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Novel acyclic carbene-substituted phospha-palladacycles ☆

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Abstract

Here, we report the synthesis of the first phospha-palladacycle substituted with an acyclic carbene. The reaction of bis(dialkyl)aminocarbenes with the very stable phospha-palladacycles leads to metastable η^1-carbene complexes, which can be converted by intramolecular reduction to zero valent palladium complexes.

Keywords: Acyclic carbene complexes; Phospha-palladacycle

1. Introduction

Phospha-palladacycles, first published by Shaw [1], Mason [2], Aleya [3], Heck [4], and in our group [5], were investigated in the past as very good catalysts in C–C coupling reactions. In this case the high air-, moisture- and thermal-stabilities are one of the important properties for these catalysts [6]. Recently, our group published the first *N*-heterocyclic carbene substituted phospha-palladacycles for C–C coupling reactions [7]; an analogous nitrogen-palladacycle was published from the Nolan group [8]. The new phospha-palladacycles combine the advantageous stability of the palladacycles with the good σ-donor ability of the carbene ligands, to be highly active catalysts for chloroarenes in the Mizoroki–Heck reaction [9–11]. A high σ-donor ability of the ligands at the palladium metal center is favourable for the Mizoroki–Heck reaction. Substitution of *N*-heterocyclic carbenes in these complexes by better σ-donating acyclic carbenes such as the bis(diisopropyl)aminocarbene [12], first published by Alder [13], should increase the catalytic potential in the Mizoroki–Heck reaction. A big disadvantage of acyclic carbenes is their possibility to act as reducing agents on palladium(II) compounds under formation of undefined palladium(0) species; in most cases palladium black was obtained [14]. With palladium(0) complexes as starting materials no complex formation could be obtained. This can be explained by the low electron affinity of the Pd(0)-metal against strong σ-donors [14]. In this case the phospha-palladacycles should give a better chance to form palladium complexes with acyclic carbene ligands, because of their high resistance against reductive decomposition and the oxidation state of two for a high electron affinity towards donor ligands.

2. Results and discussion

Trans-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]-dipalladium(II) (**1**) was used as a stable palladium(II) precursor against reduction to form the corresponding carbene palladium(II) complexes (**4**, **5**) with acyclic carbenes. As acyclic carbenes the bis(diisopropyl)aminocarbene (**3a**) [13] and the new carbene ligand **3b**

☆ Carbenes, Part 40. For Part 39, see Ref. [7a].

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(diisopropylamine-*cis*-2,6-dimethyl-*N*-piperidylmethylidene) were used [15]. Carbene **3b** was synthesized from the precursor **2b**.

To a toluene solution of the phospha-palladacycle **1** a THF-carbene solution was added at −78 °C. After 1 h the temperature was raised slowly to room temperature, and the solvent removed in vacuo, the formed orange complexes (**4**, **5**) were washed with *n*-hexane to separate an excess of the free carbenes from the products (Scheme 1). Both complexes show the expected ^{31}P NMR-signal with 24.3 ppm. Compared with NHC-phospha-palladacycles the signals are shifted downfield, due to the higher σ-donor ability of the carbene ligands. The ^{13}C NMR-signals for the carbene atoms are found in the expected range with 226.5 (**4**) and 226.1 ppm (**5**) and appear at a much lower field than in the analogous NHC complexes [7].

If complex **4** is treated with diethyl ether at −30 °C, the complex decomposes to form bis(tri-*o*-tolylphosphane)palladium(0) (**6**) and palladium black in nearly quantitative yield (Scheme 2). A similar decomposition of phospha-palladacycles was reported by Hartwig during the treatment with strong bases such as NaO*t*Bu [16]. The mechanism of this reaction is mentioned in Scheme 3.

The first step is a proton transfer from the coordinated amine to the acetate, liberating acetic acid. By a *β*-H-elimination at the amide a hydrido palladium species is formed, which dismutates after a reductive elimination to form bis(tri-*o*-tolylphosphane)palladium(0) (**6**) and palladium black. For the formed reaction mixture only one signal can be obtained in the ^{31}P NMR at −6.7 ppm (C_6D_6), which can be classified for complex **6**. The same products were obtained in the reaction of complex **4**. Because no intermediates could be characterized, we propose an intramolecular reaction mechanism without an additional base, different to the mechanism proposed by Hartwig. In the first step a proton transfer from an isopropylamine to the acetate could occur, followed by elimination of propene and liberation of acetic acid. For example such a propene elimination at an isopropylamine group was recently reported by Bertrand [17] at a free acyclic alkyl-amino carbene to form an imine, shown in Scheme 4. In our case the formed imine could now coordinate with the nitrogen and the carbon atom η^2 to the palladium. The η^2-coordinated intermediate could then decompose under elimination of another propene and H-transfer to the palladium, followed by reaction steps as postulated in the Hartwig mechanism.

In contrast, complex **5** shows no decomposition when treated with diethyl ether.

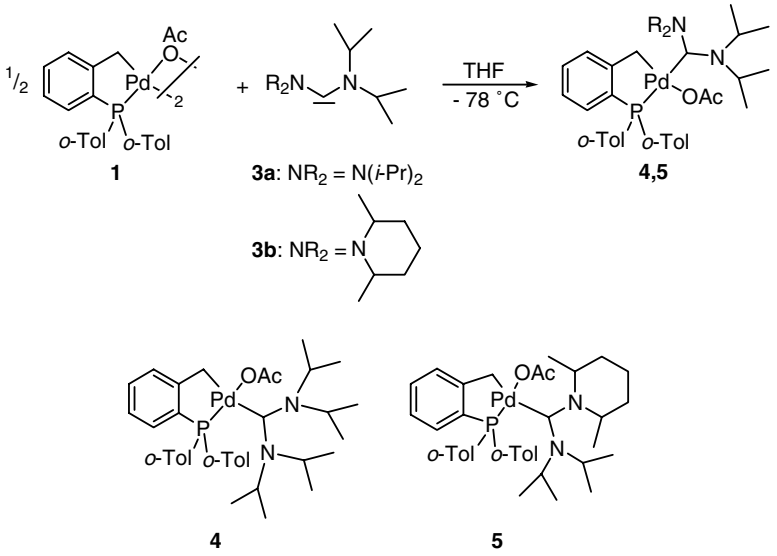
3. Conclusion

For the first time it was possible to obtain a phospha-palladacycle substituted by acyclic carbenes without reduction of the palladium(II) complex. One of the new complexes (**4**) decomposes by treating with diethyl ether under formation of **6** and palladium black.

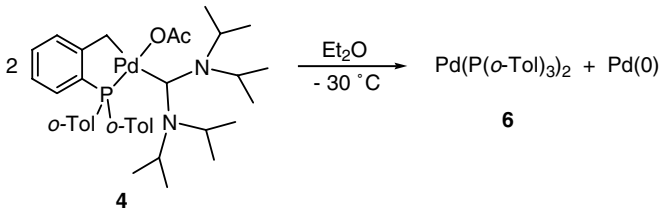
4. Experimental

4.1. General comments

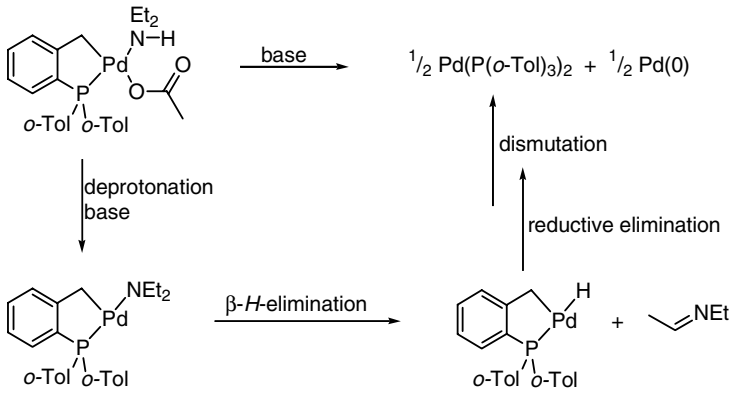
The dimer palladacycle precursor (**1**) was synthesized as reported in the literature [5]. All experiments were carried out under dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under nitrogen. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz



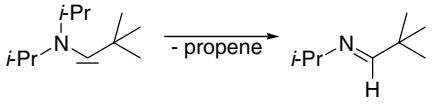
Scheme 1. Formation of phospha-palladacycles substituted with acyclic carbenes.



Scheme 2. Reduction and dismutation of complex **4**.



Scheme 3. Mechanism for the disproportion of amine-substituted phospha-palladacycles via reduction to form bis(tri-*o*-tolylphosphane)palladium(0) (**6**).



Scheme 4. Decomposition of a free carbene first published by Bertrand.

spectrometer at room temperature and referenced to the residual ^{1}H- and ^{13}C-signals of the solvents or 85% H_3PO_4 as an external standard (^{31}P). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using the CI or FAB technique. Melting points were measured with a Büchi melting point apparatus system (Dr. Tottoli).

4.2. Preparation of diisopropyl-(cis-2,6-dimethylpiperidine-1-ylmethylidene)ammonium dichlorophosphate (*2b*)

A solution of 3.2 ml (34.5 mmol) $POCl_3$ in 20 ml diethyl ether was added to a solution of 5 ml (34.5 mmol) diisopropylformamide dissolved in 50 ml diethyl ether. After stirring the combined solutions for 1 h at room temperature, the precipitate was collected by filtration. The residue was washed twice with 20 ml diethyl ether and dissolved in 30 ml dichloromethane. After cooling to −30 °C *cis*-2,6-dimethylpiperidine (4.6 ml, 34.2 mmol) was added and stirred for 45 min at 25 °C. To this solution 100 ml diethyl ether were added to precipitate a white crystalline product. The raw substance was extracted with acetone, and the product precipitated by adding diethyl ether to the acetone solution. The white hydroscopic product **2b** was dried in vacuo. Yield: 4.400 g (12.3 mmol), 36%. ^{1}H NMR (270 MHz, 300 K, $CDCl_3$): $\delta = 8.06$ (1H, s, NC*H*N), 4.34 (2H, s, C*H*$(CH_3)_2$), 4.11 (1H, br s, NC*H*(CH_3)-CH_2), 3.86 (1H, br s, NC*H*$(CH_3)CH_2$), 1.88 (2H, m, $CH(CH_3)C\mathit{H}_2CH_2$), 1.69 (2H, d, $^{3}J_{HH} = 8.7$ Hz, CH_2-$C\mathit{H}_2CH_2$), 1.59 (2H, m), 1.45 (12H, d, $^{3}J_{HH} = 6.9$ Hz, $CH(C\mathit{H}_3)_2$), 1.40 (6H, d, $^{3}J_{HH} = 6.2$ Hz, $NCH(C\mathit{H}_3)$). ^{13}C{^{1}H} NMR (67.8 MHz, 300 K, $CDCl_3$): $\delta = 154.4$ (N*C*HN), 55.4 (*C*$(CH_3)_2$), 51.2 (N*C*HCH_3), 30.2 ($C(HCH_3)C\mathit{H}_2CH_2$), 22.9, 22.0, 12.5 (*C*$H_3$). MS (FAB) *m*/*z* (%): 225.2 (100, [M^+]), 181.2 (5), 112.1 (2, [$((CH_3)_2CH)_2NC$]). Anal. Calc. for $C_{14}H_{29}N_2PO_2Cl_2$ (359.27): C, 46.80; H, 8.14; N, 7.80; P, 8.62; Cl, 19.74. Found: C, 46.91; H, 8.24; N, 7.76; P, 8.11; Cl, 19.71%.

The free carbenes (**3a** and **3b**) were prepared according to reported procedures [13,15].

4.3. Preparation of diisopropylamine-cis-2,6-dimethyl-N-piperidylmethylidene (*3b*)

Yield: 189 mg (0.84 mmol), 63%. m.p. 37 °C. ^{1}H NMR (270 MHz, 300 K, C_6D_6): $\delta = 4.22$ (2H, sept,

$^3J_{HH} = 4.7$ Hz, C*H*(CH_3)$_2$), 3.73 (2H, br s, NC*H*(CH_3)CH_2), 1.68 (4H, d, $^3J_{HH} = 5.9$ Hz), 1.36 (2H, m), 1.24 (12H, s, CH(CH_3)$_2$), 1.21 (6H, s, NCH(CH_3)). $^{13}C\{^1H\}$ NMR (67.8 MHz, 300 K, C_6D_6): $\delta = 258.9$ (N*C*N), 56.2 (*C*(CH_3)$_2$), 49.3 (N*C*HCH$_3$), 31.8 (C(HCH$_3$)*C*H$_2$CH$_2$), 24.2, 23.0, 14.6 (*C*H$_3$).

4.4. Preparation of acetato[bis(diisopropylamino)-1-ylmethylylidene][o-(di-o-tolylphosphino)benzyl] palladium(II) (4)

126 mg (0.13 mmol) *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (**1**) was dissolved in 20 ml toluene and cooled to −90 °C. The carbene solution of 59 mg (0.28 mmol) bis(diisopropylamino)-1-ylmethylylidene (**3a**) in 10 ml THF was slowly added via a syringe to the palladacycle solution, slowly heated to room temperature, and stirred for 2 h. The solvent was removed and the remaining solid was washed twice with *n*-hexane. The complex was obtained in 77 % (137 mg, 0.20 mmol) yield. By treatment of the light orange solid with diethyl ether decomposition occurs.

^{1}H NMR (270 MHz, 300 K, C_6D_6): $\delta = 7.25$–6.72 (12H, m), 5.52 (1H, sept, $^3J_{HH} = 6.9$ Hz, C*H*), 5.38 (1H, sept, $^3J_{HH} = 6.9$ Hz, C*H*), 3.71 (1H, sept, $^3J_{HH} = 7.2$ Hz, C*H*), 3.52 (1H, sept, $^3J_{HH} = 6.9$ Hz, C*H*), 2.94 (2H, m, CH_2), 2.66 (3H, s, CO$_2$CH_3), 2.39 (6H, br s), 1.37 (6H, d, $^3J_{HH} = 7.2$ Hz, CH_3), 1.30 (6H, d, $^3J_{HH} = 6.9$ Hz, CH_3), 1.16 (6H, d, $^3J_{HH} = 6.7$ Hz, CH_3), 1.12 (6H, d, $^3J_{HH} = 6.9$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, C_6D_6): $\delta = 226.5$ (s, N*C*N), 174.3 (d, *C*O$_2$CH$_3$, $J_{PC} = 29.2$ Hz), 161.0, 143.2, 142.8, 133.5, 132.8, 132.8, 132.3, 132,1, 131.7 (d, C_{Ar}, $J_{PC} = 2.3$ Hz), 130.5, 129.1, 126.6, 126.0, 56.9 (s, N*C*H-(CH$_3$)$_2$), 56.6 (br s, N*C*H(CH$_3$)$_2$), 56.3 (s, N*C*H(CH$_3$)), 30.2, 23.7, 23.6, 23.5, 21.9, 21.4, 20.2 (*C*H$_3$). $^{31}P\{^1H\}$ NMR (109 MHz, 300 K, $C_6H_5CH_3$): $\delta = 24.5$ (s). $^{31}P\{^1H\}$ NMR (161 MHz, 300 K, C_6D_6): $\delta = 24.3$ (s). MS(FAB) *m*/*z* (%): 621.4 (33, [M$^+$ − OAc]), 409.1 (18, [M$^+$ − (OAc + carbene)]), 317.1 (4, [Pd + carbene]), 211.2 (100, [carbene]), 169.2 (82).

4.5. Preparation of acetato[diisopropylamin-cis-2,6-dimethyl-N-piperidylmethylidene][o-(di-o-tolyl-phosphino)benzyl]palladium(II) (5)

375 mg (0.4 mmol) *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (**1**) was dissolved in 20 ml toluene and cooled to −90 °C. The carbene solution of 185 mg (0.82 mmol) diisopropylamin-*cis*-2,6-dimethyl-*N*-piperidylmethylidene (**3b**) in 10 ml THF was slowly added via a syringe to the palladacycle solution, slowly heated to room temperature, and stirred for 2 h. The solvent was removed and the remaining solid was washed twice with 5 ml *n*-pentane and twice with 4 ml diethyl ether. The complex was obtained as an orange solid in 73 % (405 mg, 0.58 mmol) yield.

^{1}H NMR (400 MHz, 300 K, C_6D_6): $\delta = 7.27$ (1H, dd, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 2.0$ Hz), 7.19 (1H, t, $^3J_{HH} = 8.8$ Hz), 7.11 (1H, d, $^3J_{HH} = 8.0$ Hz), 7.08–6.93 (6H, m), 6.88 (2H, t, $^3J_{HH} = 7.6$ Hz), 6.75 (1H, t, $^3J_{HH} = 7.2$ Hz), 5.06 (1H, s, C*H*), 4.70 (1H, s, C*H*), 3.99 (2H, s, C*H*), 2.94 (3H, s, CH_3), 2.92 (1H, d, $^3J_{HH} = 13.9$ Hz, CH_aH_b), 2.90 (1H, d, $^3J_{HH} = 13.9$ Hz, CH_aH_b), 2.04 (4H, s, CH_2), 1.56 (2H, m, CH_2), 1.40 (6H, d, $^3J_{HH} = 7.2$ Hz, CH_3), 1.36 (6H, d, $^3J_{HH} = 7.2$ Hz, CH_3), 1.27 (6H, br s, CH_3), 1.12 (6H, d, $^3J_{HH} = 7.2$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, C_6D_6): = 226.1 (N*C*N), 173.8 (s, *C*O$_2$CH$_3$), 161.0 (d, C_{Ar}, $J_{PC} = 29.2$ Hz), 143.6 (d, C_{Ar}, $J_{PC} = 15.3$ Hz), 135.2, 134.7, 133.0 (d, C_{Ar}, $J_{PC} = 14.6$ Hz), 132.8 (d, C_{Ar}, $J_{PC} = 23.7$ Hz), 131.3 (d, C_{Ar}, $J_{PC} = 7.6$ Hz), 130.5, 130.1, 129.9, 125.6, 125.1 (d, C_{Ar}, $J_{PC} = 6.3$ Hz), 56.9 (br s, N*C*H(CH$_3$)$_2$), 54.1 (br s, N*C*H(CH$_3$)), 33.2, 32.8, 30.5, 25.4, 23.8 (br s, *C*H$_2$), 23.4, 22.4 (d, $^3J_{PC} = 6.1$ Hz, *C*H$_3$), 22.3 (d, $^3J_{PC} = 6.9$ Hz, *C*H$_3$), 21.4, 20.6, 20.1, 14.1 (*C*H$_3$). $^{31}P\{^1H\}$ NMR (161 MHz, 300 K, C_6D_6): $\delta = 24.3$ (s). $^{31}P\{^1H\}$ NMR (161 MHz, 300 K, $C_6H_5CH_3$): $\delta = 24.2$ (s). MS(CI) *m*/*z* (%): 633.4 (14, [M$^+$ − OAc]), 409.2 (6, [M$^+$ − (OAc + carbene)]), 224.3 (31, [carbene]), 181.2 (100). Anal. Calc. for $C_{37}H_{51}N_2O_2PPd$ (693.21): C 64.11; H 7.42; N 4.04. Found: C 63.81; H 7.36; N 4.37%.

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