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A straight forward in situ preparation of NHC-substituted phosphapalladacycles ☆

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Abstract

A new simple technique for the preparation of NHC-substituted phosphapalladacycles is reported by using phosphapalladacycle acetate precursors and azolium tetrafluoroborate salts in DMSO. The one-pot synthesis avoids multi-step reactions employing free carbenes. With this technique, NHC-substituted phosphapalladacycles were thus obtained that are not accessible via the free carbene route.

Keywords: Carbenes; Phosphapalladacycle; Palladium; NHCs; In situ method

1. Introduction

Palladacycles are among the most active catalyst systems for CC-coupling reactions. Palladium(II) complexes containing a cyclopalladated (di-*o*-tolylphosphino)benzyl fragment were first characterized by Shaw [1], Mason [2], Aleya [3], and Heck [4]. They were also intensely investigated in our group [5,6], and from this work they promised to be excellent catalysts in CC-coupling reactions. As a matter of fact these catalysts exhibit high air-, moisture-, and thermal stability (up to 250 °C) for processes such as Heck- and Suzuki-catalysis [7]. Recently we presented a new class of phosphapalladacycles, the *N*-heterocyclic carbene (NHC) substituted phosphapalladacycles [8]. The latter combine the advantageous stability of phosphapalladacycles with the high σ-donor strength and steric demand of *N*-heterocyclic carbenes [9].

It is now possible to synthesize NHC-complexes without isolation of the free carbene when metal acetates are used as starting material. Palladium(II) acetate in dimethylsulfoxide reacts at elevated temperature with azolium salts via deprotonation [6,10–13]. This route is particularly useful in cases where the metal acetates are easily available and where the corresponding free carbenes are not available.

2. Results and discussion

First we tried to react an azolium chloride salt (**2a**) with the acetate-bridged phosphapalladacycle dimer **1a** in DMSO at temperatures between 70 and 120 °C. However, only a substitution of the anion occurs and the chloride bridged phosphapalladacycle **1b** was obtained as product (Scheme 1) [14].

In order to avoid halogen scrambling during the reaction, the phosphapalladacycle acetate was reacted with azolium salts bearing weak coordinating anions like BF_4^- or PF_6^-. However, an additional base is necessary for the deprotonation of the azolium salts. In this case sodium acetate showed the best performance, because it does not compete in carbene complex formation (Scheme 2). When stronger bases are applied, such as KO*t*Bu, the palladacycle precursor decomposes [15].

A temperature dependency was observed for the reactions of the different azolium salts with the phosphapalladacycles. Best results were obtained at reaction

☆ *N*-Heterocyclic carbenes, part 43. For part 42 see Ref. [22].

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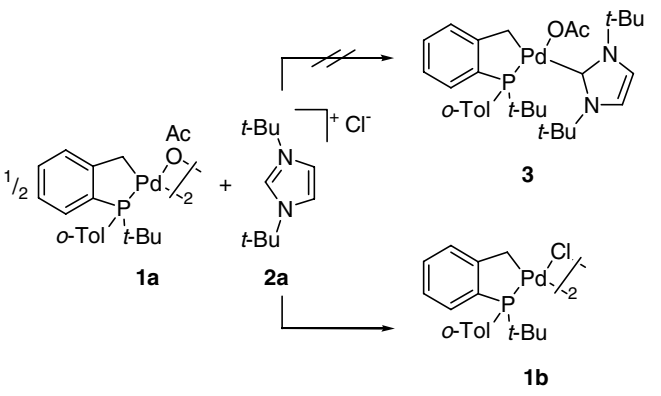
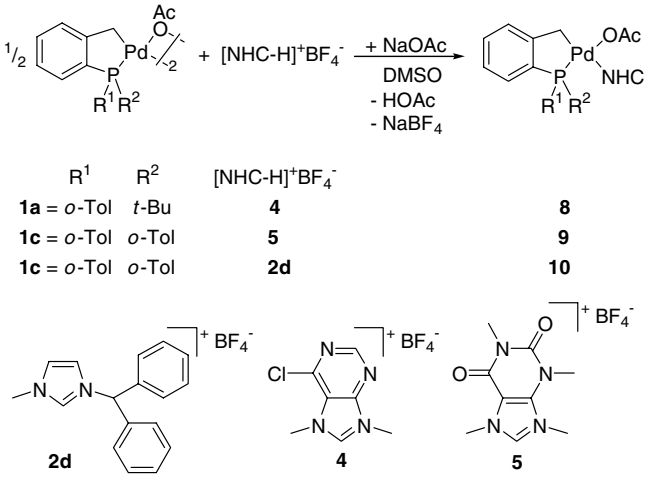


Scheme 1. Attempt for the preparation of complex **3**.



R^1	R^2	[NHC-H]$^+$BF$_4^-$	
1a = *o*-Tol	*t*-Bu	**4**	**8**
1c = *o*-Tol	*o*-Tol	**5**	**9**
1c = *o*-Tol	*o*-Tol	**2d**	**10**

Scheme 2. In situ method for the preparation of complexes **8**–**10**.

temperatures between 75 and 90 °C [13]. At higher temperatures, palladium black is formed at lower product yields.

With this preparation technique it was possible to synthesize the first dimethyl-purine-8-ylidene palladium complex **8** (Fig. 1), by reaction of 6-chloro-7,9-dimethylpurinium tetrafluoroborate (**4**) with palladacycle **1a** (Scheme 2). A 1,3,7,9-tetramethylxanthine-8-ylidene substituted complex **9** was received by reaction of azolium salt **5** with complex **1c**, analogous complex **10** was obtained. After completion of the reactions the solvent was removed in vacuo and afterwards the product was extracted in each case with toluene from the residue, to obtain light yellow or colourless products.

If less acidic azolium salts, such as 1,3-diisopropyl-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate (**12**) are applied, the basicity of sodium acetate is not high enough to form the corresponding carbene complex (**13**) (Scheme 3). In this case we used a stronger base such as KO*t*Bu at reduced temperature, and accepted a decreased yield because of partly decomposition of the phosphapalladacycle due to the stronger base.

To avoid hardly removable DMSO as solvent we tried to use another high polar solvent such as dimethylacetamide (DMAc). With this solvent no or very small yields were obtained in such reactions.

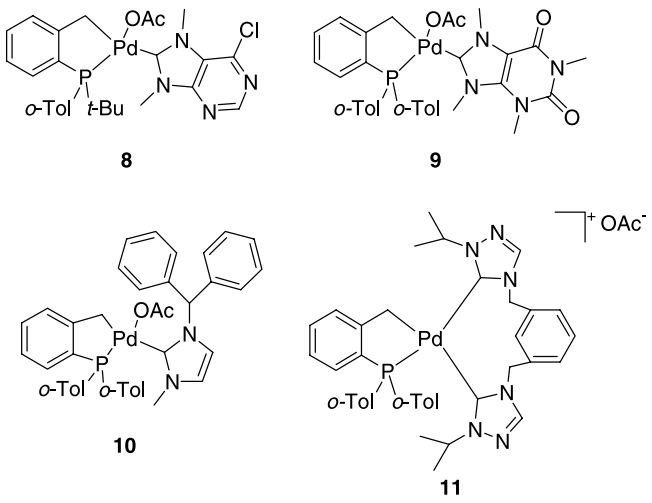
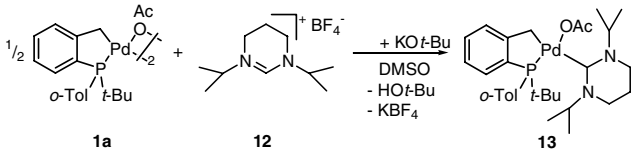


Fig. 1. Complexes **8**–**11**.

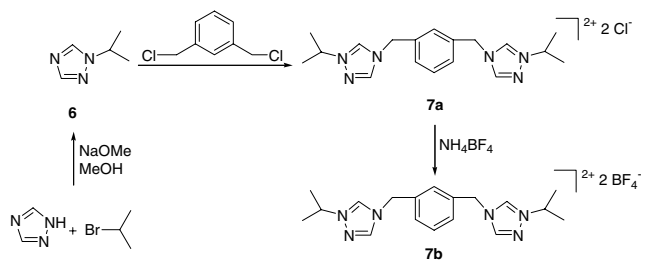


Scheme 3. Synthesis of complex **13**.

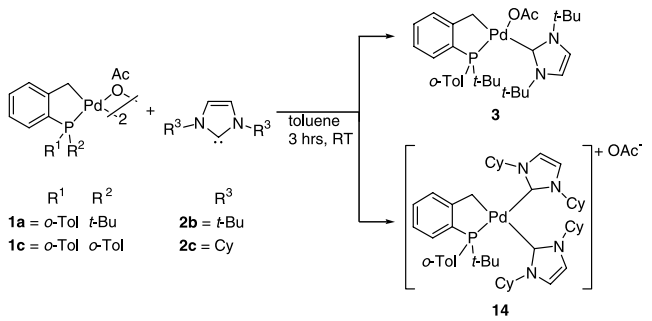
To form a bridged biscarbene palladacycle, we used α,α′-bis(1-isopropyl-triazolium)*m*-xylole ditetrafluoroborate (**7b**) as the azolium salt, prepared according to Scheme 4. The counter ion chloride in salt **7a** was exchanged to BF_4^- to form **7b**. This salt was used to synthesize **11** (Fig. 1), in a similar way to the preparation route shown in Scheme 2.

If the steric bulkiness at the nitrogens in 1,3-position of the azolium salt is increased, such as in adamantyl-, or *tert*-butyl-groups, no reaction occurs with this method. For highly sterical hindered carbene ligands, the recently published free carbene route [8] is the best way to synthesize the corresponding NHC-substituted phosphapalladacycles.

Via the free carbene route the mono substituted complex **3** and the biscarbene substituted complex **14** (Scheme 5) were synthesized. It depends on the sterical hindrance of the carbene ligand if one or two of them coordinate to the metal center, as recently published [8].



Scheme 4. Preparation of ligand **7b**.



Scheme 5. Complexes synthesized via the free carbene route.

Table 1
^{13}C NMR carbene signals of the new complexes

Complex	$^{13}C_{carbene}$ (ppm)
3	178.3, 176.9
8	185.5
9	189.3, 187.2
10	182.3
11	180.5
13[a]	200.6, 200.4
14	177.6, 177.4

[a] Small amounts of a biscarbene-substituted complex was obtained with a chemical shift in ^{13}C NMR for the carbene of 199.3 ppm.

For the complexes **3**, **8**–**11**, **14** the ^{13}C NMR signals of the carbene carbon are in the standard range of 176–190 ppm for imidazolin-2-ylidene and triazolin-2-ylidene complexes (Table 1). Complex **13** shows with 200 ppm for the carbene signal a slightly higher downfield shift because of the stronger σ-donor effect of this carbene. The complexes **3**, **9** and **13** show two carbene signals in the ^{13}C NMR spectra, because of the possible *cis*/*trans* configuration of the NHC-ligand to the phosphorous. A differentiation of the carbene signals in complex **8** and **10** could not be obtained in the ^{13}C NMR spectra, but the ^{31}P NMR spectra show two signals for the phosphorous, and gives a first hint that these complexes also form *cis*/*trans* species. In complex **11** the two carbenes should have different chemical shifts, but only one signal could be obtained. As expected the ^{31}P NMR spectra show only one signal, because no *cis*/*trans* isomerization is possible. Contrary to complex **11** for the biscarbene complex **14** two carbene signals were obtained in the ^{13}C NMR spectra. Only one signal in the ^{31}P NMR spectra was observed for the same reason as in complex **11**. In the ^{13}C NMR spectra most complexes show $^{1}J_{PC}$ (>16 Hz) and $^{2}J_{PC}$ (5–16 Hz) coupling constants for the carbons bonded directly to phosphorous and bonded not across the palladium center.

3. Experimental section

3.1. General comments

The precursors **1a** and **1c** [5i], 1,3-di-*tert*-butylimidazolin-2-ylidene (**2b**), 1,3-di-cyclohexylimidazolin-2-ylidene (**2c**), 1-diphenylbenzyl-3-methylimidazolium tetrafluoroborate (**2d**) [16], 6-chloro-7,9-dimethylpurinium tetrafluoroborate (**4**) [17], 1,3,7,9-tetramethylxanthinium tetrafluoroborate (**5**) [18], 1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazole (**6**) [19] and 3,4,5,6-tetrahydro-1,3-bis(isopropyl)pyrimidinium tetrafluoroborate (**12**) [20] were prepared according to the literature. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz 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, singulet; d, doublet; t, triplet; sept., septet; *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.

3.2. α,α′-Bis(1-isopropyl-triazolium)m-xylole dichloride (7a)

In a high pressure tube 946 mg (8.52 mmol) 1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazole **6** and 720 mg (6.52 mmol) α,α′-dichlor-*m*-xylole in 5 ml THF at 130 °C were heated for 80 h. The suspension was filtered and washed three times with 15 ml diethyl ether. Yield: 865 mg (2.18 mmol, 53%). ^{1}H NMR (400 MHz, d_6-DMSO): $\delta = 10.87$ (2H, s, CHNC*H*NCH$_2$), 9.54 (2H, s, NC*H*NCH$_2$), 7.94 (1H, s, Ar), 7.60–7.50 (3H, m, Ar), 5.57 (4H, s, CH_2), 4.82 (2H, hept., $^{3}J_{HH} = 6.4$ Hz, C*H*(CH$_3$)$_2$), 1.51 (12H, d, $^{3}J_{HH} = 6.4$ Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, d_6-DMSO): $\delta = 144.5$ (CH$_3$N*C*HNCH$_2$), 141.7 (N*C*HNCH$_2$), 134.5, 129.8, 129.7, 129.6 (Ar), 55.3 (*C*H(CH$_3$)$_2$), 50.1 (*C*H$_2$), 21.2 (*C*H$_3$).

3.3. α,α′-Bis(1-isopropyl-triazolium)m-xylole ditetrafluoroborate (7b)

Five hundred milligrams (4.77 mmol) of ammoniumtetrafluroroborate was dissolved in 5 ml water and added to a solution of 600 mg (1.51 mmol) α,α′-bis(1-isopropyl-triazolium)*m*-xylole dichloride **7a** in 5 ml water. The solution was stirred for 15 min at room temperature. The precipitate was filtered and washed twice with 4 ml water and once with 20 ml diethyl ether. Yield: 400 mg (0.97 mmol, 69%). ^{1}H NMR (400 MHz, d_6-DMSO): $\delta = 10.18$ (2H, s, CHNC*H*NCH$_2$), 9.22 (2H, s, NC*H*NCH$_2$), 7.58 (1H, s, Ar), 7.53 (3H, s, Ar), 5.49 (4H, s, CH_2), 4.79 (2H, hept., $^{3}J_{HH} = 6.4$ Hz, C*H*(CH$_3$)$_2$), 1.51 (12H, d, $^{3}J_{HH} = 6.6$ Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, d_6-DMSO): $\delta = 143.8$ (CHN*C*HNCH$_2$), 140.7 (N*C*HNCH$_2$), 133.5 (CH$_2$*C*, Ar), 129.3 (Ar), 128.9 (CH$_2$C*C*HCH), 128.5 (Ar), 54.7 (*C*H(CH$_3$)$_2$), 49.6 (*C*H$_2$), 20.5 (*C*H$_3$). MS (FAB) *m*/*z* (%): 413.0 (87, [M$^+$]), 325.0 (100, [M^{2+}]). Anal. Calc. for $C_{18}H_{26}N_6B_2F_8$ (500.05): C, 43.23; H, 5.24; N, 16.81. Found: C, 43.00; H, 5.10; N, 17.15%.

3.4. Trans-di(μ-chloro)-bis[o-(tert-butyl-o-tolylphosphino)benzyl]dipalladium(II) (**1b**) [21]

A solution of 106 mg (0.49 mmol) 1,3-di-*tert*-butylimidazolium chloride **2a** and 200 mg (0.22 mmol) *trans*-di(μ-acetato)-bis[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) **1a** were suspended in 10 ml DMSO and heated for 2 h at 120 °C. After 20 min a white solid precipitates. The precipitate was filtered and washed with 5 ml DMSO, 5 ml THF, 5 ml toluene, and 5 ml *n*-hexane. The solid is extremely insoluble in commonly used solvents. Yield: 182 mg (0.22 mmol, 99.6%). ^{1}H NMR (400 MHz, d_7-DMF): $\delta = 8.02$ (1H, s), 7.31 (2H, s), 7.25 (2H, s), 7.15 (1H, s), 7.01 (1H, s), 6.82 (1H, t, $^3J_{HH} = 7.8$ Hz), 3.36 (2H, br. s, CH_2), 2.40 (3H, s, C$H_{3,Tol}$), 1.53 (9H, d, $^3J_{PH} = 14.9$ Hz, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, d_7-DMF): $\delta = 135.4$, 134.7, 134.6, 134.1, 134.0, 132.5, 130.8, 130.0, 128.5, 125.3 (Ar), 67.9 (*C*(CH$_3$)$_3$), 41.2 (*C*H$_2$), 25.8 (C(*C*H$_3$)$_3$), 23.0 (*C*H$_3$). ^{31}P{^{1}H} NMR (161.8 MHz, (CD$_3$)$_2$SO): $\delta = 63.0$. ^{31}P{^{1}H} NMR (161.8 MHz, d_7-DMF): $\delta = 63.2$.

3.5. Acetato(1,3-di-tert-butylimidazolin-2-ylidene)[o-(tert-butyl-o-tolylphosphino)benzyl]palladium(II) (**3**)

To a solution of 300 mg (0.34 mmol) *trans*-di(μ-acetato)-bis[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) **1a** dissolved in 10 ml toluene, 123 mg (0.68 mmol) 1,3-di-*tert*-butylimidazolin-2-ylidene **2b** in 10 ml toluene was added at −90 °C. The combined solution was stirred at room temperature for 3 h. Afterwards the solvent was removed in vacuo and the residue was extracted three times with 5 ml *n*-hexane. The solvent was removed in vacuo, to obtain a yellow product. The product can be recrystallized from a *n*-hexane/*n*-pentane solution. Yield: 280 mg (0.45 mmol, 66%). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 7.67$ (2H, t, $^3J_{HH} = 7.6$ Hz), 7.06 (2H, t, $^3J_{HH} = 7.2$ Hz), 6.97 (2H, d, $^3J_{HH} = 6.4$ Hz), 6.92 (2H, m), 6.77 (2H, d, $^3J_{HH} = 17.2$ Hz, NC*H*C*H*N), 3.14 (2H, s, CH_2), 2.07(3H, s, CH_3), 1.84 (9H, s, CH_3), 1.76 (9H, s, CH_3), 1.50(3H, s, CO$_2$CH_3), 1.47 (9H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$): $\delta = 178.3$ (N*C*N), 176.9 (N*C*N), 174.2 (*C*O$_2$CH$_3$), 161.2 (d, $J = 42.0$ Hz), 143.4 (d, $J = 14.6$ Hz), 136.3, 135.9, 134.5, 132.4, 131.9 (d, $J = 6.8$ Hz), 130.8 (d, $J = 23.8$ Hz), 130.3, 129.7, 125.0 (d, $J = 5.3$ Hz), 124.2 (d, $J = 5.4$ Hz), 118.1 (d, $J = 20.0$ Hz), 58.9 (*C*(CH$_3$)$_3$), 58.3 (*C*(CH$_3$)$_3$), 34.7 (d, $J = 17.6$ Hz, *C*H$_2$), 31.7 (d, $J = 20.7$ Hz, C(*C*H$_3$)$_3$), 28.2 (d, $J = 5.4$ Hz, C(*C*H$_3$)$_3$), 25.9 (*C*H$_3$), 23.9 (CO$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (161.8 MHz, C$_6$D$_6$): $\delta = 46.9$ (s), 45.0 (s), (Intensity = 1: 14.8). MS (FAB) *m*/*z* (%): 374.5 (8, [M$^+$]), 180 (100, [carbene]).

3.6. Acetato(6-chloro-7,9-dimethylpurine-8-ylidene)-[o-(tert-butyl-o-tolylphosphino)benzyl]palladium(II) (**8**)

One hundred and eighty six milligrams (0.69 mmol) of 6-chloro-7,9-dimethylpurinium tetrafluoroborate **4**, 59 mg (0.72 mmol) sodium acetate and 260 mg (0.30 mmol) *trans*-di(μ-acetato)-bis[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) **1a** are suspended in 5 ml DMSO and heated for 2 h at 70 °C. All volatile compounds were removed in vacuo and the residue was extracted three times with 4 ml toluene. After removal of the solvent a yellow precipitate was obtained. Yield: 215 mg (0.33 mmol, 55%). ^{1}H NMR (270 MHz, C$_6$D$_6$): $\delta = 8.32$ (1H, s, NC*H*N), 7.35–6.60 (12H, m, Ar), 3.93 (3H, s, NCH_3), 3.88 (3H, s, NCH_3), 2.90 (3H, s, CO$_2$CH_3), 2.76 (2H, s, CH_2), 2.08 (3H, s, CCH_3), 1.39 (9H, m, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$): $\delta = 185.5$ (br. N*C*N), 172.8 (*C*O$_2$CH$_3$), 151.3, 149.8 (N*C*HN, *C*Cl), 132.6, 132.5, 131.8, 131.4, 130.4, 129.9, 128.7, 128.5, 128.3, 127.5, 127.3, 125.4, 125.1, 125.0, 67.5 (*C*H$_2$), 34.8 (*C*(CH$_3$)$_3$), 30.6 (N*C*H$_3$), 28.7 (d, $J_{PC} = 6.1$ Hz, *C*H$_3$, *t*-Bu), 28.4 (br., C(*C*H$_3$)$_3$), 27.8 (NCH$_3$), 22.9 (*C*H$_3$ of P-*o*-tol), 20.7 (CO$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (161.8 MHz, C$_6$H$_5$CH$_3$): $\delta = 54.0$ (s), 53.8 (s) (*cis*/*trans* = 75/25). MS (FAB) *m*/*z*: 558 [M$^+$−OAc], 375 [M$^+$−(OAc + carbene)].

3.7. Acetato(1,3,7,9-tetramethylxanthine-8-ylidene)-[o-(di-o-tolylphosphino)benzyl]palladium(II) (**9**)

Two hundred and eight milligrams (0.70 mmol) of 1,3,7,9-tetramethylxanthinium tetrafluoroborate **5**, 63 mg (0.77 mmol) sodium acetate and 300 mg (0.32 mmol) *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) **1c** were suspended in 5 ml DMSO and heated for 2 h at 80 °C. All volatile compounds were removed in vacuo and the residue was extracted three times with 4 ml toluene. After removal of the solvent a yellow precipitate was obtained. Yield: 268 mg (0.40 mmol, 62%). ^{1}H NMR (270 MHz, C$_6$D$_6$): $\delta = 7.44$–6.60 (12H, m, Ar), 4.29 (3H, s, NCH_3), 4.07 (3H, s, NCH_3), 3.76 (3H, s, NCH_3), 3.16 (3H, s, NCH_3), 3.14 (3H, s, CO$_2$CH_3), 2.11 (2H, s, CH_2), 1.76 (3H, s, CCH_3). ^{13}C{^{1}H} NMR (67.8 MHz, C$_6$D$_6$): $\delta = 189.3$ (br. N*C*N), 187.2 (br. N*C*N), 176.3 (*C*O$_2$CH$_3$), 159.5 (*C*O), 159.0 (*C*O), 143.0 (d, $^2J_{PC} = 15.6$ Hz, *ipso-C* of P-*o*-tol), 140.7 (N*CC*N), 139.2 (d, $^2J_{PC} = 15.2$ Hz, *ipso-C* of P-*o*-tol), 134.5, 133.8, 132.8 (br.), 131.8 (Ar), 131.6 (d, $^2J_{PC} = 7.8$ Hz, *ipso-C* of P-*o*-tol), 130.9, 130.3 (br.), 129.1 (Ar), 125.7 (d, $^2J_{PC} = 6.2$ Hz, *p-C* of P-*o*-tol), 125.4 (Ar), 109.1 (N*CC*N), 67.6 (*C*H$_2$), 38.6 (N*C*H$_3$), 36.5 (N*C*H$_3$), 30.5 (N*C*H$_3$), 27.7 (N*C*H$_3$), 22.6, 22.4 (*C*H$_3$ of P-*o*-tol), 17.6 (CO$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (109.1 MHz, C$_6$H$_5$CH$_3$): $\delta = 29.1$ (s). MS (FAB) *m*/*z*: 617 [M$^+$−OAc], 409 [M$^+$−(OAc + carbene)], 209 [carbene]. Anal. Calc. for C$_{32}$H$_{35}$N$_4$O$_4$PPd (677.03): C, 56.77; H, 5.21; N, 8.28. Found: C, 56.86; H, 5.31; N, 8.33%.

3.8. Acetato(1-diphenylmethyl-3-methylimidazolin-2-ylidene)[o-(di-o-tolylphosphino)benzyl]palladium(II) (**10**)

Two hundred milligrams (0.21 mmol) of *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)-benzyl]dipalladium(II)

1c, 60 mg (0.73 mmol) sodium acetate and 150 mg (0.45 mmol) 1-diphenylbenzyl-3-methylimidazolium tetrafluoroborate **2d** were suspended in 6 ml DMSO and heated for 2 h at 90 °C. All volatile compounds were removed in vacuo and the residue was extracted three times with 4 ml toluene. After removal of the solvent a yellow compound was obtained. Yield: 116 mg (0.16 mmol, 38%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.52$ (2H, br.), 7.43 (2H, br.), 7.21–6.84 (18H, m), 6.71 (1H, t, $^3J_{HH} = 7.6$ Hz, C*H*), 6.25 (2H, br. NC*H*C*H*N), 3.78 (2H, s, PdCH_2), 3.47 (3H, s, NCH_3), 3.04 (3H, s, CH_3), 2.89 (3H, s, CH_3), 2.02 (3H, s, CO_2CH_3). ^{13}C{^{1}H} NMR (67.8 MHz, C_6D_6): $\delta = 182.3$ (N*C*N), 175.5 (CO_2CH_3), 160.2 (d, $J = 36.8$ Hz), 143.4, 140.7, 140.1, 137.7, 137.2, 132.9, 132.6, 131.7, 130.0, 129.3, 128.8, 125.6, 121.4 (d, N*C*H*C*HN, $J = 20.2$ Hz), 67.5 (N*C*H), 40.8 (N*C*H_3), 37.9 (*C*H_2), 22.7, 21.4 (*C*H_3), 18.0 (CO_2CH_3). ^{31}P{^{1}H} NMR (161 MHz, $C_6D_5CD_3$): $\delta = 28.5$ (s), 27.5 (s), (Intensity = 1: 1). ^{31}P{^{1}H} NMR (161.8 MHz, $(CD_3)_2SO$): $\delta = 28.0$ (s). ^{31}P{^{1}H} NMR (161.8 MHz, d_8-THF): $\delta = 28.4$ (s), 27.9 (s), (Intensity = 1: 1). MS (FAB) *m*/*z* (%): 656.5 (60, [M$^+$]), 408.6 (14, [Pd + $PC_7H_6(C_7H_7)_2$]), 352.6 (21, [Pd + carbene]), 246.8 (100, [carbene]). Anal. Calc. for $C_{40}H_{39}N_2O_2PPd$ (717.14): C, 66.99; H, 5.48; N, 3.91. Found: C, 67.21; H, 5.38; N, 3.97%.

3.9. α,α′-Bis(1-isopropyl-4,5-dihydro-1H-1,2,4-triazolin-5-ylidene)-m-xylole[o-(di-o-tolylphosphino)benzyl]-palladium(II)acetate (**11**)

Two hundred and thirty three milligrams (0.59 mmol) of α,α′-bis(1-isopropyl-1,2,4-triazolium)*m*-xylole ditetrafluoroborate **7b**, 53 mg (0.65 mmol) sodium acetate and 250 mg (0.27 mmol) *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) **1c** were suspended in 5 ml DMSO and heated for 2 h at 80 °C. All volatile compounds were removed in vacuo and the residue was extracted three times with 4 ml toluene. After removal of the solvent a white precipitate was obtained. Yield: 291 mg (0.37 mmol, 68%). ^{1}H NMR (270 MHz, C_6D_6): $\delta = 9.01$ (2H, s, NC*H*N), 7.28–6.73 (16H, m, Ar), 5.36 (4H, br. NCH_2), 4.88 (2H, br. $(CH_3)_2CH$), 3.04 (3H, s, CO_2CH_3), 2.40 (2H, s, PdCH_2), 2.12 (6H, s, CCH_3), 1.35 (12H, br. $(CH_3)_2CH$). ^{13}C{^{1}H} NMR (67.8 MHz, C_6D_6): $\delta = 180.5$ (br. N*C*N), 175.8 (CO_2CH_3), 144.5 (N*C*HN), 143.0 (d, $^2J_{PC} = 15.6$ Hz, *ipso-C* of P-*o*-tol), 140.7 (N*C*CN), 139.2 (d, $^2J_{PC} = 15.2$ Hz, *ipso-C* of P-*o*-tol), 134.5, 133.8, 132.8 (br.), 131.8 (Ar), 131.6 (d, $^2J_{PC} = 7.8$ Hz, *ipso-C* of P-*o*-tol), 130.9, 130.3 (br.), 129.1 (Ar), 125.7 (d, $^2J_{PC} = 6.2$ Hz, *p-C* of P-*o*-tol), 125.4 (Ar), 109.1 (NC*C*N), 67.6 (Pd*C*H_2), 54.9 (N*C*H_2), 52.0 ($(CH_3)_2CH$), 22.9, 22.5, 22.2, 20.9 (*C*H_3 of P-*o*-tol, CO_2CH_3 and ($(CH_3)_2CH$)). ^{31}P{^{1}H} NMR (109.1 MHz, $C_6H_5CH_3$): $\delta = 28.8$ (s). MS (FAB) *m*/*z*: 734 [M$^+$], 691 [M$^+$−*t*-Bu]. Anal. Calc. for $C_{41}H_{47}N_6O_2PPd$ (793.24): C, 62.08; H, 5.97; N, 10.59. Found: C, 61.96; H, 6.02; N, 10.47%.

3.10. Acetato[3,4,5,6-tetrahydro-1,3-bis(1-methylethyl)-pyrimidine-2-ylidene][o-(tert-butyl-o-tolylphosphino)benzyl]palladium(II) (**13**)

Two hundred and fifty milligrams (0.29 mmol) of *trans*-di(μ-acetato)-bis[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]-dipalladium(II) **1a**, 65 mg (0.58 mmol) potassium-*tert*-butylate and 160 mg (0.63 mmol) 3,4,5,6-tetrahydro-1,3-bis(1-methylethyl)pyrimidinium tetrafluoroborate **12** were combined in 5 ml DMSO at room temperature. The solution was heated up slowly to 80 °C and reacted for further 2 h, while the color changed from white to brown. The solvent was removed in vacuo and the residue was extracted three times with 4 ml toluene. After the solvent was removed in vacuo a yellow solid was obtained, containing three isomers. Yield: 73 mg (0.12 mmol, 21%). ^{1}H NMR (400 MHz, $(CD_3)_2SO$): $\delta = 8.06$ (1H, s), 7.32 (1H, s), 7.24–7.18 (4H, m), 7.11 (1H, d, $^3J_{HH} = 4.9$ Hz), 6.94 (1H, m), 3.71 (2H, sept., $^3J_{HH} = 7.4$ Hz, C*H*$(CH_3)_2$), 3.34 (2H, s, CH_2Pd), 3.06 (4H, m, NCH_2), 2.26 (2H, m, CH_2), 2.03 (3H, s, CH_3), 1.80 (3H, s, CH_3), 1.39 (12H, d, $^3J_{HH} = 13.5$ Hz, CH(CH_3)$_2$), 1.11 (9H, d, $^3J_{PH} = 6.2$ Hz, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): $\delta = 200.6$ (N*C*^{1}N), 200.4 (N*C*^{2}N), 199.3 (N*C*^{3}N), 175.5 (br. s, CO_2CH_3), 172.9 (s, CO_2CH_3), 162.7 (C^1_{Aryl}), 162.2 (C^2_{Aryl}), 162.1 (C^3_{Aryl}), 159.6 (d, $J_{PC} = 37.4$ Hz, C^3), 158.4 (d, $J_{PC} = 28.2$ Hz, C^2), 159.6 (d, $J_{PC} = 27.4$ Hz, C^1), 142.5 (d, $J = 14.4$ Hz), 142.2 (d, $J = 11.4$ Hz), 137.3, 134.1, 132.3, 131.9, 131.7 (d, $J = 5.3$ Hz), 131.6 (d, $J = 7.6$ Hz), 131.1 (d, $J = 8.4$ Hz), 130.4, 130.3, 130.0 (d, $J_{PC} = 8.4$ Hz), 129.3, 128.9, 128.2, 128.0 (d, $J = 10.7$ Hz), 127.7 (d, $J_{PC} = 6.1$ Hz), 125.3, 124.9, 124.4 (d, $J_{PC} = 5.3$ Hz, C_{Aryl}), 57.3, 57.1 (*C*H$(CH_3)_2$), 48.9 (*C*$(CH_3)_3$), 40.4 (N*C*H_2), 37.6 (C^3H_2Pd), 37.3 (C^1H_2Pd), 37.2 (C^2H_2Pd), 27.9 (br. CO_2CH_3), 21.7 ($CH_2CH_2CH_2$), 19.9, 19.7 ($CH_{3,Tol}$). ^{31}P{^{1}H} NMR (109.1 MHz, $(CD_3)_2SO$): $\delta = 52.4$ (s), 50.5, 50.4 (*cis*/*trans*). MS (FAB) *m*/*z* (%): 542.6 (46, [M$^+$−OAc]), 374.6 (60), 270.8 (12, [Pd + carbene]), 166.9 (100, [carbene]).

3.11. Bis(1,3-di-cyclohexylimidazolin-2-ylidene)[o-(tert-butyl-o-tolylphosphino)benzyl]palladium(II)acetate (**14**)

To a solution of 300 mg (0.34 mmol) *trans*-di(μ-acetato)-bis[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) (**1a**) dissolved in 15 ml toluene a solution of 200 mg (0.86 mmol) 1,3-di-cyclohexylimidazolin-2-ylidene **2c** in 10 ml *n*-hexane was added at −90 °C. After the solution was concentrated in vacuo to 15 ml and stirred for 12 h at room temperature, a white solid precipitated. The solution was filtered off and the precipitate was washed twice with 5 ml toluene. Yield: 545 mg (0.61 mmol, 88%). ^{1}H NMR (270 MHz, $(CD_3)_2SO$): $\delta = 7.99$ (1H, m), 7.85 (1H, s), 7.65 (1H, m), 7.59 (1H; s), 7.41 (2H, t, $^3J_{HH} = 3.6$ Hz), 7.31 (2H, d, $^3J_{HH} = 2.1$ Hz), 7.09 (2H, m), 6.81 (2H, t, $^3J_{HH} = 7.4$ Hz), 4.70 (4H, m, NCH_{Cy}), 3.30 (2H, m, CH_2), 2.02 (3H, s, CO_2CH_3), 2.28–1.15 (43H, m), 1.35

(9H, $^{3}J_{PH} = 14.7$ Hz, C(CH_3)$_3$), 1.09–0.88 (m, *n*-hexane). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): $\delta = 177.6$ (N*C*N), 177.4 (N*C*N), 174.4 (*C*O_2CH_3), 158.3 (d, $J_{PC} = 32.7$ Hz, C_{Aryl}), 142.7 (d, $J_{PC} = 14.0$ Hz, C_{Aryl}), 133.2, 132.9, 132.0, 130.9, 130.4, 129.1, 128.2, 127.9, 126.2 (d, $J_{PC} = 7.8$ Hz, C_{Aryl}), 125.3 (d, $J_{PC} = 5.7$ Hz, C_{Aryl}), 120.8, 120.4, 120.0, 119.3 (N*C*H*C*HN), 60.1, 58.9, 58.4, 58.0 (*C*H_{Cy}), 55.2 (*C*(CH_3)$_3$), 35.5, 35.0, 34.5, 34.4, 34.1, 34.1, 33.7, 33.0 (*C*H_2), 31.7, 31.5, 30.9, 30.7 (*C*H_2), 25.9 (CO_2*C*H_3), 24.1 (C(*C*H_3)), 22.0 (d, $J_{PC} = 11.4$ Hz, *C*$H_{3,Tol}$). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, $(CD_3)_2SO$): $\delta = 49.3$ (s). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, THF): $\delta = 48.3$ (s). MS (FAB) *m*/*z* (%): 839.0 (14, [M^+]), 606.9 (52, [M^+−[OAc + carbene]]), 570.0 (7, [Pd + 2*carbene]), 334.9 (8, [Pd + carbene]), 233.1 (100, [carbene]).

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