10), 118.7 (s; C-Quin), 119.9 (d, J_{PC} = 7.9 Hz; C-Quin), 121.7 (s; C-Quin), 123.0 (s; C-6), 128.0 (s; C-Quin), 128.0 (d, ³J_{PC} = 12.5 Hz; C-13), 128.3 128.8 (s, C3,4), 130.3 (d, ⁴J_{PC} = 2.9 Hz; C-14), 133.0 (d, ²J_{PC} = 10.3 Hz; C-12), 137.1 (d, ¹J_{PC} = 92.0 Hz; C-11), 150.2 (s; C-1), 161.5 (bs; C-9). ³¹P{¹H} NMR (162.0 MHz, C₆D₆): δ 41.3. Anal. Calcd for C₂₂H₁₇ClNPS: C, 66.23; H, 5.93; N, 2.57; S, 5.89. Found: C, 65.76; H, 6.23; N, 2.50; S, 5.69.

Preparation of 4a. To 238 mg (481 μ mol) of carbenoid 3a in 13 mL of THF was added 30 μ L (481 μ mol) of MeI. The mixture was stirred for 3 h and the solvent was subsequently removed in vacuo. NMR spectroscopic studies showed the clean formation of the product. For further purification the slightly brown oil was purified by flash chromatography on silica with DCM ($R_f = 0.8$) as eluent, thus giving the product as a colorless solid (120 mg, 335 μ mol, 70%). ¹H NMR (400.1 MHz, CDCl₃): δ 2.33 (d, ${}^{3}J_{PH}$ = 15.2 Hz, 3H; CH₃), 7.14-7.18 (m 1H; H-2), 7.35-7.40 (m, 2H; H-9), 7.43-7.57 (m, 6H; H-3,4,9,10), 7.95-8.00 (m, 2H; H-8), 8.13-8.19 (m, 2H; H-8), 8.44-8.47 (bd, 1H; H-1). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ 27.4 (d, ${}^{2}J_{\rm PC}$ = 4.4 Hz; CH₃), 71.4 (d, ${}^{2}J_{\rm PC}$ = 46.8 Hz; C-6), 123.1 (d, ${}^{5}J_{\rm PC}$ = 2.2 Hz; C-4), 124.9 (d, ${}^{3}J_{PC} = 2.7$ Hz; C-2), 127.9 (d, ${}^{3}J_{PC} = 12.3$ Hz; C-9), 128.1 (d, ${}^{3}J_{PC}$ = 12.2 Hz; C-9), 129.0 (d, ${}^{1}J_{PC}$ = 80.8 Hz; C-7), 129.9 (d, ${}^{2}J_{PC} = 79.9$ Hz; C-7), 131.9 (d, ${}^{4}J_{PC} = 3.0$ Hz; C-10), 132.0 (d, ${}^{4}J_{PC}$ = 2.9 Hz; C-10), 133.9 (d, ${}^{2}J_{PC}$ = 9.5 Hz; C-8), 134.0 (d, ${}^{2}J_{PC}$ = 9.5 Hz; C-8), 135.8 (d, ${}^{4}J_{PC} = 1.9$ Hz; C-3), 147.8 (d, ${}^{4}J_{PC} = 1.6$ Hz; C-1), 156.9 (d, ${}^{2}J_{PC} = 1.1$ Hz; C-5). ${}^{31}P{}^{1}H$ NMR (162.0 MHz, CDCl₃): δ 59.6. Anal. Calcd for C₂₂H₁₇ClNPS: C, 63.77; H, 4.79; N, 3.91; S, 8.96. Found: C, 63.85; H, 4.90; N, 3.84; S, 9.05.

Preparation of 4b. A 30 mg portion (61.0 μmol) of carbenoid **3a** and 12.8 mg (64.0 μmol) of trimethylchlorostannane were placed in a J. Young NMR tube and dissolved in 0.8 mL of C₆D₆. The slightly yellow mixture was shaken, and NMR data were recorded, which showed quantitative formation of the stannylated product. ¹H NMR (500.1 MHz, C₆D₆): δ 0.36 (s, 9H; CH₃), 6.42 (m, 1H; H-2), 6.84 (m, 1H; H-4), 6.96–7.03 (m, 3H; H-9/10), 7.08–7.10 (m, 3H; H-9/10), 7.14–7.16 (m, 1H; H-3), 8.04–8.09 (m. 3H; H-8/1), 8.53–8.56 (m, 2H; H-8). ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ –2.9 (s, ¹J_C^{117/19}Sn = 183.7 Hz, 175.6 Hz; CH₃), 69.2 (d, ¹J_{PC} = 23.4 Hz; C-6), 122.2 (d, 2.9 Hz; C-2), 124.2 (d, ³J_{PC} = 3.9 Hz; C-4), 127.7 (d, ³J_{PC} = 11.7 Hz; C-9), 128.0 (d, ³J_{PC} = 11.9 Hz; C-9), 131.3 (d, ⁴J_{PC} = 2.9 Hz; C-10), 131.4 (d, ¹J_{PC} = 75.2 Hz; C-7), 131.6 (d, ⁴J_{PC} = 2.9 Hz; C-10), 132.4 (d, ¹J_{PC} = 81.0 Hz; C-7), 134.2 (bd, ²J_{PC} = 13.4 Hz; C-8), 136.1 (d, ⁴J_{PC} = 2.5 Hz; C-3), 147.0 (d, ⁴J_{PC} = 1.82 Hz; C-1), 159.6 (d, ²J_{PC} = 2.7 Hz; C-5). ³¹P{¹H} NMR (162.0 MHz, C₆D₆): δ 50.1 (²J_P^{μτ/μ9}Sn = 16.4, 37.4 Hz).

Attempted Cyclopropanation with Cyclohexene and *trans*-Stilbene. Carbenoid 3a and 1.1 equiv of olefin (cyclohexene, *trans*stilbene) were placed in a J. Young NMR tube and dissolved in THF and toluene, respectively. The mixture was stirred for several hours at room temperature (and at 60 °C). NMR spectroscopy showed no conversion and decomposition of the carbenoid, respectively, after a prolonged reaction time at elevated temperature.

Preparation of 5. A 10 mL portion of diethyl ether was added to 120 mg (244 μ mol) of carbenoid **3a** and 282 mg (244 μ mol) of tetrakis(triphenylphosphine)palladium(0) at -78 °C. The yellow suspension was slowly warmed to room temperature and stirred for 3

days. Subsequently the solvent was removed in vacuo and the residue taken up in 20 mL of toluene. After filtration to remove the formed lithium chloride, the solvent was reduced to approximately 1 mL and 5 mL of hexane was added. The solvent was removed with a syringe and the solid washed with hexane $(6 \times 10 \text{ mL})$, giving the product as a yellow solid (94 mg, 139 μ mol; 57%). ¹H NMR (500.1 MHz, C₆D₆): δ 6.00-6.03 (m, 1H; H-2), 6.71-6.75 (m, 1H; H-3), 6.75-6.80 (m, 2H; H-10), 6.81-6.86 (m, 4H; H-9), 6.90-6.95 (m, 9H; H-13/14), 7.65-7.68 (m, 1H; H-1), 7.69-7.72 (m, 1H; H-4), 7.87-7.96 (m, 6H; H-12), 8.35–8.42 (m, 4H, H-8). ${}^{13}C{}^{1}H{}$ NMR (500.1 MHz, d_8 -THF): δ 39.0 (dd, ${}^{1}J_{PC}$ = 111.0 Hz, ${}^{2}J_{PC}$ = 103.0 Hz; C-6), 113,8 (C-2), 121.8 $(dd, {}^{3}J_{PC} = 9.0 \text{ Hz}, {}^{4}J_{PC} = 4.1 \text{ Hz}; \text{ C-4}), 128.1 (d, {}^{3}J_{PC} = 12.2 \text{ Hz}; \text{ C-9}),$ 128.4 (d, ${}^{3}J_{PC}$ = 12.6 Hz; C-13), 128.8 (dd, ${}^{1}J_{PC}$ = 91.8 Hz, ${}^{4}J_{PC}$ = 1.2 Hz; C-11), 129.6 (d, ${}^{4}J_{PC}$ = 2.9 Hz; CH-10), 131.5 (d, ${}^{4}J_{PC}$ = 2.9 Hz; C-14), 132.5 (d, ${}^{2}J_{PC}$ = 10.6 Hz; C-8), 133.7 (bs, C-3), 135.2 (d, ${}^{2}J_{PC}$ = 9.7 Hz; C-12), 139.6 (dd, ${}^{1}J_{PC}$ = 86.26, ${}^{4}J_{PC}$ = 4.1 Hz; C-7), 146.6 (d, ${}^{3}J_{PC}$ = 4.0 Hz; C-1), 162.7 (d, ${}^{2}J_{PC}$ = 10.0 Hz; C-5). ${}^{31}P{}^{1}H$ NMR (500.1 MHz, C_6D_6) δ 19.1 (d, ${}^{3}J_{PP}$ = 46.2 Hz; PdPPh₃), 40.6 (d, ${}^{3}J_{PP}$ = 46.2 Hz; PPh₂). ESI-MS: calcd for C₃₆H₃₀NP₂SPd 676.06163, found 676.06191.

Single-Crystal X-ray Structure Determination. Single crystals were selected from a Schlenk flask under an argon atmosphere and covered with an inert oil (perfluoropolyalkyl ether). Data were collected on a Bruker APEX-CCD instrument (D8 three-circle goniometer) (Bruker AXS). Integration was conducted with SAINT, and an empirical absorption correction (SADABS) was applied. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F² (SHELXL-97).¹⁸ All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined using the riding model. Relevant details about the structure refinements are given in Tables S1 and S2 in the Supporting Information. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-967265 (compound 1b), CCDC-967266 (compound 2a), CCDC-967267 (compound 2b), CCDC-967268 (compound 3a), and CCDC-967269 (compound 3b). Copies of the data can be obtained free of charge on application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam. ac.uk).

Computational Details. All calculations were performed without symmetry restrictions. Starting coordinates were obtained directly from the crystal structure analyses. All calculations were done with the Gaussian 03 and Gaussian 09 program package.¹⁹ Geometry optimizations were performed at the density functional theory level using the B3LYP and M062X functionals.²⁰ For the calculation of the carbenoids 3a,b the 6-311++G** basis set was used, for the Pd complexes the 6-31G(d) basis set was used for hydrogen, the LANL2TZ(f)²¹ basis set augmented with a f polarization function of exponent 1.472^{22} was used for palladium, and the 6-311+g(d) basis set was used for all other atoms. Harmonic vibrational frequency analyses were performed at the same levels of theory to confirm that the structures were indeed minima on the potential energy surface (PES). NBO analyses were carried out on the optimized systems using the NBO 5.0 program interfaced to the Gaussian 03 program and the same level of theory.²³

ASSOCIATED CONTENT

S Supporting Information

CIF files, text, tables, and figures giving crystallographic data for structures of **1b**, **2a**,**b**, and **3a**,**b**, plots of the molecular structures of **1b** and **2b**, ¹H and ³¹P{¹H} NMR spectra for all of the synthesized compounds, crystallographic and computational details, and coordinates of the energy-optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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