ORGANOMETALLICS

Formation of a Palladium Thioketone Complex from a Thiophosphinoyl Stabilized Li/Cl Carbenoid

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Supporting Information

ABSTRACT: An in situ generated thiophosphinoyl stabilized Li/Cl carbenoid reacts with $Pd(PPh_3)_4$ with formation of a palladium thioketone complex. The presence of both the thiophosphinoyl and silyl groups as anion-stabilizing substituents is insufficient to stabilize the expected alkylidene complex and instead results in a rearrangement to the thioketone compound.

 \ensuremath{S} ince the pioneering work by Fischer and Schrock, transition-metal complexes with a metal-carbon double bond have found wide-ranging applications.¹ These complexes are generally divided into two classes: the Fischer-type carbene and the Schrock-type alkylidene complexes. The former usually bear π donor substituents and are viewed as singlet species, forming the C=M bond via σ donation to the metal center and π backbonding from the metal into the empty p_{π} orbital. In contrast, Schrock-type complexes usually bear alkyl substituents and the metal center interacts with a triplet fragment with formation of a covalent metal-carbon bond. In this context, carbene complexes formed from geminal dilithiated bis(thiophosphinoyl)methane or bis(iminophosphorano)methane have gained special interest, as they seem to contradict this general classification pattern (Figure 1).² Here, the metal-carbon bond is formed by a fourelectron donation from the ligand to the metal, leaving a highly nucleophilic carbon atom bound to anion stabilizing groups."



Figure 1. Classifications of metal carbene complexes.

Fascinated by the unique properties of these carbene complexes derived from geminal dianions, we were interested in expanding this chemistry to further systems and functionalities. We assumed that changing the substitution pattern at carbon should significantly influence the electronic situation and thus the reactivity of the complex. However, geminal dianions are extremely sensitive species and, apart from the bis(thiophosp-



hinoyl)- and bis(iminophosphorano)methanediides, difficult to synthesize and isolate in high yields.^{5,6} Thus, we aimed at geminal dianions with sufficient stabilization of the negative charge to allow for quantitative deprotonation. Several functional groups are known as "anion-stabilizers", in particular silyl groups, due to the high polarizability of Si and the presence of low-lying σ^* -SiR orbitals, which allow for negative hyperconjugation.^{7,8} Herein, we report our attempts to access a dianionic ligand from an α -silyl-substituted phosphine sulfide. We show that, due to the lower anion stabilization capability of the silyl group, the carbene complex is no longer stable and rearranges to an unexpected palladium thioketone complex.

The starting phosphine sulfide 1 was obtained in 76% yield by straightforward lithiation of methyldiphenylphosphine sulfide and subsequent treatment with trimethylchlorosilane (Scheme 1). Addition of the lithium reagent to a solution of the electrophile is of crucial importance to minimize the formation of the disilylsubstituted compound by deprotonation of the more CH acidic α -silyl phosphine sulfide 1 already formed in the reaction mixture. To examine the possible dilithiation of the methylene moiety to the geminal dianion 2, compound 1 was treated with 2 equiv of lithium base (MeLi, *n*BuLi, and *t*BuLi), which resulted in a yellow ether solution. Monitoring of the reaction process by ³¹P NMR spectroscopy showed the immediate consumption of 1 and the formation of a single species at δ 44.0 ppm. Trapping of the reaction mixture with different electrophiles, however, only afforded the products derived from the monometalated species. Comparison with a monolithiation experiment identified the formed lithium compound as the monolithiated compound 3. An even longer reaction time and the addition of additives (TMEDA, PMDETA) did not result in the clear formation of 2. This observation clearly demonstrates the considerable loss of stabilization of the negative charge by replacing the phosphonium substituent with the SiMe3 group. In the case of the bis(thiophosphinoyl)- and bis(iminophosphorano)methanes

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double deprotonation usually occurs with simple organolithium bases. Only in the case of sterically demanding systems is the use of additional activating bases required.⁵

This result prompted us to aim for an alternative approach to the desired alkylidene complex. Le Floch and co-workers have demonstrated the accessibility of the palladium complexes A via the corresponding lithium carbenoid, which in their case could be prepared by mild oxidation of the dilithium species.⁹ To follow an approach via a carbenoid species, we aimed at the synthesis of the chlorinated compound 4, which we expected to undergo a preferred deprotonation reaction in comparison to a competitive substitution of the chloride. At first, the chlorinated compound 4 was prepared in 95% yield by lithiation of 1 with *n*-butyllithium followed by treatment with hexachloroethane (Scheme 1). For the formation of the lithium carbenoid 5, 4 was treated in diethyl ether with 1 equiv of methyllithium at -78 °C, which instantly resulted in a yellow color. However, warming of the solution of 5 to room temperature resulted in decomposition at around -20 °C, which was accompanied by a color change to black.¹⁰ This thermolability of 5 also prevented its isolation. Nevertheless, treatment with iodomethane at -78 °C gave the methylated racemic product 6 and thus unequivocally confirmed the lithium carbenoid as an intermediate species (Scheme 1). The methylation proceeds quantitatively, and 6 could be isolated in 94% yield after workup. 1, 4, and 6 were characterized by elemental analyses, mass spectrometry, and multinuclear NMR. Due to the chiral centers in 4 and 6, the phenyl substituents at the adjacent prochiral phosphorus atom are diastereotopic (see the Supporting Information). 1 was additionally characterized by X-ray crystallography (see the Supporting Information). Overall, the formation of 6 confirmed the preferred deprotonation of 4 over a possible substitution reaction and thus the in situ accessibility of the lithium carbenoid.¹¹



To test the applicability of lithium carbenoid 5 for the synthesis of alkylidene complexes, freshly prepared 5 was reacted with tetrakis(triphenylphosphine)palladium (Scheme 2). Addition of 5 to a THF solution of $[Pd(PPh_3)_4]$ at -30 °C immediately resulted in an orange color. ³¹P NMR studies of the reaction mixture showed the formation of triphenylphosphine and a second phosphorus species characterized by a set of three doublets of doublets at δ 9.4, 21.3, and 25.8 ppm, the first signal being shifted somewhat upfield to the expected alkylidene complex 7a (see the Supporting Information). After workup aimed at eliminating PPh₃ and LiCl formed during the reaction, the product was obtained as a yellow solid in 79% yield (Scheme 2). However, when single crystals of 7 were obtained, an X-ray diffraction study revealed that it was not the expected alkylidene, but the thioketone complex 7b (Figure 2a). 7b features a Pd-C-S three-membered ring as the central structural motif and a noncoordinating phosphine unit, which is consistent with the observed upfield-shifted signal in the ³¹P NMR spectrum. Complex 7b is formed as a racemic mixture. The stereogenic carbon atom results in diastereotopic phenyl substituents at the adjacent prochiral phosphorus atom and thus in the corresponding splitting in the ¹H and ¹³C NMR spectra (see the Supporting Information).





^{*a*} Reagents and conditions (yields): (a) 1 equiv of *n*BuLi, THF, -78 °C to -30 °C, Me₃SiCl, H₂O; (b) 1 equiv of MeLi, Et₂O, -78 °C to -30 °C, quantitative by ³¹P NMR; (c) C₂Cl₆, -78 °C (95%); (d) 1 equiv of MeLi, Et₂O, -78 °C to -50 °C; (e) CH₃I (94%).

Scheme 2. Formation of the Thioketone Complex 7b and the Proposed Mechanism



Compound 7b crystallizes in the triclinic space group $P\overline{1}$. The central motif consists of a Pd-C-S moiety, in which the palladium adopts a strongly distorted square planar (Figure 2c) coordination (angles between 45.94(7) and 155.28(3) $^{\circ}$) due to the short bite of the C-S linkage. The same is true for the coordination sphere around carbon, which considerably deviates from the ideal tetrahedral arrangement. The Pd-C (2.182(3) Å) as well as the C–Si and C–P distances are in the typical range of a single bond. In contrast, the C–S bond of 1.747(3) Å is shorter than a typical C–S single bond, indicating some π character. Both the short C–S bond and the flattened carbon coordination sphere (torsion angle Si-C-P-S of 151.6(3)°) (Figure 3b) are comparable to those for known thioketone transition-metal complexes. Thus, 7b can be viewed as a side-on coordination complex of the Pd(0) species to the C=S double bond.¹² This is also confirmed by computational studies of the model system 7b', in which the PPh₃ ligands are replaced by PH₃ (for computational details see the Supporting Information).¹ The optimized geometry of 7b' (e.g., Pd–C = 2.158 Å, C–S = 1.745 Å) is in good agreement with the experimental data. Natural bond orbital (NBO) analysis shows a typical C=S double bond with a roughly sp² hybridized carbon atom. As evidenced by second-order perturbation theory, the π bond interacts with the palladium fragment by strong donation into a vacant metal orbital and back-bonding from the filled metal d_{xz} orbital into the π^* (LUMO, Figure 3).



Figure 2. Palladium complex 7b: (a) molecular structure; (b, c) views of the Pd coordination sphere. Selected bond lengths (Å) and angles (deg): C(4)-S(1) = 1.747(3), C(4)-P(1) = 1.833(3), C(4)-Si(1) = 1.891(3), C(4)-Pd(1) = 2.182(3), P(2)-Pd(1) = 2.3142(9), P(3)-Pd(1) = 2.3465(8), Pd(1)-S(1) = 2.2865(9); S(1)-C(4)-P(1) = 123.09(15), S(1)-C(4)-Si(1) = 113.47(14), P(1)-C(4)-Si(1) = 116.40(14), S(1)-C(4)-Pd(1) = 70.18(9), P(1)-C(4)-Pd(1) = 114.19(13), Si(1)-C(4)-Pd(1) = 110.07(13), C(4)-Pd(1)-S(1) = 45.94(7), P(2)-Pd(1)-P(3) = 109.03(3), C(4)-S(1)-Pd(1) = 63.87(9). For crystallographic details see the Supporting Information.



Figure 3. LUMO of model complex 7b'.

The selective formation of thioketone complexes has not been reported before for analogous systems. Usually, thionation reactions are preformed with Lawesson reagent or diphenylphosphinodithioic acid on oxidized carbon compounds, particularly carbonyls, amides, or esters.¹⁴ In the case of the lithium carbenoid **5** the thionation reaction only occurred by treatment with $[Pd(PPh_3)_4]$.¹⁵ The formation of an analogous thiocarbonyl complex has been observed as a byproduct of the synthesis of a uranium carbene complex.¹⁶ Accordingly, we propose that carbenoid **5** also initially reacts with $[Pd(PPh_3)_4]$ with formation of the corresponding alkylidene complex **7a**, which further reacts to **7b** by attack of the nucleophilic carbon atom at sulfur



Figure 4. (a) Calculated model systems and (b) KS-HOMO and KS-LUMO of the energy-optimized structure of hypothetical alkylidene complex 7a'.

(Scheme 2). But why is 7b and not the alkylidene complex 7a the stable product? It is noteworthy that the π interaction of the M–C double bond is rather weak. This results from the unusual electronic situation in complexes derived from geminal dianions or carbenoid compounds. The energy-optimized model system 7a' (PPh₃ replaced by PH₃) features a Pd–C bond, which is formed by a π -type interaction of the n $_{\pi}$ orbital with the d_{xy} orbital of palladium (HOMO) and an interaction between the n $_{\sigma}$ orbital and the d_{xz} orbital (LUMO) (Figure 4). As the HOMO is of antibonding nature, the π -type interaction is weaker and thus the M–C bond longer than in "classical" metal carbene complexes.⁹

This "weakness" of the alkylidene complex also becomes evident from the energy optimization of the model systems 7a'and 7b'. Although the alkylidene complex was also revealed to be a minimum on the reaction coordinate, it is considerably less stable ($\Delta H = 22.0 \text{ kcal mol}^{-1}$) than the thioketone complex 7b'. Remarkably, in the system A' this difference only amounts to 2 kcal mol^{-1} , which is also the result of the chelating nature of the bis(thiophosphinoyl)methanide ligand. This is in line with the higher negative charge at the carbenic atom in 7a' (NPA charge $q_{\rm C}$ = -1.41) compared with that in A' ($q_{\rm C}$ = -1.38). This suggests the negative charge to be the driving force for the transformation of 7a to 7b ($q_{\rm C} = -1.15$), which is the result of the lower anion-stabilizing capability of the silyl group compared to that of the thiophosphinoyl substituent. The lower stabilization is also in line with the so far failed dilithiation of 1 under mild reaction conditions and the instability of the lithium carbenoid 5.

In conclusion, we have presented the unexpected formation of a palladium thioketone complex 7b by reaction of $Pd(PPh_3)_4$ with a thiophosphinoyl-stabilized Li/Cl carbenoid. The presence of both the thiophosphinoyl and a silyl group as anion-stabilizing substituents was found insufficient to stabilize the analogous alkylidene complex 7a, as known for the bis(thiophosphinoyl)methanide ligand. These results clearly indicate the crucial influence of the substituents at the carbon atom on the electronic situation and thus the reactivity of the corresponding metal complex. We are currently studying the influence of the substitution pattern at silicon and phosphorus on the formation of the thioketone complex to obtain more detailed information about the mechanistic features of this reaction.

ASSOCIATED CONTENT

Supporting Information. Text, figures, tables, and CIF files giving experimental procedures, synthesis of all compounds, spectroscopic and computational details, and crystallographic data of the presented compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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