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Preparation of NHC-substituted phosphitepalladacycles ☆

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Dedicated to Dr. Karl Öfele on the occasion of his 75th birthday.

Abstract

The preparation of unsaturated NHC-substituted phosphitepalladacycles via phosphitepalladacycle acetato and chloro precursors and azolium salts with non-coordinating anions in DMSO is reported. With this one-pot synthesis NHC-substituted phosphitepalladacycles are obtained avoiding multi-step reactions. The molecular structures of an acetate-bridged phosphitepalladacycle dimer, an unsaturated NHC-substituted palladacyclic complex and one acetylacetonato phosphapalladacycle complex have been determined by single-crystal X-ray analysis.

Keywords: Carbenes; Palladacycle; Palladium; Phosphite; NHCs; In situ method

1. Introduction

Palladacycles have been known for over 30 years [1–4] and have been used recently as catalysts [5,6]. Many groups also use *ortho*-metallated complexes as Pd(II)-precatalysts in which an aromatic carbon atom adjacent to a functional group is bound to the metal center. Milstein produced efficient catalysis with aryl-metallated "pincer" complexes [7], and also acetylacetonate-substituted phosphapalladacycles were used as catalyst systems for the Mizoroki–Heck reaction [8,9].

Another class of potential catalysts was introduced in 1993; those featuring *N*-heterocyclic carbene (NHC) ligands [10]. *N*-Heterocyclic carbenes have the advantageous property of forming strong σ-bonds to metal centers, with little tendency towards dissociation [11,12]. This is particularly beneficial in their use as ligands in organometallic catalysis [13]. Most of the palladium complexes can be used as catalysts for various carbon–carbon bond formations and related reactions [14]. Hartwig and co-workers demonstrated that catalysts containing saturated NHCs could be used in the room-temperature "Buchwald–Hartwig" amination of non-activated aryl chlorides [15], while Caddick and Kofie demonstrated the efficiency of palladium catalysts based on these saturated NHCs (formed in situ by deprotonation of the imidazolium salt) in intramolecular Mizoroki–Heck couplings of aryl chloride substrates [16].

The combination of a palladacycle framework with an NHC was reported first in 1997 by our group [17–19], and became an important class of novel NHC-substituted palladium complexes for catalysis. These catalysts, with unsaturated NHC ligands, have proved to be effective in the coupling of aryl chloride substrates with arylalkenes [19,20]. NHC substituted phosphapalladacycles combine the advantageous stability of phosphapalladacycles with the steric bulk and high σ-donor strength of *N*-heterocyclic carbenes [19].

☆ *N*-Heterocyclic carbenes, Part 50. For part 49, see Ref. [31].

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Bedford and co-workers published in 1998 an *ortho*-metallated triaryl phosphite chloro palladium complex, which was found to be a highly active catalyst in biaryl coupling reactions [21]. The analogous acetate complex was synthesized in 2004 [22]. A monograph about *N*-heterocyclic carbene adducts of both chloro- and acetato-*ortho*-palladated phosphite complexes was published at the beginning of 2005 [20]; almost simultaneously Bedford et al. reported a small variety of saturated *N*-heterocyclic carbene adducts of *ortho*-palladated triarylphosphite complexes and their catalytic activities in the Suzuki–Miyaura coupling [23].

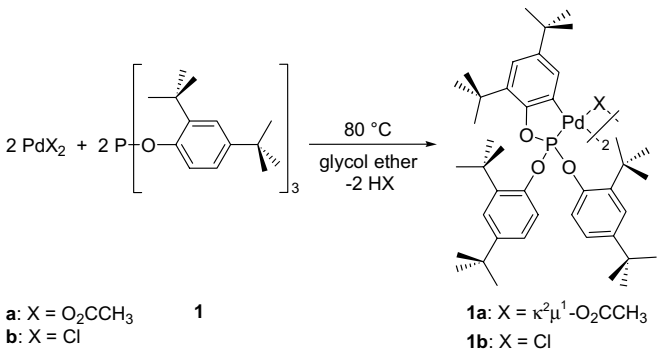
Because of the high stability of these acetato and chloro NHC-phosphitepalladacycles, we extended our previous work [20] by varying the carbenes and the palladacycles to investigate their chemical properties.

2. Results and discussion

2.1. ortho-Metallated dimeric complex

The acetate-bridged phosphitepalladacycle dimer **1a** is prepared in a similar way to these of Bedford and co-workers for the analogous chloride complex **1b** [21]. When $Pd(OAc)_2$ (**a**) or $PdCl_2$ (**b**) is treated with the sterically demanding tris-(2,4-di-*tert*-butylphenyl)phosphite (**1**) in monomethylglycol ether at 80 °C, the colorless complexes **1a** and **1b** are formed in high yields (93–96%) (Scheme 1) [20,21].

Complex **1a** could be identified as a mixture of *cis*- and *trans*-isomers in solution, with two signals in the ^{31}P NMR spectrum (126.7 and 124.8 ppm; intensity = 1:1), in agreement with the published values of complex **1b** (119.2 and 118.7 ppm) [20,21]. The remarkable air, moisture, and thermal stability of complex **1a** is comparable to the analogous chloride complex **1b**. Complex **1a** has been characterized by spectroscopic methods and elemental analysis. Suitable single crystals of complex **1a** for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane solution. The solid state structure of the complex **1a** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2.



Scheme 1. Preparation of Bedford-type phosphitepalladacycles **1a** and **1b**.

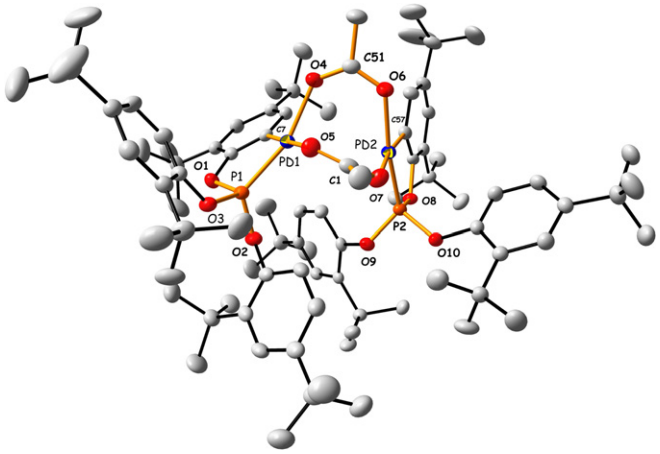


Fig. 1. ORTEP style plot [30h] of compound **1a** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

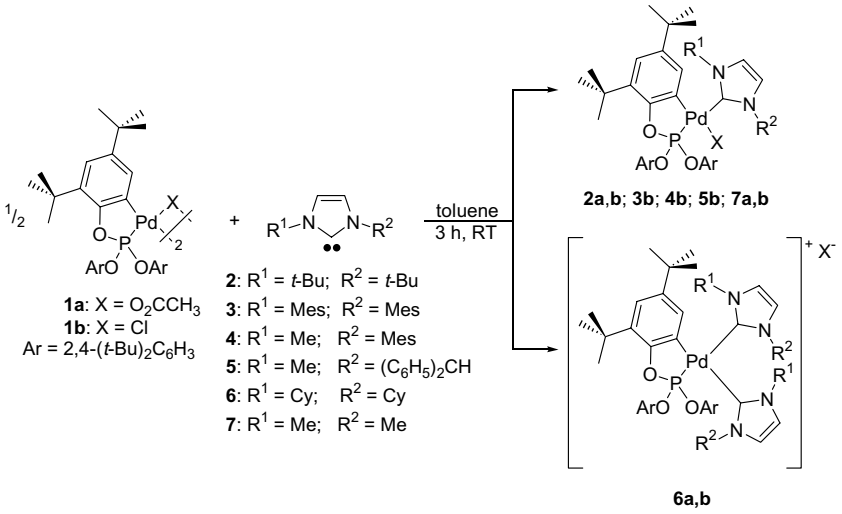
Most of the crystal structures of *ortho*-palladated triaryl-phosphite dimers indicate that in the solid state, the *trans* isomer crystallizes preferentially, where the two phosphorus atoms are coordinated *trans* to each other at the palladium center, although in our case the solid state structure of **1a** depicts the *cis* isomer, in contrast to previously reported *ortho*-palladated triarylphosphane dimer [19,24]. The two Pd atoms in **1a** adopt square planar geometry and are connected by two bridging acetate ligands. The angles around the palladium center deviate from 90° due to the bite angle of the cyclometalated ligand [P1–Pd1–C7 79.21(6)°; P2–Pd2–C57 80.86(6)°]. No significant differences of the bond lengths between the coordinated atoms and the palladium center were observed compared to other published palladaphosphites [21,23].

2.2. NHC-substituted phosphitepalladacycles

Nowadays it is possible to synthesize NHC-palladacycle complexes in two different ways. Firstly we used the "free carbene" route [19] for highly sterically hindered carbene ligands (Scheme 2), or without isolation of the free carbene the "in situ" method, when palladium acetate is used as the starting material [24] (Scheme 3).

Reaction of the bulky *ortho*-palladated triarylphosphite complexes **1a** and **1b** with the free carbene ligands (**2**–**7**), in THF at room temperature, give the mono- and disubstituted complexes **2a**–**7b.**

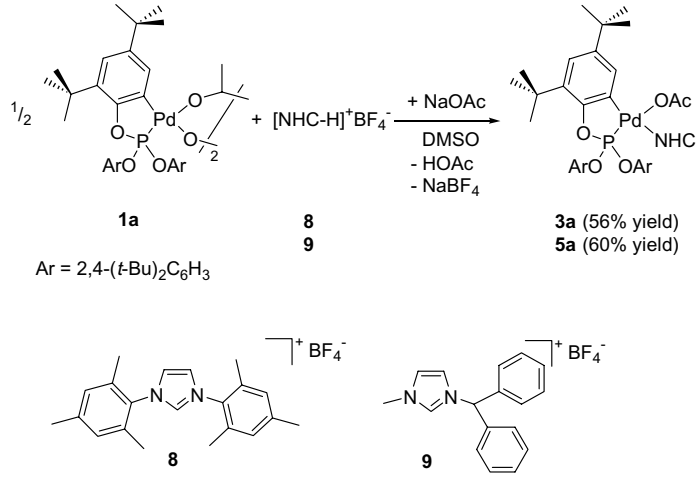
If the palladacycles **1a** and **1b** are treated with 2.1 equiv. of a less sterically hindered carbene such as 1,3-dicyclohexylimidazolin-2-ylidene (**6**), the acetate and chloride products with two *N*-heterocyclic carbene ligands are formed (**6a**,**b**) (Scheme 2). The coordination of two carbenes at one metal center is a good illustration that NHC ligands are much stronger ligands than the acetate ligand. These complexes were purified by extraction of the obtained residue with *n*-hexane and toluene to remove traces of unreacted free carbene (**6**). Using bulky groups



Complex	R_1	R_2	X	Yield [%]
2a / **2b**	*t*-Bu	*t*-Bu	OAc / Cl	50 / 59
- / **3b**	Mes	Mes	- / Cl	- / 72
- / **4b**	Me	Mes	- / Cl	- / 86
- / **5b**	Me	$(C_6H_5)_2CH$	- / Cl	- / 63
6a / **6b**	Cy	Cy	OAc / Cl	49 / 60
7a / **7b**	Me	Me	OAc / Cl	79 / 75

Scheme 2. Synthesis of mono- and disubstituted NHC-phosphitepalladacycles via the *"free carbene"* route.

on the carbene ligand, such as for example the *tert*-butyl group, only monocarbene substituted complexes (**2a**,**b**, **3b**–**5b** and **7a**,**b**) were obtained, in accordance with previously published results [19,24]. The monocarbene-substituted complexes are obtained in most cases as a mixture of *cis* and *trans* isomers. The reaction of **1a**,**b** with the free carbene **7**, did not proceed as we expected when stoichiometry was held at 2:1 and 1:1, but rather gave a mixture of mono- and dicarbene substituted compounds as determined by FAB mass spectrometry and ^{31}P NMR spectra. When the reaction was repeated and the free carbene **7** was added very slow to a highly diluted metal precursor toluene solution, at very low temperatures (−90 °C), the ^{31}P NMR spectra showed two signals in the region for monocarbene *cis*/*trans* products **7a**,**b**. Under these conditions the formation of the mono-substituted NHC complexes **7a**,**b** over the expected di-substituted complexes is favoured. The formation of a mono-substituted NHC complex shows that the coordination of two NHCs to the palladium center is not always necessary, especially when the steric demand of the ligand would disfavour such a conformation.



Scheme 3. In situ method for the preparation of the complexes **3a** and **5a**.

Table 1
^{13}C NMR carbene carbon nuclei signals of complexes **2**–**7**

Complex	$^{13}C_{carbene}$ (ppm)
2a/2b	175.7/177.5
3a/3b	182.1/no carbene signal was observed
–/4b	–/186.2
5a/5b	185.2/186.1
6a/6b	178.4/175.1 and 173.0
7a/7b	178.3/178.2

The acetate-bridged phosphapalladacycle **1a** in dimethyl sulfoxide reacts at elevated temperatures with azolium salts (**8**, **9**) bearing weakly coordinating anions like BF_4^- or PF_6^- via deprotonation to form the corresponding carbene complexes (**3a** and **5a**) [17,25,26]. An additional base (NaOAc) is necessary for the complete deprotonation of the azolium salts. For this reaction a temperature dependency was observed; best results were obtained at reaction temperatures between 75 and 90 °C [24]. The yields of the products **3a** and **5a** are shown in Scheme 3.

For the complexes **2a**–**7b** the ^{13}C NMR signals of the carbene carbon are in the expected range of 176–190 ppm for imidazolin-2-ylidene complexes (Table 1). The carbene signals in complexes **5a**,**b** could not be differentiated in the ^{13}C NMR spectra, but the ^{31}P NMR spectra show clearly two signals for the phosphorus, suggesting a *cis*/*trans* product mixture. In the case of dicarbene complex **6a** the two coordinated carbene carbon atoms should be inequivalent, but only one signal was observed for both carbenes. In contrast to complex **6a**, two carbene signals were obtained in the ^{13}C NMR spectra of **6b** (175.1 and 173.0 ppm). As expected the ^{31}P NMR spectra shows only one signal, because no *cis*/*trans* isomerization is possible for these complexes. In the ^{13}C NMR spectra most of the prepared complexes show $^1J_{PC} > 16$ Hz and $^2J_{PC}$ 5–16 Hz for the carbene carbon nuclei.

Colorless crystals of complex **7b** suitable for X-ray diffraction were obtained by slow evaporation of a saturated CH_2Cl_2/*n*-pentane solution (Fig. 2). The palladium center reveals a slightly distorted square-planar structure [Cl1*(2)*–Pd1*(2)*–C1*(51)* 88.91(7)°, *87.31(7)*°; Cl1*(2)*–Pd1*(2)*–C7*(57)* 94.26(7)°, *93.89(7)*°; P1*(2)*–Pd1*(2)*–C1 *(51)* 98.64(7)°, *99.50(7)*°; P1*(2)*–Pd1*(2)*–C7*(57)* 79.11 (7)°, *79.42(7)*°]. In contrast to the known saturated carbene-substituted phosphitepalladacycles [27], the NHC-ligand in complex **7b** is coordinated *cis* to the phosphorus donor [23]. The Pd1*(2)*–C7*(57)* bond lengths of the *ortho*-metallated phosphite ligand is slightly longer (2.052(2), *2.063(2)* Å) compared to complex **1a** (1.995(2), *2.005(2)* Å) and **1b** (1.998(6) Å). In contrast the Pd–P bond

Table 2
Selected bond lengths (Å) and bond angles (°) for **1a** · (CH_2Cl_2), **7b** · 3(CH_2Cl_2), and **11**

Compound	**1a** · (CH_2Cl_2)	**7b** · 3(CH_2Cl_2)	**11**
Bond lengths (Å)			
Pd1(2)–Cl1(2)		2.3804(7)/*2.3584(7)*	
Pd1(2)–P1(2)	2.1630(6)/*2.1535(6)*	2.1590(7)/*2.1554(7)*	
Pd1(2)–O4(6)	2.103(2)/*2.100(2)*		
Pd1(2)–O5(7)	2.127(2)/*2.106(2)*		
Pd1(2)–C1(51)		2.069(2)/2.077(3)	
Pd1(2)–C7(57)	1.995(2)/*2.005(2)*	2.052(2)/*2.063(2)*	
Pd–P			2.217(2)
Pd–O1			2.111(4)
Pd–O2			2.092(4)
Pd–C6			2.000(6)
Bond angels (°)			
Cl1(2)–Pd1(2)–P1(2)		169.88(3)/*172.89(3)*	
Cl1(2)–Pd1(2)–C1(51)		88.91(7)/*87.31(7)*	
Cl1(2)–Pd1(2)–C7(57)		94.26(7)/*93.89(7)*	
P1(2)–Pd1(2)–C1(51)		98.64(7)/*99.50(7)*	
P1(2)–Pd1(2)–C7(57)	79.21(6)/*80.86(6)*	79.11(7)/*79.42(7)*	
C1(51)–Pd1(2)–C7(57)		172.17(9)/*176.74(9)*	
P1(2)–Pd1(2)–O4(6)	161.45(4)/*172.00(5)*		
P1(2)–Pd1(2)–O5(7)	100.36(4)/*96.53(5)*		
O4(6)–Pd1(2)–O5(7)	88.12(6)/*88.47(6)*		
O4(6)–Pd1(2)–C7(57)	91.47(7)/*93.33(7)*		
O5(7)–Pd1(2)–C7(57)	177.04(7)/*171.81(7)*		
P–Pd–O1			100.1(1)
P–Pd–O2			169.1(1)
P–Pd–C6			84.1(2)
O1–Pd–O2			89.7(2)
O1–Pd–C6			173.4(2)
O2–Pd–C6			86.6(2)

The corresponding values of the second part of the molecule (**1a**) or a second crystallographically independent molecule in the asymmetric unit (**7b**) are shown in italic.

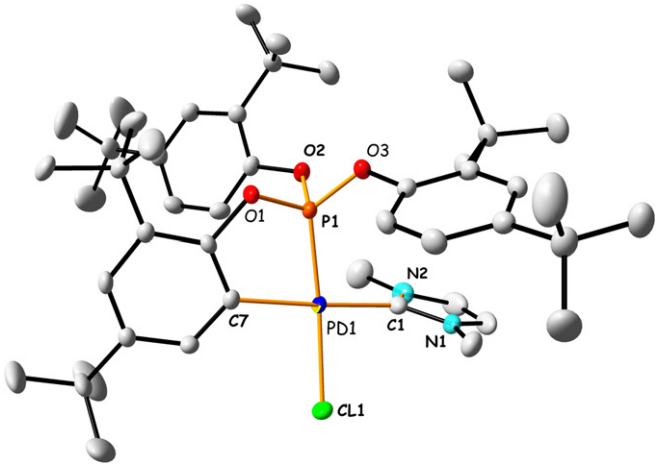
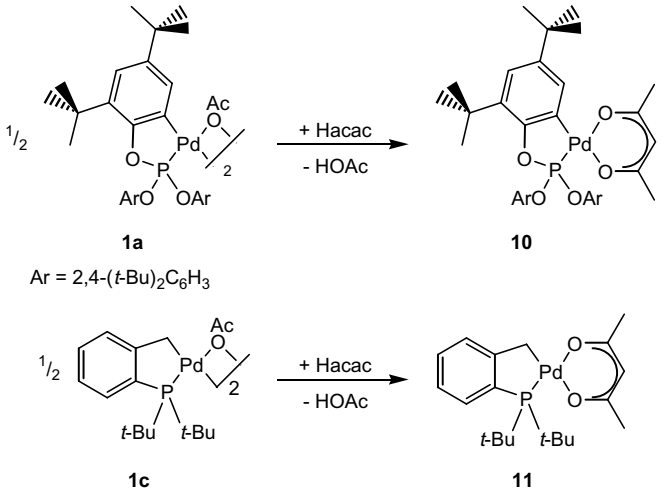


Fig. 2. ORTEP style plot [30h] of compound **7b** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



Scheme 4. Synthesis of acetylacetonate phospha- and phosphite-palladacycles.

length is shorter in complex **7b** (2.1590(7), *2.1554(7)* Å) compared to **1a** (2.1630(6), *2.1535(6)* Å) and **1b** (2.1668 (17) Å). The Pd–C(1) bond lengths for complex **7b** are within the esd for carbene-substituted phosphitepalladacycles. The heterocyclic five-membered ring in complex **7b** [Pd1*(2)*–C7*(57)*–C8*(58)*–O1*(4)*–P1*(2)*] adopts an envelope conformation, with bond angles similar to those observed in the saturated carbene complexes [23].

2.3. Acetylacetonates of phospha- and phosphitepalladacycles

It is well established that acetylacetonate substituted palladacycles show very high turnover numbers (TONs) in the Mizoroki-Heck coupling reactions of iodobenzene with styrene, therefore the preparation and characterization of new phospha- and phosphitepalladacycles has been performed in this work.

The acetylacetonate phospha/phosphitepalladacycles were prepared by treatment of the acetate bridged palladacycles **1a** and **1c** with 2,4-pentanedione (Hacac) in dichloromethane to afford the acetylacetonate products **10** and **11** in nearly quantitative yields according to established methods [1,9,17] (Scheme 4). In a previous report it was mentioned that the acetylacetonate substituted palladacycle **11** (Fig. 3) shows high TONs of 3500 [mole product per mole **11**] in Mizoroki–Heck coupling reactions for the coupling of chlorobenzene with styrene [9].

The compounds **10** and **11** show broad ^{1}H NMR signals at 25 °C [9]. Acetylacetonate complexes of phospha- and phosphitepalladacycles show excellent air and thermal stability even at elevated temperatures. The structure of complex **11** was determined by single-crystal X-ray diffraction studies. Suitable single were grown from dichloromethane by slow evaporation of the solvent at ambient temperature (Fig. 3).

According to previously described solid state structures of acetylacetonate-substituted palladacycles [9], we found

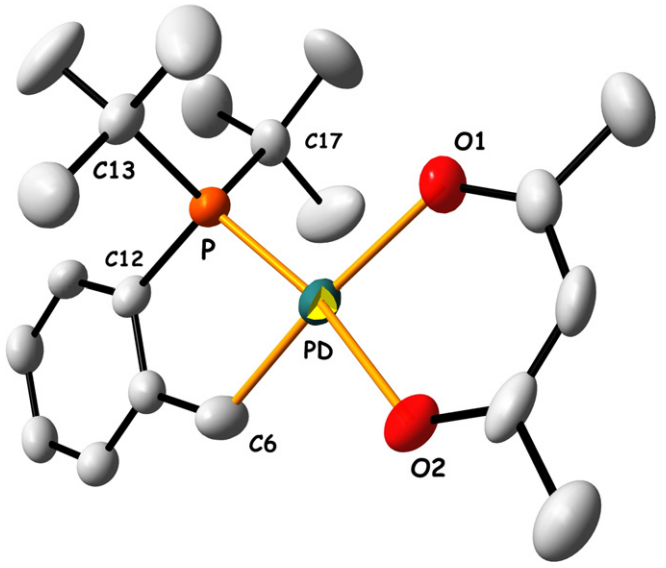


Fig. 3. ORTEP style plot [30h] of compound **11** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

for complex **11** that the two Pd–O distances differ significantly. The oxygen atom O1 coordinated *trans* to the carbon atom shows a slightly longer bond length (2.111(4) Å) compared to the oxygen atom O2 coordinated *trans* to the phosphine (2.092(4) Å), because of the donating effect of the carbanion. This behaviour was observed for the first time for the di-*ortho*-tolyl-substituted palladacycle complex ($C_{26}H_{27}O_2PPd$) with bond lengths of 2.112 and 2.078 Å [28].

3. Conclusion

The compounds **1a**,**b** make excellent precursors for the generation of both mono- and di-substituted carbene

adducts of phosphitepalladacycles in good yields. New NHC-substituted phosphitepalladacycles were prepared using a similar procedure to that used to prepare NHC substituted phosphine complexes, in order to investigate their chemical properties. Acetylacetonate complexes of phospha- and phosphitepalladacycles show excellent air and thermal stability even at elevated temperatures. The structural identity of three compounds was settled by single-crystal X-ray diffraction studies. We are currently investigating the catalytic activity of these complexes in different types of CC-coupling reactions, and this work will be reported at a later date.

4. Experimental

4.1. General comments

The precursors **1b** [17], and free carbenes and azolium salts (**2**–**9**) were prepared according to the literature [29]. ^{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 = singlet, 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 CI or FAB techniques. Melting points were measured with a Büchi melting point apparatus system (Dr. Tottoli).

4.2. trans-Di(μ-acetato)-bis[2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC]dipalladium(II) (*1a*)

To a solution of 750 mg (3.34 mmol) $Pd(OAc)_2$ dissolved in 50 mL monomethylglycol ether, 2.38 g (3.68 mmol) tri[2,4-di-*tert*-butylphenyl]phosphite was added and heated for 2 h at 80 °C. After 10 min. a colorless product started to precipitate from the solution. The solution was cooled to room temperature and the solvent was removed by filtration, the solid was washed with the same amount of 5 mL monomethylglycol ether, toluene and *n*-hexane. The obtained product **1a** is soluble in THF and DCM. Yield: 252 mg (1.55 mmol, 93%).

M.p. 247–248 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): $\delta = 7.80$ (2H, d, $^{3}J_{HH} = 9.2$ Hz), 7.34 (2H, s), 7.23 (2H, t, $^{3}J_{HH} = 8.0$ Hz), 7.16 (2H, d, $^{3}J_{HH} = 6.6$ Hz), 7.12 (2H, s), 6.97 (2H, t, $^{3}J_{HH} = 9.6$ Hz), 6.84 (2H, s), 6.67 (2H, d, $^{3}J_{HH} = 8.4$ Hz, CH_{Aryl}), 1.84 (6H, s, CO_2CH_3), 1.40 (18H, s, $C(CH_3)_3$), 1.33 (18H, s, $C(CH_3)_3$), 1.23 (18H, s, $C(CH_3)_3$), 1.21 (18H, s, $C(CH_3)_3$), 1.20 (18H, s, $C(CH_3)_3$), 1.15 (18H, s, $C(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8): $\delta = 152.4$ (CO_2CH_3), 148.9 (d, C_{Aryl}, $J_{PC} = 5.4$ Hz), 147.8, 139.8, 135.5, 133.5, 131.5, 129.7, 128.9, 126.0, 125.5, 124.6, 122.0 (C_{Aryl}), 35.4, 35.2, 32.2, 31.9, 30.9, 29.9 (CH_3), 21.5 (CO_2CH_3). $^{31}P\{^{1}H\}$ NMR (161 MHz, THF-d_8): $\delta = 126.7$ (s), 124.8 (s) ($I = 1{:}1$). MS (CI) m/z (%): 1622.7 (10, [M^+]), 1563.5 (65, [M^+−OAc]), 1386.7 (40, [M^+−2,4-di-*t*-Bu-C_6H_5O]), 976.3 (35, [M^+−(2,4-di-*t*-Bu-$C_6H_5O)_3$]), 810.6 (100, [$\frac{1}{2}$palladacycle]), 751 (50, [(2,4-di-*t*-Bu-$C_6H_5O)_3$PPd]), 441.5 (20, [(2,4-di-*t*-Bu-$C_6H_5O)_2P^+$]), 191.3 (10, [2,4-di-*t*-Bu-$C_6H_5^+$]). Anal. Calc. for $C_{88}H_{130}O_{10}P_2Pd_2 \cdot THF$ (1694.86): C, 65.20; H, 8.21. Found: C, 66.20; H, 7.98%.

4.3. Acetato-(1,3-di-tert-butylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (*2a*)

To a suspension of 300 mg (0.19 mmol) *trans*-di(μ-acetato)-bis[2-[[bis[2,4-bis(1,1-dimethylethyl)phenoxy]phosphino-κP]oxy]-3,5-bis(1,1-dimethylethyl)phenyl-κC]dipalladium(II) (**1a**) in 10 mL toluene, a solution of 100 mg (0.55 mmol) 1,3-di-*tert*-butylimidazolin-2-ylidene **2** in 7 mL THF was added at −70 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 mL *n*-hexane. Yield: 245 mg (0.25 mmol, 50%).

^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.44$ (1H, s), 8.07 (1H, d, $^{3}J_{HH} = 7.2$ Hz), 7.55 (1H, s), 7.45 (1H, s), 7.29 (1H, d, $^{3}J_{HH} = 7.6$ Hz), 7.03 (1H, s), 6.66 (1H, s), 6.60 (1H, s), 6.51 (2H, s, NC*H*C*H*N), 2.42 (3H, s, OAc), 1.65 (9H, s, $C(CH_3)_3$), 1.58 (9H, s, $C(CH_3)_3$), 1.43 (9H, s, $C(CH_3)_3$), 1.37 (9H, s, $C(CH_3)_3$), 1.32 (9H, s, $C(CH_3)_3$), 1.31 (9H, s, $C(CH_3)_3$), 1.13 (9H, s, $C(CH_3)_3$), 0.97 (9H, s, $C(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6): $\delta = 175.7$ (d, N*C*N, $J_{PC} = 16.8$ Hz), 154.7 (s, C_6H_5), 153.9, 153.7 (s, C_6H_5), 148.4, 148.3 (s, C_6H_5), 146.4, 144.8 (s, C_6H_5), 142.1, 140.3, 138.3 (s, C_6H_5), 135.6, 134.9, 131.8, 131.5 (s, C_6H_5), 131.0 (s, O*C*O), 124.2, 124.0, 123.5, 123.4 (s, C_6H_5), 123.1, 120.3, 119.6, 118.7 (s, C_6H_5), 116.7 (N*C*H*C*HN), 60.0 (N*C*$(CH)_3$), 35.0, 34.9, 34.7, 34.3, 34.2 (s, $C(CH_3)_3$), 31.2 (d, C(CH_3)$_3$, $J_{PC} = 9.2$ Hz), 30.4 (s, $C(CH_3)_3$), 30.2 (s, $C(CH_3)_3$), 29.7 (d, C(CH_3)$_3$, $J_{PC} = 12.2$ Hz), 29.5 (s, $C(CH_3)_3$). $^{31}P\{^{1}H\}$ NMR (161 MHz, C_6D_6): $\delta = 136.9$ (s), 135.9 (s); ($I = 5{:}1$). MS (FAB) m/z (%): 930.2 (100, [M^+−OAc]), 286.8 (50, [Pd+carbene]), 228.8 (45, [Pd+carbene−*t*-Bu]), 181 (58, [carbene]), 123 (50, [carbene−*t*-Bu]). Anal. Calc. for $C_{55}H_{86}N_2O_5PPd$ (992.53): C, 66.55; H, 8.73; N, 2.82. Found: C, 66.37; H, 8.99; N, 2.17%.

4.4. Chloro-(1,3-di-tert-butylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (*2b*)

To a suspension of 300 mg (0.19 mmol) *trans*-di(μ-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1b**) in 10 mL toluene, a solution of 100 mg (0.55 mmol)

1,3-di-*tert*-butylimidazolin-2-ylidene **2** in 7 mL THF was added at −70 °C. The reaction mixture was stirred at room temperature for 3 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 mL *n*-hexane. Yield: 273 mg (0.26 mmol, 61%).

^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.34$ (1H, s), 8.08 (1H, s), 7.48 (2H, s), 7.43 (2H, s), 7.30 (1H, s), 6.78 (1H, d, $^3J_{HH} = 7.6$ Hz), 6.51 (2H, s, NC*H*C*H*N), 1.75 (9H, s, C(CH_3)$_3$), 1.61 (9H, s, C(CH_3)$_3$), 1.53 (9H, s, C(CH_3)$_3$), 1.46 (9H, s, C(CH_3)$_3$), 1.39 (9H, s, C(CH_3)$_3$), 1.32 (9H, s, C(CH_3)$_3$), 1.19 (9H, s, C(CH_3)$_3$), 1.07 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 177.5$ (d, N*C*N, $J_{PC} = 16.8$ Hz), 163.7, 161.3, 155.6, 148.9, 146.7, 144.8, 140.7, 138.9, 138.1, 135.1, 133.5, 124.6, 123.9, 122.8, 122.2, 121.2, 120.1, 119.1, 117.4 (N*C*HCHN), 68.1 (N*C*(CH$_3$)$_3$), 35.8, 35.1, 35.0, 34.9, 34.5, 34.1, 34.1 (*C*(CH$_3$)$_3$), 32.5 (d, C(*C*H$_3$)$_3$, $J_{PC} = 7.7$ Hz), 31.8, 30.4, 30.1 (d, C(*C*H$_3$)$_3$, $J_{PC} = 9.2$ Hz), 30.1 (d, C(*C*H$_3$)$_3$, $J_{PC} = 9.2$ Hz). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): $\delta = 141.1$ (s), 135.9 (s); ($I = 1$:8). MS (FAB) *m*/*z* (%): 931.3 (22, [M$^+$−Cl]), 751.1 (7, [1/2palladacycle−Cl]), 284.7 (27, [Pd+carbene]), 180.9 (100, [carbene]). Anal. Calc. for $C_{53}H_{83}N_2O_3PPdCl$ (967.49): C, 65.69; H, 8.63; N, 2.89. Found: C, 65.28; H, 8.44; N, 2.57%.

4.5. Acetato-(1,3-di-mesitylimidazolin-2-ylidene) {2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (*3a*)

Three hundred milligrams of (0.19 mmol) *trans*-di(μ-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1a**), 30 mg (0.36 mmol) sodium acetate and 144 mg (0.37 mmol) 1,3-di-mesitylimidazolium tetrafluoroborate **8** were suspended in 5 mL DMSO and heated for 2 h at 90 °C. The volatile compounds were removed in vacuo and the residue was extracted three times with 4 mL toluene to obtain a yellow product. Yield: 246 mg (0.22 mmol, 60%).

^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.15$ (2H, d, $^3J_{HH} = 7.9$ Hz), 8.04 (1H, br. s), 7.44 (2H, br. s), 6.99 (1H, dd, $^3J_{HH} = 10.1$ Hz, $^4J_{HH} = 2.4$ Hz), 6.61 (2H, br. s, mesityl), 6.65 (2H, br. s, mesityl), 6.53 (2H, br s), 3.81 (2H, m, NCHC*H*N), 2.32 (6H, s, CH$_{3,mesityl}$), 2.21 (6H, s, CH$_{3,mesityl}$), 2.03 (6H, s, CH$_{3,mesityl}$), 1.95 (9H, s, C(CH_3)$_3$), 1.78 (18H, s, C(CH_3)$_3$), 1.75 (9H, br. s, C(CH_3)$_3$), 1.44 (9H, s, C(CH_3)$_3$), 1.23 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 182.1$ (s, N*C*N), 163.6 (d, $C_{metallated}$, $^2J_{PC} = 18.1$ Hz), 148.9, 147.6 (s, C_{Aryl}), 139.8, 138.3, 136.9, 136.5, 132.6, 131.6, 130.2 (d, C_{Aryl}, $J_{PC} = 7.4$ Hz), 126.0, 125.3 (d, C_{Aryl}, $J_{PC} = 4.6$ Hz), 124.9, 124.8, 124.4, 122.5, 121.5, 119.7, 119.6, 115.9 (s, C_{Aryl}), 50.2 (s, N*C*H*C*HN), 40.8, 35.7, 35.6, 35.5, 35.4, 34.8 (s, *C*(CH$_3$)$_3$), 32.4, 31.9, 31.7, 30.7, 30.4, 29.8 (s, C(*C*H$_3$)$_3$), 21.7, 21.2, 18.5, 18.1 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 134.1$(s), 133.1 (s); ($I = 2$:1). MS (FAB) *m*/*z* (%): 1115.2 (5, [M$^+$]), 1101.1 (18, [M$^+$−CH$_3$]), 1086.1 (5, [M$^+$−OCH$_3$]), 1056.4 (19, [M$^+$−OAc]), 305.0 (100, [carbene]), 189.0 (45, [2,4-di-*t*-Bu-C$_6$H$_5$]). Anal. Calc. for $C_{65}H_{89}N_2O_5PPd$ (1115.81): C, 69.97; H, 8.04; N, 2.51. Found: C, 69.40; H, 8.21; N, 2.41%.

4.6. Chloro-(1,3-di-mesitylimidazolin-2-ylidene) {2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (*3b*)

To a suspension of 300 mg (0.19 mmol) *trans*-di(μ-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1b**) in 15 mL toluene, a solution of 152 mg (0.49 mmol) 1,3-di-mesitylimidazolin-2-ylidene **3** in 10 mL THF was added at −90 °C. The reaction mixture was stirred at room temperature for 2 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed with 5 mL *n*-hexane and 5 mL *n*-pentane. Yield: 398 mg (0.37 mmol, 72%).

^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.65$ (2H, dd, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 2.0$ Hz), 7.44 (1H, dd, $^3J_{HH} = 5.59$ Hz, $^4J_{HH} = 2.3$ Hz), 7.03 (2H, dd, $^3J_{HH} = 7.9$ Hz), 6.92 (1H, dd, $^3J_{HH} = 10.7$ Hz, $^4J_{HH} = 2.0$ Hz), 6.74 (2H, br. s, mesityl), 6.65 (2H, br. s, mesityl), 6.34 (2H, dd, $^3J_{HH} = 10.7$ Hz, $^4J_{HH} = 2.3$ Hz), 3.59 (2H, m, NC*H*C*H*N), 2.69 (6H, s, CH$_3$), 2.37 (6H, s, CH$_3$), 2.12 (6H, s, CH$_3$), 1.48 (9H, s, C(CH_3)$_3$), 1.28 (18H, s, C(CH_3)$_3$), 1.18 (18H, s, C(CH_3)$_3$), 1.11 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): no signal was detected for the carbene carbon nucleus, $\delta = 167.5$ (s, C_{Aryl}), 163.1, 159.9 (s, C_{Aryl}), 152.3 (d, $J_{PC} = 21.2$ Hz), 147.1, 146.9, 144.6, 140.2 (d, C_{Aryl}, $J_{PC} = 5.4$ Hz), 140.0, 139.5 (d, C_{Aryl}, $J_{PC} = 4.6$ Hz), 148.9, 148.4, 147.5, 146.7, 145.9, 139.2, 136.3, 132.1, 130.8, 129.8, 129.1, 125.5, 124.5, 124.4, 121.3, 120.5 (d, NC*H*C*H*N, $^4J_{PC} = 6.9$ Hz), 35.3, 35.1, 34.6, 34.4, 34.3 (s,*C*(CH$_3$)$_3$), 31.7, 30.6, 30.5, 29.7 (s, C(*C*H$_3$)$_3$), 24.0, 21.2, 18.0 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 121.3$ (s), 133.7(s); ($I = 1$:2). MS (FAB) *m*/*z* (%): 1057.5 (10, [M$^+$−Cl]), 751.4 (5, [M$^+$−(Cl+carbene)]), 645.4 (5, [P(OC$_6$H$_2$-2,4-*t*-Bu$_2$])), 305.0 (100, [carbene]), 189.0 (45, [2,4-di-*t*-Bu-C$_6$H$_5$]). Anal. Calc. for $C_{63}H_{86}N_2O_3PPdCl$ (1092.22): C, 69.28; H, 7.94; N, 2.56. Found: C, 69.31; H, 7.93; N, 2.48%.

4.7. Chloro-(1-mesityl-3-methylimidazolin-2-ylidene) {2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (*4b*)

To a suspension of 300 mg (0.19 mmol) *trans*-di(μ-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1b**) in 15 mL toluene, a solution of 100 mg (0.49 mmol) 1-mesityl-3-methylimidazolin-2-ylidene **4** in 10 mL THF was added at −85 °C. The reaction mixture was stirred at room temperature for 2 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 mL *n*-pentane. Yield: 424 mg (0.43 mmol, 86%).

^{1}H NMR (400 MHz, C_6D_6): $\delta = 9.28$ (2H, dd, $^3J_{HH} = 8.5$ Hz), 7.91 (1H, d, $J_{HH} = 8.56$ Hz), 7.46 (2H, dd, $^3J_{HH} = 9.6$ Hz, $^4J_{HH} = 2.4$ Hz), 7.33 (1H, br. t, $J_{HH} = 4.0$ Hz), 6.68 (2H, br. d, $^3J_{HH} = 8.4$ Hz, CH_{Aryl}), 6.32 (2H, br. s, mesityl), 3.54 (2H, m, NC*H*CHN), 1.78 (3H, s, CH_3), 1.66 (6H, s, CH_3), 1.52 (6H, s, CH_3), 1.49 (6H, s, CH_3), 1.32 (9H, s, C(CH_3)$_3$), 1.26 (18H, s, C(CH_3)$_3$), 1.13 (18H, s, C(CH_3)$_3$), 0.87 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 186.2$ (s, N*C*N), 179.9 (d, $J_{PC} = 14.8$ Hz), 154.5 (d, $J_{PC} = 16.5$ Hz), 149.0 (d, C_{Aryl}, $J_{PC} = 6.5$ Hz), 148.8, 148.0, 147.7, 146.7, 146.3, 144.1, 141.2 (s, C_{Aryl}), 139.6 (d, C_{Aryl}, $J_{PC} = 5.5$ Hz), 138.5, 138.2, 137.7, 136.1, 135.2, 134.5, 133.9 (s, C_{Aryl}), 129.8 (d, C_{Aryl}, $J_{PC} = 11.4$ Hz), 125.6, 124.5, 123.9, 121.8 (s, C_{Aryl}), 121.3 (d, C_{Aryl}, $J_{PC} = 6.7$ Hz), 120.6 (d, N*C*H*C*HN, $J_{PC} = 8.2$ Hz), 35.5, 35.3, 34.5, 34.3 (s, *C*(CH_3)$_3$), 32.2, 31.9, 31.8, 31.5, 31.3 (s, C(*C*H_3)$_3$), 21.2, 20.3, 19.6, 19.3, 18.8 (s, $CH_{3,mesityl}$), 14.2 (s, *C*H_3). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 138.5$ (s), 137.3 (s); ($I = 1{:}3$). MS (FAB) *m*/*z* (%): 951.5 (10, [M$^+$−Cl]), 543.2 (5, [(2,4-di-*t*-Bu-C_6H_5-O)$_2$PPd]), 333.2 (8, [carbene+Pd+P]), 306.0 (8, [carbene+Pd]), 199.1 (100, [carbene]), 185.0 (10, [carbene−Me]). Anal. Calc. for $C_{55}H_{78}N_2O_3PPdCl$ (988.07): C, 66.86; H, 7.96; N, 2.84. Found: C, 66.07; H, 7.97; N, 2.25%.

*4.8. Acetato-(1-diphenylmethyl-3-methylimidazolin-2-ylidene)-{2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]-oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (**5a**)*

Three hundred and fifty-four milligrams of (0.22 mmol) *trans*-di(μ-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1a**), 60 mg (0.73 mmol) sodium acetate and 150 mg (0.30 mmol) imidazolium tetrafluoroborate salt **9** were suspended in 5 mL DMSO and heated for 2 h at 80 °C. The volatile compounds were removed in vacuo and the residue was extracted three times with 4 mL toluene to obtain a yellow product. Yield: 273 mg (0.26 mmol, 60%).

^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.57$ (1H, dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.2$ Hz), 7.91 (1H, dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1.2$ Hz), 7.56 (2H, s), 7.53 (1H, dd, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 2.2$ Hz), 7.41 (2H, s), 7.29 (1H, s), 7.28 (1H, d, $^4J_{HH} = 2.4$ Hz), 7.12–6.93 (7H, m, CH_{Aryl}), 6.84 (2H, d, $J_{HH} = 1.8$ Hz), 6.30 (1H, s, NC*H*), 6.24 (1H, d, $^4J_{HH} = 1.0$ Hz, NC*H*CHN), 6.05 (1H, s, NC*H*CHN), 3.76 (3H, s, NCH_3), 2.10 (3H, s, CO_2CH_3), 1.52 (9H, s, C(CH_3)$_3$), 1.40 (9H, s, C(CH_3)$_3$), 1.38 (9H, s, C(CH_3)$_3$), 1.21 (9H, s, C(CH_3)$_3$), 1.15 (9H, s, C(CH_3)$_3$), 1.01 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 185.2$ (s, N*C*N), 176.5 (s, *C*O$_2$CH$_3$), 155.3, 154.8, 154.5, 149.2, 149.0 (d, C_{Aryl}, $J_{PC} = 6.2$ Hz), 147.1, 146.9, 144.6, 140.2 (d, C_{Aryl}, $J_{PC} = 5.4$ Hz), 140.0, 139.5 (d, C_{Aryl}, $J_{PC} = 4.6$ Hz), 139.4, 137.8, 135.1, 129.3, 129.1, 129.1, 128.9, 128.7, 128.5, 128.4, 125.6, 124.8, 124.7, 124.5, 124.1, 123.7, 123.4, 122.2 (d, C_{Aryl}, $J_{PC} = 24.4$ Hz), 121.3, 118.8 (d, N*C*HCHN, $J_{PC} = 21.2$ Hz), 68.0 (N*C*H), 38.5 (N*C*H$_3$), 35.4, 35.3, 35.1, 34.6, 34.4, 34.3 (*C*(CH$_3$)$_3$), 31.8, 31.5, 31.4, 30.6, 30.5, 30.1 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (161 MHz, $(CD_3)_2SO$): $\delta = 139.5$ (s), 138.3 (s); ($I = 1{:}4$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 139.9$ (s), 138.9 (s); ($I = 1{:}4$). MS (FAB) *m*/*z* (%): 998.5 (11, [M$^+$]), 353.6 (12, [Pd+carbene]), 246.8 (43, [carbene]), 166.8 (100, [carbene−Ph]). Anal. Calc. for $C_{61}H_{81}N_2O_5PPd$ (1059.72): C, 69.14; H, 7.70; N, 2.64. Found: C, 69.34; H, 7.68; N, 2.67%.

*4.9. Chloro-(1-diphenylmethyl-3-methylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (**5b**)*

To a suspension of 394 mg (0.25 mmol) *trans*-di(μ-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1b**) in 15 mL toluene, a solution of 200 mg (0.55 mmol) 1-diphenylmethyl-3-methylimidazolin-2-ylidene **5** in 10 mL THF was added at −90 °C. The reaction mixture was stirred at room temperature for 3 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 mL *n*-hexane. Yield: 282 mg (0.27 mmol, 63%).

^{1}H NMR (270 MHz, C_6D_6): $\delta = 8.43$ (1H, dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.0$ Hz), 8.33 (1H, dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1.7$ Hz), 7.91 (1H, s), 7.53 (2H, dd, $^3J_{HH} = 10.6$ Hz, $^4J_{HH} = 2.0$ Hz), 7.40 (2H, dd, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 1.8$ Hz), 7.23 (1H, s), 7.12–6.93 (10H, m, CH_{Aryl}), 6.38 (1H, t, $^3J_{HH} = 1.7$ Hz, NC*H*), 6.20 (1H, s, NC*H*CHN), 6.16 (1H, t, $^3J_{HH} = 1.7$ Hz, NC*H*CHN), 3.32 (3H, s, NCH_3), 1.70 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.39 (9H, s, C(CH_3)$_3$), 1.21 (9H, s, C(CH_3)$_3$), 1.11 (9H, s, C(CH_3)$_3$), 1.08 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 186.1$ (N*C*N), 154.0 (d, C_{Aryl}, $J_{PC} = 27.5$ Hz), 149.1, 146.8 (d, C_{Aryl}, $J_{PC} = 6.7$ Hz), 144.5, 139.7, 137.3 (d, C_{Aryl}, $J_{PC} = 6.2$ Hz), 134.8, 133.7 (d, C_{Aryl}, $J_{PC} = 16.6$ Hz), 129.8, 128.8, 128.7, 128.6, 128.5, 128.2, 124.5 (d, C_{Aryl}, $J_{PC} = 5.7$ Hz), 124.2 (d, C_{Aryl}, $J_{PC} = 6.2$ Hz), 121.6 (N*C*HCHN), 121.2 (N*C*HCHN), 67.6 (N*C*H), 38.0 (N*C*H$_3$), 35.5, 35.4, 35.3, 34.6, 34.5, 34.2 (*C*(CH$_3$)$_3$), 31.8, 31.6, 31.5, 30.8, 30.6, 30.1 (C(*C*H$_3$)$_3$), 23.6 (CO_2CH_3). ^{31}P{^{1}H} NMR (161 MHz, $(CD_3)_2SO$): $\delta = 140.2$ (s). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 138.8$ (s), 137.6 (s); ($I = 8.5{:}1$). MS (FAB) *m*/*z* (%): 998.4 (15, [M$^+$]), 353.6 (15, [Pd+carbene]), 246.8 (59, [carbene]), 166.8 (100, [carbene−Ph]). Anal. Calc. for $C_{59}H_{78}N_2O_3PPdCl$ (1036.11): C, 68.39; H, 7.59; N, 2.70. Found: C, 68.23; H, 7.43; N, 2.65%.

*4.10. Bis(1,3-di-cyclohexylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) acetate (**6a**)*

To a suspension of 300 mg (0.19 mmol) *trans*-di(μ-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1a**) in 15 mL toluene, a solution of 128 mg (0.55 mmol)

1,3-di-cyclohexylimidazolin-2-ylidene **6** in 10 mL THF was added at −80 °C. The reaction mixture was stirred at room temperature for 3 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 mL *n*-hexane and 5 mL *n*-pentane. Yield: 346 mg (0.27 mmol, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.28$ (2H, d, $J_{HH} = 6.4$ Hz), 8.49 (1H, t, $^3J_{HH} = 8.4$ Hz), 7.55 (2H, br. dd, $^3J_{HH} = 9.6$ Hz, $^4J_{HH} = 2.7$ Hz, CH_{Aryl}), 7.05 (1H, br. t, $^3J_{HH} = 8.4$ Hz, CH_{Aryl}), 6.68 (2H, br. d, $^3J_{HH} = 8.4$ Hz, CH_{Aryl}), 6.54 (m, NC*H*C*H*N), 6.41 (m, NC*H*C*H*N), 4.94 (2H, t, $^3J_{HH} = 10.6$ Hz, CH_{Cy}), 4.08 (2H, t, $^3J_{HH} = 4.7$ Hz, CH_{Cy}), 1.78–1.41 (br. m, C$H_{2,Cy}$) 1.36 (9H, s, C(CH_3)$_3$), 1.21 (18H, s, C(CH_3)$_3$), 0.61 (18H, s, C(CH_3)$_3$), 0.39 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 178.4$ (s, N*C*N), 176.8 (s, *C*O$_2$CH$_3$), 164.1, 161.3, 148.6, 147.0 (s, C_{Aryl}), 146.1 (d, C_{Aryl}, $J_{PC} = 3.9$ Hz), 145.3, 143.1 (s, C_{Aryl}), 138.7 (d, C_{Aryl}, $J_{PC} = 5.7$ Hz), 136.1, 133.4, 132.4, 132.2, 130.9 (s, C_{Aryl}), 126.7, 126.2, 125.3, 124.3, 121.9 (s, C_{Aryl}), 120.9 (d, C_{Aryl}, $J_{PC} = 6.7$ Hz), 118.4 (s, C_{Aryl}), 117.4 (s, N*C*HCHN), 116.5 (s, N*C*HCHN), 69.4 (br, N*C*H$_{Cy}$), 58.1 (br, N*C*H$_{Cy}$), 34.1, 33.9, 33.7 (s, *C*H$_{2,Cy}$), 31.9, 31.6, 30.4, 30.8 (s, *C*(CH$_3$)$_3$), 29.2, 29.0, 28.7, 28.6 (s, C(*C*H$_3$)$_3$), 25.8 (CO$_2$*C*H$_3$), 24.3–23.6 (br, *C*H$_{2,Cy}$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 139.4$ (s). MS (FAB) *m*/*z* (%): 1215.5 (40, [M$^+$−OAc]), 983.3 (35, [M$^+$−(OAc+1NHC])), 337.1 (15, [Pd+carbene]), 233.1 (100, [carbene]), 151.8 (42, [carbene−Cy]). Anal. Calc. for $C_{74}H_{113}N_4O_5PPd \cdot 1/2CH_2Cl_2$ (1318.58): C, 67.86; H, 8.71; N, 4.25. Found: C, 68.44; H, 8.83; N, 3.22%.

4.11. Bis(1,3-di-cyclohexylimidazolin-2-ylidene) {2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) chloride (6b)

To a suspension of 300 mg (0.19 mmol) *trans*-di (μ-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1b**) in 15 mL toluene a solution of 128 mg (0.55 mmol) 1,3-dicyclohexylimidazolin-2-ylidene **6** in 10 mL THF was added at −80 °C. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed in vacuum and the residue was washed twice with 5 mL *n*-hexane and 5 mL *n*-pentane. Yield: 375 mg (0.29 mmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.49$ (2H, d, $^3J_{HH} = 4.4$ Hz), 8.26 (1H, d, $^3J_{HH} = 8.4$ Hz), 7.85 (2H, d, $^3J_{HH} = 8.4$ Hz), 7.47 (1H, br. t, $^3J_{HH} = 9.7$ Hz, CH_{Aryl}), 6.52 (2H, d, $^3J_{HH} = 4.8$ Hz, CH_{Aryl}), 6.43 (2H, br. s, NC*H*CHN), 4.92 (2H, t, $^3J_{HH} = 4.7$ Hz, CH_{Cy}), 4.63 (2H, t, $^3J_{HH} = 4.7$ Hz, CH_{Cy}), 1.66 (9H, s, C(CH_3)$_3$), 1.46 (18H, s, C(CH_3)$_3$), 1.45 (9H, s, C(CH_3)$_3$), 1.42–1.31 (m, 20H, C$H_{2,Cy}$), 1.23 (18H, s, C(CH_3)$_3$), 1.10 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 175.1$ (s, N*C*N), 173.0 (s, N*C*N), 171.0 (d, C_{Aryl}, $J_{PC} = 16.7$ Hz), 153.5 (d, C_{Aryl}, $J_{PC} = 23.9$ Hz), 148.2, 147.6, 147.2, 146.6, 146.0, 145.5 (s, C_{Aryl}), 141.5, 138.9, 134.3, 133.6 (s, C_{Aryl}), 133.5 (d, C_{Aryl}, $J_{PC} = 5.6$ Hz), 124.9, 123.8, 123.2, 122.6 (s, C_{Aryl}), 119.5 (d, C_{Aryl}, $J_{PC} = 8.5$ Hz), 118.5 (N*C*HCHN), 60.1 (br. s, *C*H$_{Cy}$), 59.3 (br. s, *C*H$_{Cy}$), 35.0, 34.8, 34.6, 34.3 (*C*(CH$_3$)$_3$), 33.1–31.3(*C*H$_{2,Cy}$), 30.2, 30.1, 29.7, 29.5 (C(*C*H$_3$)$_3$), 26.4 (CO$_2$*C*H$_3$), 25.0, 24.9, 24.5, 24.4 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 141.0$ (s). MS (FAB) *m*/*z* (%): 1215.5 (40, [M$^+$−Cl]), 983.3 (35, [M$^+$−(Cl+1NHC])), 336.9 (15, [Pd+carbene]), 233.1 (100, [carbene]), 151.8 (42, [carbene−Cy]). Anal. Calc. for $C_{72}H_{110}N_4O_3PPdCl$ (1252.52): C, 69.04; H, 8.85; N, 4.47. Found: C, 69.23; H, 8.64; N, 3.98%.

4.12. Acetato-(1,3-di-methylimidazolin-2-ylidene) {2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (7a)

To a suspension of 101 mg (0.125 mmol) *trans*-di (μ-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1a**) in 15 mL toluene, a solution of 48 mg (0.55 mmol) 1,3-dimethylimidazolin-2-ylidene **7** in 10 mL THF was added at −90 °C. The reaction mixture was stirred at room temperature for 4 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 mL *n*-hexane. Yield: 198 mg (0.19 mmol, 79%).

^{1}H NMR (270 MHz, C_6D_6): $\delta = 8.45$ (2H, d, $J_{HH} = 4.3$ Hz), 7.91 (1H, t, $^3J_{HH} = 6.3$ Hz), 7.43 (2H, br. d, $^3J_{HH} = 8.6$ Hz), 7.31 (1H, br. t, $J_{HH} = 2.5$ Hz), 6.57 (2H, d, $^3J_{HH} = 7.3$ Hz), 3.16 (2H, s, NC*H*C*H*N), 1.58 (6H, s, CH_3), 1.42 (9H, s, C(CH_3)$_3$), 1.33 (18H, s, C(CH_3)$_3$), 1.16 (18H, s, C(CH_3)$_3$), 1.08 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 178.3$ (N*C*N), 170.1 (*C*O$_2$CH$_3$), 154.9, 148.6, 147.5 (s, C_{Aryl}), 145.5, 140.6, 139.2, 139.2, 135.1, 132.5, 125.8, 125.4 (s, C_{Aryl}), 124.6 (t, C_{Aryl}, $J_{PC} = 7.9$ Hz), 124.3, 124.2, 123.8, 123.3 (s, C_{Aryl}), 122.1, 121.5 (s, C_{Aryl}), 121.2 (d, C_{Aryl}, $J_{PC} = 10.4$ Hz), 116.8 (s, N*C*H*C*HN), 70.8 (N*C*H), 36.7 (N*C*H$_3$), 35.4, 35.3, 35.2, 35.1 (*C*(CH$_3$)$_3$), 31.8, 31.6, 31.5, 31.4 (C(*C*H$_3$)$_3$), 30.4, 30.1, 29.9, 29.8 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 128.4$ (s), 130.7 (s); ($I = 1{:}1$). MS (FAB) *m*/*z* (%): 943.4 (55, [M$^+$−OAc]), 847.3 (100, [M$^+$−(OAc+NHC)]), 831.3 (10, [M$^+$−(OAc+NHC + CH$_3$)]), 439.2 (5, [2,4-di-*t*-Bu-C$_6$H$_5$OPPd + carbene]). Anal. Calc. for $C_{49}H_{73}N_2O_5PPd$ (907.51): C, 64.67; H, 8.11; N, 3.09. Found: C, 64.74; H, 8.22; N, 2.10%.

4.13. Chloro-(1,3-di-methylimidazolin-2-ylidene) {2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (7b)

To a suspension of 200 mg (0.13 mmol) *trans*-di (μ-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) (**1b**) in 15 mL toluene, a solution of 48 mg (0.55 mmol) 1,3-methylimidazolin-2-ylidene **7** in 10 mL THF was added at −90 °C. The reaction mixture was stirred at room

temperature for 4 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 mL *n*-hexane. Yield: 185 mg (0.19 mmol, 75%).

^{1}H NMR (270 MHz, C_6D_6): $\delta = 8.31$ (2H, d, $^3J_{HH} = 9.8$ Hz), 7.68 (1H, d, $J_{HH} = 7.3$ Hz), 7.39 (2H, br. d, $^3J_{HH} = 9.1$ Hz), 7.34 (1H, br. t, $J_{HH} = 3.1$ Hz), 7.18 (2H, d, $^3J_{HH} = 7.3$ Hz), 3.74 (1H, m, NC*H*CHN), 3.21 (1H, d, $^3J_{HH} = 10.8$ Hz, NCHC*H*N), 1.76 (6H, s, CH_3), 1.42 (9H, s, C(CH_3)$_3$), 1.32 (18H, s, C(CH_3)$_3$), 1.26 (18H, s, C(CH_3)$_3$), 1.03 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 178.2$ (d, $J_{PC} = 14.5$ Hz, N*C*N), 154.8 (t, $J_{PC} = 23.9$ Hz,C_{Aryl}), 148.6, 147.4, 145.8, 145.4, 140.9 (s, C_{Aryl}), 139.1 (d, C_{Aryl}, $J_{PC} = 5.2$ Hz), 134.9, 134.2 (s, C_{Aryl}), 132.3 (d, C_{Aryl}, $J_{PC} = 18.4$ Hz), 129.2, 125.6, 125.1, 124.9, 123.8, 122.13 (s, C_{Aryl}), 120.6 (d, $J_{PC} = 10.2$ Hz, N*C*H*C*HN), 67.5 (N*C*H), 36.4 (N*C*H$_3$), 35.2, 34.9, 34.4, 34.3 (*C*(CH$_3$)$_3$), 32.0, 31.8, 31.5, 31.3 (C(*C*H$_3$)$_3$), 30.5, 30.2, 29.9, 29.8 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): $\delta = 132.4$ (s), 135.4 (s); ($I = 1{:}2$). MS (FAB) *m*/*z* (%): 847.3 (100, [M$^+$−(OAc+NHC)]), 645.5 (10, [(2,4-di-*t*-Bu-C_6H_5O)$_3$P]), 202.1 (8, [Pd + NHC]). Anal. Calc. for $C_{47}H_{70}N_2O_3PPdCl$ (883.92): C, 63.77; H, 8.09; N, 3.17. Found: C, 63.72; H, 8.40; N, 3.58%.

4.14. Acetylacetonato-{[bis[2,4-di-tert-butylphenoxy]phosphino-P]oxy]-3,5-di-tert-butylphenyl-C}-dipalladium(II) (**10**)

To a solution of 405 mg (0.25 mmol) acetate bridged dimer **1a** in 20 mL dichloromethane 150 mg (1.50 mmol) acetylacetone was added and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed in vacuo and the residue was washed with cold diethyl ether. The product was recrystallized from dichloromethane as a pale yellow solid. Yield: 821 mg (0.96 mmol, 96.6%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.11$ (1H, d, $J_{HH} = 8.1$ Hz, H_{Aryl}), 7.72 (2H, d,$J_{HH} = 8.6$ Hz, H_{Aryl}), 7.51 (2H, d, $J_{HH} = 8.2$ Hz, H_{Aryl}), 7.12 (1H, br. t, $J_{HH} = 5.2$ Hz), 7.03 (2H, m,H_{Aryl}), 5.27 (1H, s, CH_{acac}), 2.06 (3H, s, C$H_{3,acac}$), 1.66 (3H, s, C$H_{3,acac}$), 1.36 (9H, s, C(CH_3)$_3$), 1.29 (18H, s, C(CH_3)$_3$), 1.25 (18H, s, C(CH_3)$_3$), 1.03 (9H, s, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 187.9$ (s, *C*O$_{acac}$), 186.9 (s, *C*O$_{acac}$), 148.2 (d, C_{Aryl}, $J_{PC} = 19.3$ Hz), 146.8 (s, C_{Aryl}), 144.8 (s, C_{Aryl}), 139.0 (d, $J_{PC} = 5.4$ Hz, C_{Aryl}), 127.3 (s, C_{Aryl}), 124.4 (d, C_{Aryl}, $J_{PC} = 17.3$ Hz), 123.7 (d, C_{Aryl}, $J_{PC} = 12.1$ Hz), 122.0 (s, C_{Aryl}), 119.8 (d, C_{Aryl}, $J_{PC} = 8.9$ Hz), 99.6 (s, *C*H$_{acac}$), 53.1 (s, *C*H$_{3,acac}$), 45.9 (s, *C*H$_{3,acac}$), 35.1, 35.0, 34.9, 34.5 (*C*(CH$_3$)$_3$), 31.8, 30.3, 29.7, 28.1 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): $\delta = 127.5$ (s). MS (FAB) *m*/*z* (%): 850.4 (38, [M$^+$]), 751.4 (100, [M$^+$−acac]), 692.3 (17, [M$^+$−(acac+*t*-Bu])), 636.7 (41, [M$^+$−(acac+2*t*-Bu])). Anal. Calc. for $C_{47}H_{69}O_5PPd$ (851.44): C, 66.30; H, 8.17; P, 3.64; Pd 12.46. Found: C, 66.21; H, 8.13; P, 3.78; Pd 12.80%.

4.15. Acetylacetonato-[o-(di-t-butylphosphino)-benzyl]palladium(II) (**11**)

To a solution of 401 mg (0.5 mmol) acetate bridged dimer **1c** in 20 mL dichloromethane, 150 mg (1.5 mmol) acetylacetone was added and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed in vacuo and the residue was washed with cold diethyl ether. The product was recrystallized from dichloromethane as a colorless solid. Yield: 440 mg (0.99 mmol, 99.8%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.43$ (1H, t, $^3J_{HH} = 7.1$ Hz, H_{Aryl}), 7.3–7.2 (2H, m, H_{Aryl}), 7.11 (1H, t, $^3J_{HH} = 6.7$ Hz, H_{Aryl}), 5.23 (1H, s, CH_{acac}), 3.30 (2H, d, $J_{HH} = 4.2$ Hz, PdCH_2), 1.93 (3H, s, C$H_{3,acac}$), 1.36 (18H, d, $J_{HH} = 14$ Hz, C$H_{3,t\text{-}Bu}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 189.0$ (s, *C*O$_{acac}$), 187.9 (s, *C*O$_{acac}$), 160.9 (d, C_{Aryl}, $J_{PC} = 25$ Hz), 134.8 (d, C_{Aryl}, $J_{PC} = 43$ Hz), 133.2 (s, C_{Aryl}), 132.0 (s, C_{Aryl}), 130.2 (d, C_{Aryl}, $J_{PC} = 21$ Hz), 126.1 (d, C_{Aryl}, $J_{PC} = 7$ Hz), 100.6 (s, *C*H$_{acac}$), 38.2 (s, *C*H$_{3,acac}$), 38.0 (s, *C*H$_{3,acac}$), 31.4 (s, *C*H$_{3,t\text{-}Bu}$). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): $\delta = 89.3$ (s). MS (FAB) *m*/*z* (%): 439.7 (12, [M$^+$]), 340.7 (100, [M$^+$−acac]), 284.7 (17, [M$^+$−(acac+*t*-Bu])), 240.7 (41, [M$^+$−(acac+2*t*-Bu])). Anal. Calc. for $C_{20}H_{31}O_2PPd$ (440.84): C, 54.49; H, 7.09; P, 7.03; Pd 24.14. Found: C, 54.40; H, 7.10; P, 7.10; Pd 24.60%.

4.16. Single-crystal X-ray structure determination of compounds **1a** · (CH_2Cl_2), **7b** · 3(CH_2Cl_2), and **11**

General: Crystal data and details of the structure determination are presented in Table 3. Suitable single crystals for the X-ray diffraction studies were grown with standard cooling techniques. Crystals were stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collections were performed at low temperatures (OXFORD CRYOSYSTEMS cooling device). Each crystal was measured with a couple of data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0°$. Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso}(H) = 1.5U_{eq}(C)$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and aromatic d_{C-H} distances of 0.99 and 0.95 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$. Full-matrix least-squares refinements

Table 3
Crystallographic data for **1a** · (CH_2Cl_2), **7b** · $3(CH_2Cl_2)$, and **11**

Compound	**1a** · (CH_2Cl_2)	**7b** · $3(CH_2Cl_2)$	**11**
Formula	$C_{89}H_{132}Cl_2O_{10}P_2Pd_2$	$C_{97}H_{146}Cl_8N_4O_6P_2Pd_2$	$C_{20}H_{31}O_2PPd$
Formula weight	1707.63	2022.56	440.84
Color/habit	Colorless/fragment	Colorless/fragment	Colorless/plate
Crystal dimensions (mm)	$0.28 \times 0.33 \times 0.46$	$0.23 \times 0.28 \times 0.48$	$0.10 \times 0.23 \times 0.30$
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no.2)	$P\bar{1}$ (no.2)	*Pbca* (no. 61)
a (Å)	15.3542 (1)	11.1224 (1)	8.4230 (3)
b (Å)	16.8517 (1)	20.7167 (2)	15.8029 (6)
c (Å)	18.4679 (2)	24.1982 (2)	31.2520 (15)
α (°)	91.4991 (3)	100.1638 (4)	90
β (°)	95.5910 (3)	103.0992 (4)	90
γ (°)	92.0949 (3)	94.0864 (3)	90
V (Å^3)	4750.43 (7)	5309.31 (8)	4159.9 (3)
Z	2	2	8
T (K)	173	173	173
D_{calc} (g cm^{-3})	1.194	1.265	1.408
μ (mm^{-1})	0.519	0.619	0.978
$F(000)$	1804	2124	1824
θ Range (°)	1.21–25.36	1.46–25.36	1.30–23.25
Index ranges (h, k, l)	±18, ±20, ±22	±13, ±24, ±29	±9, ±17, ±34
Number of reflections collected	74051	55808	13426
Number of independent reflections/R_{int}	17380/0.036	18623/0.032	2868/0.075
Number of observed reflections [$I > 2\sigma(I)$]	14563	15639	1937
Number of data/restraints/parameters	17380/0/984	18623/0/1151	2868/0/225
R_1/wR_2 [$I > 2\sigma(I)$][a]	0.0307/0.0728	0.0339/0.0795	0.0453/0.0800
R_1/wR_2 (all data)[a]	0.0409/0.0763	0.0447/0.0847	0.0882/0.0924
Goodness-of-fit (GOF) (on F^2)[a]	1.032	1.030	1.025
Largest difference in peak and hole (e Å^{-3})	+0.65 and −0.48	+0.68 and −0.88	+0.60 and −0.68

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.003. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium 4 PC, with the WINGX system, including the programs DIAMOND, PLATON, SHELXL-97, and SIR-92 [30]. *Specials*: **1a** · (CH_2Cl_2): a second solvent molecule could not be resolved and modeled without a doubt. This problem was cured be using the PLATON "calc squeeze" procedure. Compound **7b** · $3(CH_2Cl_2)$: A disorder over two positions observed for each of the three independent solvent molecules CH_2Cl_2 [0.68(1)/0.32(1), 0.61(2)/0.39(2), and 0.68(3)/0.32(3)] could be resolved and modeled clearly. The asymmetric unit contains two crystallographic independent molecules **A** and **B** of the target compound **7b**.

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Appendix A. Supplementary material

CCDC 638462, 638461 and 638460 contain the supplementary crystallographic data (excluding structure factors) for [**1a** · (CH_2Cl_2)], [**7b** · $3(CH_2Cl_2)$] and **11**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.03.020.

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