Synthesis and Characterization of *N*-Heterocyclic Carbene Phospha-Palladacycles and Their Properties in Heck Catalysis†

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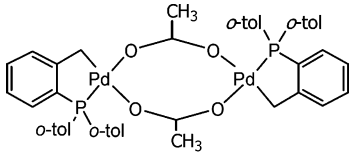
Palladacycles are among the most active catalyst systems for the Mizoroki−Heck reaction to date. We present *N*-heterocyclic carbene (NHC) substituted phospha-palladacycles as a new class of catalysts. This new type of palladacycles combines the advantageous stability of phospha-palladacycles with the steric demand and high σ-donor strength of *N*-heterocyclic carbenes. In this work NHC-substituted phospha-palladacycles are tested in Heck catalysis. The activity of these catalysts allows the coupling of even aryl chlorides in good yields.

Introduction

Since its discovery in 1971 the Mizoroki−Heck reaction has developed into a standard method of C−C coupling, for instance styrene derivatives and iodo- or bromoarenes.[1,2] However, to date it remains a challenge to submit inexpensive chloroarenes to the Heck olefination.[3] Important classes of catalysts for the transformation of these unreactive reagents are palladacycles, such as **1**. Palladium(II) complexes containing a cyclopalladated (di-*o*-tolylphosphino)benzyl fragment were first characterized by Shaw,[4] Mason,[5] Aleya,[6] and Heck,[7] e.g., *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II). They were intensely investigated in our group[8] and promised to be excellent catalysts in Heck-type reactions.



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Reviews by Pfeffer[9] and Bedford[10] demonstrate their high air-, moisture-, and thermal-stability (stable up to 250 °C) for processes such as Heck and Suzuki catalyses. Milstein[11] performed efficient Heck catalysis with an *ortho*-metalated Pd(II) complex, in which an aromatic carbon atom adjacent to a functional group binds to the metal center. Bedford published in 1998 the *N*-palladacycle **20**[12] and another palladacycle system that contains phosphites coordinated to a Pd(II) species.[13]

However, the high price associated with bulky tertiary phosphines and difficulties to remove the ligands and their degradation byproducts have encouraged many research groups to explore alternatives for phosphines, such as *N*-heterocyclic carbenes (NHCs).[14] The NHCs have the advantage of being better σ-donors than phosphines, rendering the oxidative addition of aryl

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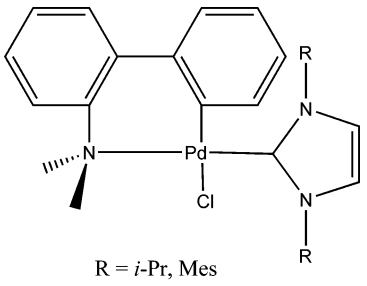
halides to palladium facile.[15b,16] A second advantage is that no excess of NHC ligands is necessary during the catalysis. Furthermore NHCs allow an easy elimination of the coupling product because of their steric demand brought about by the presence of bulky substituents.[15b]

Recently, a combination of a palladacycle framework and a NHC has been reported by Reisinger.[17] This catalyst combines the stability induced by the presence of a palladacycle framework with the high activity commonly associated with palladium-phosphine complexes. The NHC-substituted phospha-palladacycles show extreme high thermostability.

In 2003 Nolan et al. published NHC-modified *N*-palladacycles **2** as good catalysts in the Suzuki–Miyaura cross-coupling and the reaction of aryl halides with amines.[15]



R = *i*-Pr, Mes

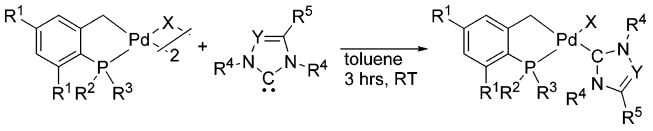
2

A disadvantage of these nitrogen-palladacycles is proposed in the catalyst activation pathway, which assumes a decomposition of the palladacycle to obtain the catalytically active Pd(0)-imidazolin-2-ylidene species. Because of the high stability of phospha-palladacycles, the work of Reisinger[17] is now continued by varying the carbenes and the palladacycles to investigate their chemical properties.

Results and Discussion

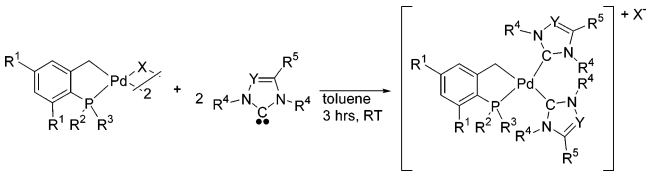
During the preparation of *N*-heterocyclic carbene-substituted palladacycles we obtained three different substitution patterns, depending on the bulkiness of the azoline-ylidenes (Table 1, Table 2, Scheme 1). Bulky substituents such as adamantyl, mesityl, or *tert*-butyl groups in the 1,3-position of the imidazolin-2-ylidenes give a monosubstituted NHC-palladium complex by cleaving the acetate bridge of the dimeric palladacycle during the reaction (Table 1). The end of the reaction can be monitored via ^{31}P NMR; for example in reaction 4 (Table 1) the signal of the starting material (34.2 ppm) decreases and a new signal at 26.8 ppm appears. All these monocarbene-substituted complexes are soluble in nonpolar solvents such as toluene, and the carbene coordinates in most cases *cis* and *trans* to the phosphine ligand.

Table 1. Synthesis of Monosubstituted NHC-Palladacycles



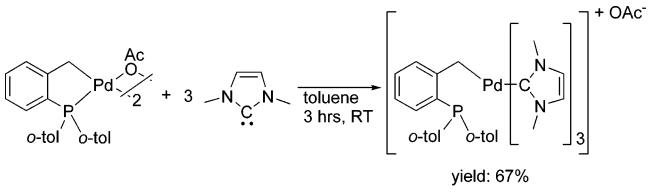
complex	R_1	R_2	R_3	R_4	R_5	Y	X	yield [%]
3	H	*o*-tol	*o*-tol	Ad	H	CH	OAc	89
4	H	*o*-tol	*o*-tol	*t*-Bu	H	CH	OAc	93
5	H	*o*-tol	*o*-tol	Mes	H	CH	OAc	84
6	H	*o*-tol	*o*-tol	Ph	Ph	N	OAc	92
7	H	*o*-tol	*t*-Bu	Mes	H	CH	OAc	83
8a	H	*o*-tol	*t*-Bu	Ph	Ph	N	OAc	93
9	H	*o*-tol	Cy	Ph	Ph	N	OAc	82
10	H	Cy	Cy	Ph	Ph	N	Br	77
11	CH_3	Mes	Mes	Mes	H	CH	Br	74
12	CH_3	Mes	Mes	Ph	Ph	N	OAc	65

Table 2. Synthesis of Complexes 8b, 13, and 14



complex	R_1	R_2	R_3	R_4	R_5	Y	X	yield [%]
8b	H	*o*-tol	*t*-Bu	Ph	Ph	N	OAc	86
13	H	*o*-tol	*o*-tol	Cy	H	CH	OAc	84
14	H	Cy	Cy	Cy	H	CH	Br	93

Scheme 1. Synthesis of Complex 15



1 **15**

Complex **6** can be obtained after recrystallization from dichloromethane/*n*-pentane as a colorless crystalline material. The X-ray single-crystal diffraction study of **6** reveals a *trans*-conformation of the NHC ligand to the phosphorus (Figure 1). The ^{13}C NMR spectrum showed that the typical *cis*–*trans* product mixture was obtained during the preparation of this complex.

If palladacycle **1** is treated with 2 equiv of a less sterically hindered carbene such as 1,3-dicyclohexylimidazolin-2-ylidene, the ionic product with two carbene ligands and a cyclopalladated phosphine forms (Table 2). The acetate ion acts as a counterion in the outer-space ligand sphere. These complexes are on one hand less soluble in toluene and are obtained during the reaction as light yellow precipitates (**8b**, **13**, **14**). On the other hand, their solubility in polar solvents such as acetone or THF is very good. The complexes can be purified by extraction of the obtained residue with *n*-hexane and toluene. The dicarbene palladium complexes are light-, air-, and moisture-stable.

Suitable pale yellow crystals of complex **13** for X-ray diffraction were obtained by slow evaporation of a saturated acetone/4-hydroxy-4-methyl-2-pentanone solution. The X-ray single-crystal diffraction study of **13** reveals a slightly distorted square-planar structure (Figure 2). The coordination of two carbenes at one metal center is an excellent example to demonstrate

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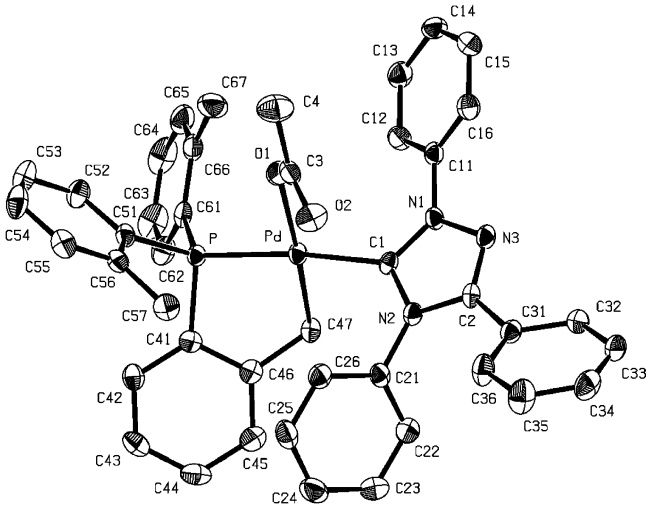


Figure 1. ORTEP style plot of compound **6** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd−P 2.2910(5), Pd−O1 2.097(2), Pd−C1 2.046(2), Pd−C47 2.058(2), C1−N1 1.329(3), C1−N2 1.369(3); P−Pd−O1 94.16(4), P−Pd−C1 173.58(6), P−Pd−C47 81.51(6), O1−Pd−C1 91.45(7), O1−Pd−C47 175.25(7), C1−Pd−C47 92.98(8), N1−C1−N2 103.4(2).

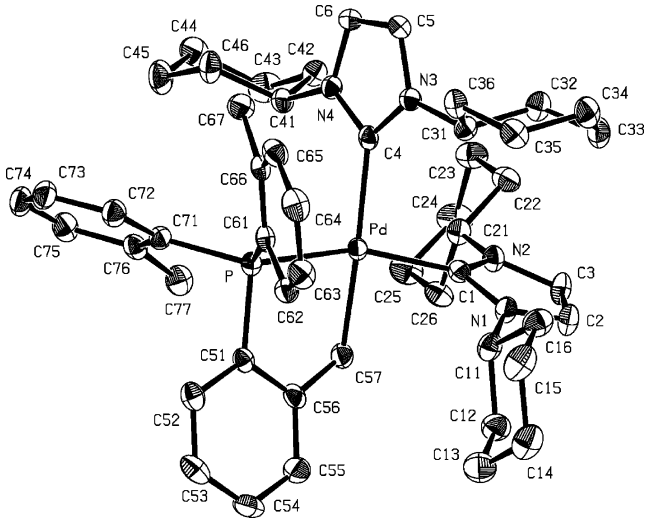
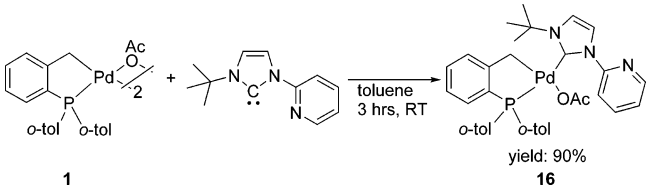


Figure 2. ORTEP style plot of the cationic part of compound **13**·($C_6H_{12}O_2$) in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd−P 2.3259(7), Pd−C1 2.048(2), Pd−C4 2.123(2), Pd−C57 2.089(2), C1−N1 1.361(3), C1−N2 1.349(3), C4−N3 1.359(3), C4−N4 1.362(3); P−Pd−C1 156.69(7), P−Pd−C4 99.11(6), P−Pd−C57 82.72(6), C1−Pd−C4 97.91(9), C1−Pd−C57 82.62(9), C4−Pd−C57 172.05(9), N1−C1−N2 104.8(2), N3−C4−N4 103.3(2).

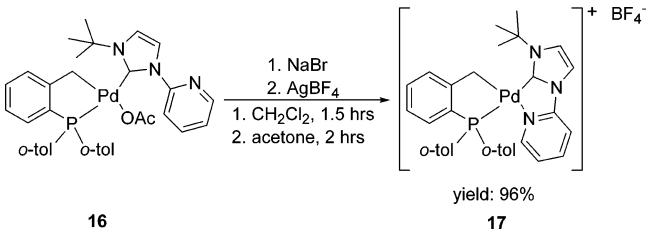
that NHC ligands are much stronger ligands than acetate. There will always be a coordination of two NHCs to the palladium center if the steric demand of the ligands allows such a conformation.

Treating palladacycle **1** with 3 equiv of 1,3-dimethylimidazolin-2-ylidene results in the formation of a new complex, **15** (Scheme 1), as a yellow precipitate in 67% yield. Mass spectroscopy and NMR indicate a 3:1 ratio of NHC ligand to palladacycle in the newly formed complex. We propose that in complex **15** the P−Pd bond

Scheme 2. Preparation of Complex 16



Scheme 3. Preparation of Complex 17



is cleaved and another NHC coordinates to the palladium. This assumption is supported by ^{31}P NMR: a singlet appears at −26.31 ppm in benzene and small amounts of free P(*o*-tol)$_3$ are formed during the reaction by decomposition of the palladacycle at −29.01 ppm. Because of the lower steric demand of 1,3-dimethylimidazolin-2-ylidene, three carbenes can coordinate at the palladium center.

If the bidentate carbene (3-(*tert*-butyl)-1-(2-pyridyl)-imidazolin-2-ylidene) is added to palladacycle **1**, a monocarbene species forms (Scheme 2). However, without the exchange of the anion from a coordinating to a weakly coordinating ion such as BF_4^-, the pyridine substituent does not coordinate to the metal center.

Complex **16** can be obtained after recrystallization from dichloromethane/*n*-pentane as colorless crystalline material in 90% yield. The crystal structure of complex **16** is shown in Figure 3.

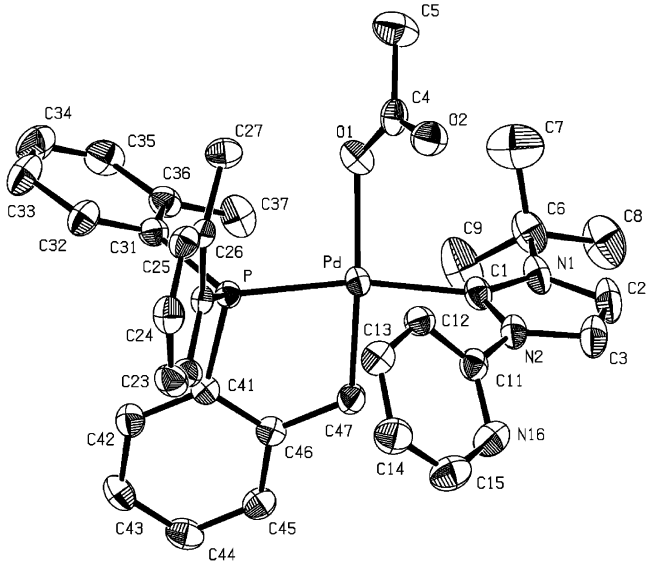


Figure 3. ORTEP style plot of compound **16** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd−P 2.2666(6), Pd−O1 2.122(2), Pd−C1 2.070(2), Pd−C47 2.058(3), C1−N1 1.354(3), C1−N2 1.365(3); P−Pd−O1 94.95(5), P−Pd−C1 165.55(7), P−Pd−C47 83.49(7), O1−Pd−C1 96.04(9), O1−Pd−C47 169.41(9), C1−Pd−C47 87.4(1), N1−C1−N2 104.1(2).

Scheme 4. Preparation of Complexes 19a and 19b

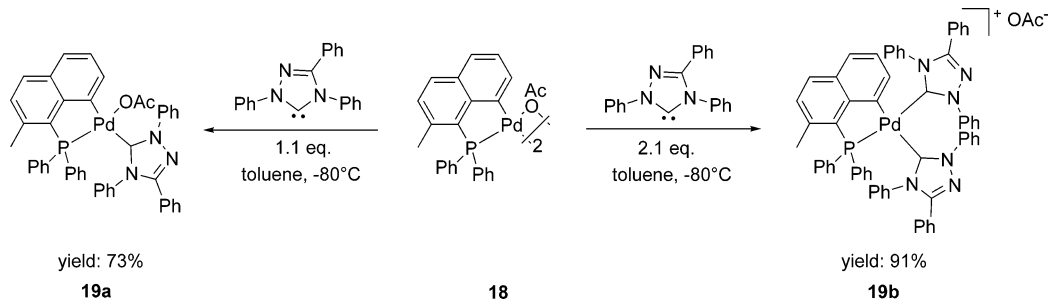
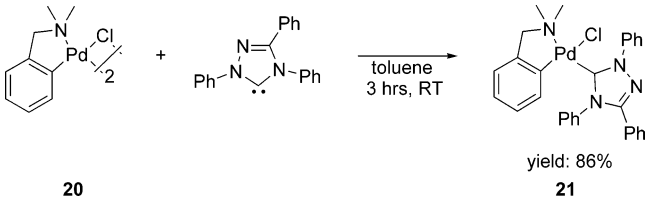


Table 3. Selected Bond Distances (pm) and Bond Angles (deg) for the Prepared Palladacycles

complex	N−$C_{carbene}$−N angle (deg)	Pd−$C_{carbene}$ (pm)	P−Pd−$C_{carbene}$ angle (deg)	C−Pd−O($C_{carbene}$) angle (deg)
6	103.4(2)	204.6(2)	173.58(6)	175.25(7)
13	104.8(2)	204.8(2)	156.69(7)	172.05(9)
	103.3(2)	212.3(2)		
16	104.1(2)	207.0(2)	165.55(7)	169.41(9)

Scheme 5. Preparation of Complex 21



An exchange of the acetate of complex **16** by a bromide anion introduces BF_4^- via $AgBF_4$ in a two-step reaction. This creates a new open coordination side at which the nitrogen atom of the pyridine ring coordinates in complex **17** and the BF_4^- ion acts as a counterion in the outer-space ligand sphere. (Scheme 3). Complex **17** was obtained as a white solid in 96% yield.

The *ortho*-metalated naphthyl-phospha-palladacycle **18** was prepared according to the literature[18] and treated with 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene to form complexes **19a**,**b** (Scheme 4). When 1.1 equiv of carbene was applied, complex **19b** was also formed as a byproduct. If the temperature during the addition of 1.1 equiv of carbene was reduced to −78 °C, the amount of byproduct **19b** was minimized. However, addition of 2.1 equiv of free carbene resulted in complex **19b** in almost quantitive yield over complex **19a**, which is formed as an intermediate.

Furthermore a NHC-*N*-palladacycle **21** was prepared (Scheme 5), by treating palladacycle **20**, which was first published by Bedford,[12] with the free triazolin-5-ylidene to obtain complex **21** as a white solid in 86% yield.

Crystal Structure Discussion

The molecular structures of the complexes **6**, **13**, and **16** in the solid state are depicted in Figure 1, 2, and 3. A selection of characteristic bond angles and bond distances are given in Table 3. Crystal data and details of the structure determination of the three crystal structures are presented in Table 6.

The favored square-planar coordination sphere of the palladium center is best accomplished in complex **6**, in contrast to complex **16**, which has a disturbed square-planar coordination.

The palladium−carbene bond length is in all complexes in the range of Pd(0) and Pd(II) complexes reported in the literature.[15b,19] The bond length with more than 204 pm for a palladium−carbene bond in these complexes is longer than the ones reported for Pd(II) complexes (195−200 pm) in the literature. [20] This effect can be explained by the bulkiness of the coordinated phosphine. Another not neglected possibility is the coordinated metalated carbanion of the benzyl group. This carbanionic species can charge electron density to the palladium atom, to reduce the electron deficit at the metal atom.[18] The fact that the two carbene−Pd bonds in complex **13** are not equal is an indication of the steric demand of the system and the *trans*-effect of the metalated carbanion The carbene−Pd distance of 212.3(2) pm for the carbene coordinated *trans* to the carbanion is in the region of Pd(0)−carbene bonds.[19] The two NHC ligands are coordinated perpendicular to each other to minimize the steric hindrance at the palladium center and to minimize the sterical hindrance between the cyclohexyl ring (C41−C46) and the *ortho*-tolyl group (C61−C67) of the phosphine. The phosphine−palladium bond in the complexes **6**, **13**, and **16** is in the range of Pd(II)−P complexes (224−235 pm) with 226.66(6) pm for complex **16**, 229.10(5) pm for **6**, and 232.59(7) pm for **13**.[21]

The methyl groups of the tolyl rings are directed to the palladium, which is in agreement with analogous X-ray crystal structures in the literature.[4,6−8] In all complexes the N−C−N angles of the carbene ligands

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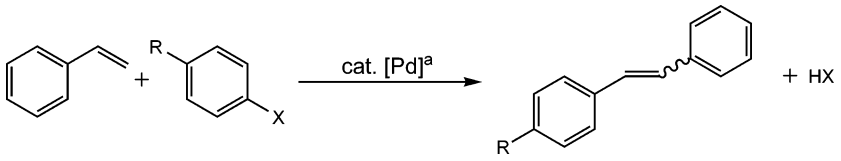
Table 4. Heck Olefination of Aryl Halides with Styrene and Palladacycles 6, 7, 10, 13, 14, 16, and 21 as Catalysts



entry	R	X	base	catalyst	cocatalyst	mol %	yield (%)[b]	*trans*/*cis*
1	$C(O)CH_3$	Br	NaOAc	**6**	NBu_4Br	1	100	18.61
2	$C(O)CH_3$	Br	NaOAc	**6**	NBu_4Br	0.1	70	10.68
3	$C(O)CH_3$	Br	NaOAc	**6**		1	59	16.65
4	$C(O)CH_3$	Br	Cs_2CO_3	**6**	NBu_4Br	1	64	5.10
5	H	Br	NaOAc	**6**	NBu_4Br	1	96	5.31
6	H	Br	NaOAc	**6**		1	40	12.65
7	H	Br	Cs_2CO_3	**6**	NBu_4Br	0.1	51	12.95
8	OCH_3	Br	NaOAc	**6**	NBu_4Br	1	92	7.23
9	OCH_3	Br	NaOAc	**6**		1	15	1.15
10	OCH_3	Br	Cs_2CO_3	**6**	NBu_4Br	1	41	11.97
11	$C(O)CH_3$	Cl	NaOAc	**6**	NBu_4Br	1	33	14.82
12	$C(O)CH_3$	Cl	NaOAc	**6**		1	1	no *cis*
13	$C(O)CH_3$	Cl	Cs_2CO_3	**6**	NBu_4Br	1	73	84.21
14	$C(O)CH_3$	Cl	$Ca(OH)_2$	**6**	NBu_4Br	1	31	23.82
15	$C(O)CH_3$	Cl	$Ca(OH)_2$	**6**		1	34	25.36
16	$C(O)CH_3$	Br	NaOAc	**7**	NBu_4Br	1	85	11.11
17	$C(O)CH_3$	Br	NaOAc	**7**		1	82	9.88
18	$C(O)CH_3$	Br	Cs_2CO_3	**7**	NBu_4Br	1	58	10.35
19	OCH_3	Br	NaOAc	**7**	NBu_4Br	1	77	7.39
20	OCH_3	Br	NaOAc	**7**		1	48	8.45
21	$C(O)CH_3$	Cl	$Ca(OH)_2$	**7**	NBu_4Br	1	63	32.83
22	$C(O)CH_3$	Cl	$Ca(OH)_2$	**7**		1	36	68.23
23	$C(O)CH_3$	Cl	Cs_2CO_3	**7**	NBu_4Br	1	28	49.12
24	$C(O)CH_3$	Cl	NaOAc	**7**	NBu_4Br	1	10	23.16
25	$C(O)CH_3$	Cl	NaOAc	**7**		1	5	no *cis*
26	$C(O)CH_3$	Br	NaOAc	**10**	NBu_4Br	1	81	16.47
27	$C(O)CH_3$	Br	NaOAc	**10**		1	91	18.01
28	OCH_3	Br	Cs_2CO_3	**10**	NBu_4Br	1	0	
29	H	Br	NaOAc	**13**		1	0	
30	OCH_3	Br	NaOAc	**14**	NBu_4Br	1	6	no *cis*
31	OCH_3	Br	NaOAc	**14**		1	18	12.02
32	OCH_3	Br	$Ca(OH)_2$	**14**	NBu_4Br	1	23	14.05
33	OCH_3	Br	$Ca(OH)_2$	**14**		1	54	9.20
34	$C(O)CH_3$	Cl	Cs_2CO_3	**14**	NBu_4Br	1	0	
35	$C(O)CH_3$	Cl	NaOAc	**14**	NBu_4Br	1	13	8.71
36	$C(O)CH_3$	Cl	NaOAc	**14**		1	0	
37	$C(O)CH_3$	Cl	$Ca(OH)_2$	**14**	NBu_4Br	1	15	28.24
38	$C(O)CH_3$	Cl	$Ca(OH)_2$	**14**		1	32	34.82
39	$C(O)CH_3$	Br	NaOAc	**16**	NBu_4Br	1	95	13.17
40	$C(O)CH_3$	Br	NaOAc	**16**		1	34	31.04
41	$C(O)CH_3$	Br	Cs_2CO_3	**16**	NBu_4Br	1	52	no *cis*
42	OCH_3	Br	NaOAc	**16**		1	7	8.27
43	$C(O)CH_3$	Cl	Cs_2CO_3	**16**	NBu_4Br	1	54	no *cis*
44	$C(O)CH_3$	Br	NaOAc	**21**	NBu_4Br	1	97	15.56
45	$C(O)CH_3$	Br	NaOAc	**21**		0.01	92	14.00
46	$C(O)CH_3$	Br	Cs_2CO_3	**21**	NBu_4Br	1	85	4.06
47	H	Br	NaOAc	**21**		1	40	11.35
48	OCH_3	Br	NaOAc	**21**	NBu_4Br	1	58	6.70
49	OCH_3	Br	NaOAc	**21**		1	79	8.16
50	OCH_3	Br	Cs_2CO_3	**21**	NBu_4Br	1	81	no *cis*
51	OCH_3	Br	Cs_2CO_3	**21**		1	55	17.20
52	$C(O)CH_3$	Cl	NaOAc	**21**	NBu_4Br	1	4	no *cis*
53	$C(O)CH_3$	Cl	K_2CO_3	**21**	NBu_4Br	1	8	no *cis*
54	$C(O)CH_3$	Cl	Cs_2CO_3	**21**	NBu_4Br	1	21	no *cis*
55	$C(O)CH_3$	Cl	Cs_2CO_3	**21**		1	21	no *cis*
56	$C(O)CH_3$	Cl	$Ca(OH)_2$	**21**	NBu_4Br	1	70	20.98
57	$C(O)CH_3$	Cl	$Ca(OH)_2$	**21**		1	97	24.61

[a] One equiv of aryl halide, 1.5 equiv of styrene, 1.5 equiv of base, 20 mol % of cocatalyst, dimethylacetamide (DMAc), $T = 130$ °C, $t = 14$ h. [b] GC yields using diethyleneglycol-di-*n*-butyl ether as the internal standard.

are in accordance with coordinated imidazole or triazole rings reported in the literature.[15b,19]

Catalysis

The palladium-catalyzed coupling of arenes and olefins is known as the Mizoroki−Heck reaction.[1,2b,22] Regularly, aryl halides are used as the arene source.[23] Aryl olefins are frequent building blocks for pharmaceuticals,[24] for fine chemicals,[25] and for building blocks of polymers,[26] making the Mizoroki−Heck reaction one of the most important synthetic methods.[2b]

The activity of nitrogen-palladacycles is comparable to phospha-palladacycles when both are NHC-substi-

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Table 5. Determination of Turnover Numbers[a] in the Heck Olefination of Different Aryl Halides with Styrene and Palladacycles 6, 7, and 21 as Catalysts

entry	R	X	base	catalyst	cocatalyst	mol %	yield (%)[b]	TON[c]
1	$C(O)CH_3$	Br	NaOAc	**6**	NBu_4Br	2.5×10^{-4}	86	343 000
2	H	Br	NaOAc	**6**	NBu_4Br	2.0×10^{-3}	79	39 600
3	$C(O)CH_3$	Cl	Cs_2CO_3	**6**	NBu_4Br	2.0×10^{-3}	22	10 800
4	$C(O)CH_3$	Br	NaOAc	**7**	NBu_4Br	1.6×10^{-4}	18	109 000
5	H	Br	NaOAc	**7**	NBu_4Br	1.6×10^{-3}	8	4900
6	$C(O)CH_3$	Br	NaOAc	**21**	NBu_4Br	1.6×10^{-4}	89	533 000
7	H	Br	NaOAc	**21**	NBu_4Br	1.6×10^{-3}	7	4200

[a] One equiv of aryl halide, 1.5 equiv of styrene, 1.5 equiv of base, 20 mol % of cocatalyst, dimethylacetamide (DMAc), $T = 130$ °C, $t = 72$ h. [b] GC yields using diethyleneglycol-di-*n*-butyl ether as the internal standard. [c] (mol product)/(mol Pd).

Table 6. Crystallographic Data for Compounds 6, 13·($C_6H_{12}O_2$), and 16

	6	**13**·($C_6H_{12}O_2$)	**16**
formula	$C_{43}H_{38}N_3O_2PPd$	$C_{59}H_{83}N_4O_4PPd$	$C_{35}H_{38}N_3O_2PPd$
fw	766.15	1049.68	670.07
color/habit	colorless/fragment	pale yellow/fragment	colorless/needle
cryst dimens (mm^3)	$0.20 \times 0.30 \times 0.84$	$0.20 \times 0.23 \times 0.30$	$0.08 \times 0.10 \times 0.43$
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	*Pbca* (no. 61)
a, Å	10.4761(1)	10.6600(1)	12.6248(1)
b, Å	12.1957(1)	13.4585(2)	17.9528(1)
c, Å	16.3896(1)	38.2426(9)	27.0927(2)
α, deg	109.4464(4)	90	90
β, deg	92.8248(4)	94.103(1)	90
γ, deg	112.4486(3)	90	90
V, $Å^3$	1787.13(3)	5472.51(16)	6140.57(7)
Z	2	4	8
T, K	123	123	173
D_{calcd}, g cm^{-3}	1.424	1.274	1.450
μ, mm^{-1}	0.606	0.417	0.693
$F(000)$	788	2232	2768
θ range, deg	1.90−25.33	1.60−25.34	4.10−25.37
index ranges (h, k, l)	±12, ±14, ±19	±12, ±16, ±46	±15, ±21, ±32
no. of rflns collected	40 884	83 297	136 328
no. of indep rflns/R_{int}	6532/0.036	9981/0.039	5611/0.058
no. of obsd rflns ($I > 2\sigma(I)$)	5888	7779	4793
no. of data/restraints/params	6532/0/603	9981/0/630	5611/0/531
R1/wR2 ($I > 2\sigma(I)$) [a]	0.0250/0.0563	0.0350/0.0753	0.0291/0.0679
R1/wR2 (all data) [a]	0.0303/0.0583	0.0554/0.0813	0.0384/0.0717
GOF (on F^2)[a]	1.050	1.023	1.035
largest diff peak and hole, e $Å^{-3}$	+0.77/−0.40	+0.65/−0.42	+0.64/−0.51

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

tuted. The tested nitrogen-palladacycle is the only one that coupled a chloroarene in quantitative yield. However, during catalysis with nitrogen-palladacycles palladium black is formed, in contrast to the tested phospha-palladacycles. Leaching of the phospha-palladacycles is nonexistent.

As reported earlier, the addition of NBu_4Br as a cocatalyst increases the activity of most catalytic system.[4c,8a−d,13c,27,28] The use of the base Cs_2CO_3 is not favorable to NaOAc for the coupling of bromoacetophenone. However, in the case of chloroarenes $Ca(OH)_2$ proves to be the best base, followed by Cs_2CO_3 and NaOAc. Application of $Ca(OH)_2$ resulted in the only catalytic system that was not improved by the cocatalyst NBu_4Br. There is no general prediction possible whether a certain base or the addition of a cocatalyst gives better results or not. For instance, the tested nitrogen-palladacycle **21** shows a lower activity than complexes **6** and **7** for the coupling of chloroacetophenone when Cs_2CO_3 and NBu_4Br were added. Nevertheless complex **21** is superior to all tested catalysts when $Ca(OH)_2$ and no cocatalyst were added. Introducing two carbene ligands to the palladacycle leads to ionic dicarbene palladacycles, which are far less active than mono-carbene palladacycles. Again, an optimization of the reaction conditions also for dicarbene palladacycles results in higher yields, whereas our chosen standard conditions gave very few or no product.

Compared to the results for the Mizoroki−Heck reaction of complex **18**,[29a] the carbene-substituted complexes **6**, **7**, and **21** show a much higher yield and TON [mol product per mol catalyst]. Dicarbene complexes such as **8b**, **13**, **14**, and **19b** did not show high catalytic

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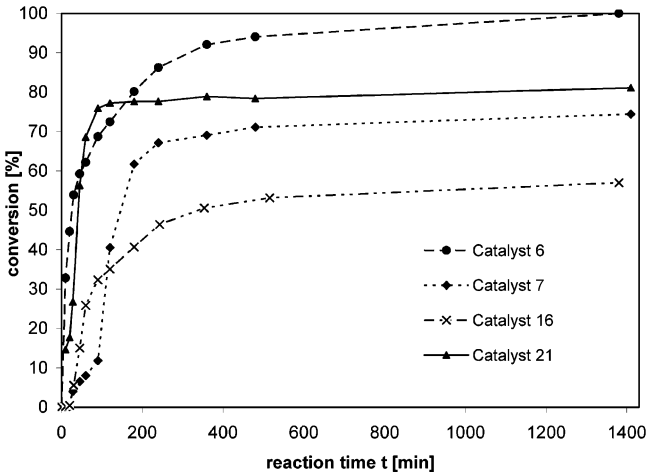

Figure 4. Diagram of the conversion [in %] vs reaction time (t) of the Heck olefination of 4-bromoanisole with styrene at 130 °C to form 4-methoxystilbene. 1 equiv of 4-bromoanisole, 1.5 equiv of styrene, 1.5 equiv of NaOAc, 1 mol % catalyst, dimethylacetamide, $T = 130$ °C.

activity in the Heck coupling experiments[29] and were not further investigated in this work.

The best performance was expected for the monosubstituted carbene complexes, with sterically bulky substituents at the nitrogens of the carbene ligand. Another influence should be the basicity of the phosphine group. We found in the past that a lower basicity of the phosphine group increases the catalytic activity.[8] Therefore we tried to use mostly complexes with low basicity, for instance phenyl groups at the phosphine. A TON of more than 10 000 for the coupling of chloroacetophenone with styrene is one of the best TONs for phospha-palladacycle-catalyzed Heck reactions.

The *N*-palladacycle **21** shows a very high TON of up to 533 000 for the activated substrate bromoacetophenone. However, for less active aryl halides the TON is lower than the other two phospha-palladacycles (**6**, **7**), which were tested for TON determination. These phospha-palladacycles gave TONs of up to 343000, although the reaction conditions are not optimized yet. For activated bromoaryls there are much better catalysts described in the literature than the catalysts prepared in this work.[8] The great advantage of catalyst **6** is the possibility of coupling an activated aryl chloride with styrene with a TON of 10 800 at 130 °C.[29] In comparison, complex **1** gives under these conditions a TON of only 690. Such a high TON for the CC coupling of chloroarenes with styrene is known only from a pincer-type palladium catalyst at a much higher temperature (180 °C).[30] Recently a TON of 3500 was obtained in our group with acetylacetonate-substituted phosphapalladacycles.[18]

In Figure 4 the catalytic properties of complexes **6**, **7**, **16**, and **21** are monitored in the Heck olefination of bromoanisole with styrene via a reaction profile of bromoanisole. Complex **6** shows the shortest induction period and a complete conversion of bromoanisole. Other good catalysts are complexes **7** and **21**, which convert bromoanisole between 70 and 80%. Compared to complex **21**, complex **7** has a much longer induction period of 45 min, but after this induction period catalyst **7** shows a high TOF of 55 min^{-1}. Catalysts **6**, **7**, and **16** can be recovered after the reaction as halide-substituted phosphapalladacycles. When catalyst **21** was used, only palladium black was obtained. The longer induction period of catalyst **7** compared to catalyst **6** is due to the *tert*-butyl group of the phosphine. Because of the alkyl group, the phosphine is more basic than an aryl phosphines, whereby the oxidation state of palladium(II) is thermodynamically stabilized by the strong σ-donor ability of the alkyl groups.[31]

Conclusion

NHC-phospha-palladacycles constitute a new class of well-defined catalysts or efficient catalyst precursors for the Heck olefination of haloarenes. An improved catalyst efficiency compared to all previously described homogeneous palladium-containing catalysts has been realized for the reactions with deactivated aryl bromides and activated aryl chlorides. The advantage of the new phosphapalladacycles is the possibility of coupling 4-chloroacetophenone with styrene in a very high TON of 10 800. An optimized carbene-substituted phosphapalladacycle should be a mono-carbene-substituted complex with a good σ-donor NHC ligand and bulky groups at the nitrogens of the heterocycle. Also a less basic cyclometalated phosphine has a positive effect and increases the catalytic activity.

Experimental Section

General Considerations. The imidazolium salts and corresponding carbenes were prepared according to reported procedures. The free carbene (1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene) was prepared according to the literature.[32]The palladacycle dimer precursors were synthesized as reported in the literature.[8,12]

^{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, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. GC-MS spectra were measured on a Hewlett-Packard GC 5890 A gas chromatograph equipped with a MS 5970 B mass selective detector. Quantitative analyses were performed on a Hewlett-Packard GC 5890 A equipped with a flame ionization detector (GC/FID).

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.

General Procedure for the Mizoroki−Heck Reaction. The base (1.5 mmol) and tetrabutylammonium bromide (0.2 mmol), in the cases when it was used, were placed in a Schlenk tube equipped with a stirring bar. The flask was put under an atmosphere of argon, and aryl halide (1.0 mmol), styrene (156 mg, 170 mL, 1.5 mmol), 50 mg of diethyleneglycol-di-*n*-butyl ether, and 2 mL of degassed DMAc (dimethylacetamide) were added. After thermostating at 130 °C for 10 min the catalyst was added against a positive stream of argon. To

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determine the yield, the mixture was stirred for 14 h. To finish the reaction, the mixture was allowed to cool to room temperature and 3 mL of 1 M HCl (aq) was added. The aqueous phase was extracted three times with 2 mL of dichloromethane, the combined organic phases were dried over $MgSO_4$, and the solution was analyzed on a gas chromatograph.

Preparation of Complexes 3−8a, 9−12, 16, and 19a. The free carbene (0.55 mmol) and the palladacycle dimer (0.25 mmol) were each dissolved in dry toluene (10 mL) and cooled to −80 °C. The carbene solution was slowly added via a syringe to the palladacycle solution, slowly heated to room temperature, and stirred for 3 h. The solvent was removed in a vacuum, and the remaining solid was washed twice with anhydrous *n*-hexane.

Acetato(1,3-diadamantylimidazolin-2-ylidene)[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (3). Yield: 89%. ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ 6.69−7.27 (14H, m), 3.22 (1.5H, s, CH_3(*cis*/*trans*)), 3.10 (1.5H, s, CH_3(*cis*/*trans*)), 2.91 (4H, m), 2.72 (6H, d, $^3J_{HH}$ = 11.2 Hz), 2.56 (4H, d, $^3J_{HH}$ = 10.0 Hz), 2.07 (3H, s, CH_3), 1.93 (3H, s, CH_3), 1.46−1.58 (6H, m), 1.38 (12H, s). ^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ 177.2 (s, *C*O_2CH$_3$), 175.8 (s, N*C*N), 161.9 (d, J_{PC} = 43.0 Hz), 133.7, 132.5, 132.1, 131.7, 131.3, 130.9, 130.4, 130.0, 126.6 (d, J_{PC} = 5.5 Hz), 125.4 (d, J_{PC} = 6.8 Hz), 124.9 (d, J_{PC} = 6.1 Hz), 117.2 (d, J = 37.5 Hz, N*CHCH*N,), 59.3 (d, J = 30.6 Hz, Ad), 44.3 (d, J = 17.6 Hz), 37.2, 35.9 (*C*H$_2$), 30.4 (d, J = 9.0 Hz), 24.0 (d, J = 6.9 Hz, CO$_2$*C*H$_3$), 23.2 (d, J_{PC} = 13.0 Hz, *C*H$_3$), 21.3 (d, J_{PC} = 7.1 Hz, *C*H$_3$). ^{31}P{^{1}H} NMR (161 MHz, 300 K, C_6D_6): δ 25.33 (s). MS (FAB) *m/z* (%): 745.5 (40, [M$^+$ − OAc]), 441.3 (14, [Pd + carbene]), 409.1 (9, [M$^+$ − (OAc + carbene)]), 337.4 (68, [carbene]), 135.1 (100). Anal. Calcd for $C_{46}H_{55}N_2O_2PPd$ (805.33 g mol^{-1}): C, 68.60; H, 6.88; N, 3.48. Found: C, 68.46; H, 6.92; N, 3.63.

Acetato(1,3-di-*tert*-butylimidazolin-2-ylidene)[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (4). Yield: 93%. ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ 7.39−7.29 (4H, m), 7.11 (2H, m), 7.00 (2H, t, $^3J_{HH}$ = 7.6 Hz), 6.92−6.84 (3H, m), 6.74 (1H, t, $^3J_{HH}$ = 7.6 Hz), 6.57 (2H, s, N*CHCH*N), 3.25 (3H, s, CO$_2$*C*H$_3$), 2.70 (1H, d, $^3J_{HH}$ = 15.2 Hz, C*H*$_2$), 2.19 (1H, d, $^3J_{HH}$ = 14.8 Hz, C*H*$_2$), 1.84 (3H, s, C*H*$_3$), 1.69 (3H, s, C*H*$_3$), 1.26 (18H, s, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ 177.5 (s, N*C*N), 174.6 (s, *C*O$_2$CH$_3$), 160.5 (d, *C*$_{Ar}$, J_{PC} = 36.8 Hz), 143.6, 143.2, 133.4, 132.8, 132.2, 131.4 (d, *C*$_{Ar}$, J_{PC} = 7.2 Hz), 130.6, 130.5 (d, *C*$_{Ar}$, J_{PC} = 2.3 Hz), 129.9, 126.6, 125.5 (d, *C*$_{Ar}$, J_{PC} = 7.4 Hz), 118.0 (d, J = 3.6 Hz, N*CHCH*N), 58.6 (s, N*C*(CH$_3$)$_3$), 31.5 (br s, C(*C*H$_3$)$_3$), 29.7 (s, CH$_2$), 25.7 (d, J_{PC} = 11.9 Hz, CO$_2$*C*H$_3$), 22.5 (br s, *C*H$_{3-tolyl}$), 22.0 (br s, *C*H$_{3-tolyl}$). ^{31}P{^{1}H} NMR (161 MHz, 300 K, $C_6H_5CH_3$): δ 26.75 (s). ^{31}P{^{1}H} NMR (109 MHz, 300 K, C_6D_6): δ 27.97 (s). MS (CI) *m/z* (%): 588.4 (7, [M$^+$ − OAc]), 466.4 (4, [M$^+$ − carbene]), 375.2 (50, [M$^+$ − (carbene + *o*-tolyl)]), 359.3 (100, [M$^+$ − (carbene + *o*-tolyl + CH$_3$)]), 289.3 (61, [Pd + carbene]), 181.4 (10). Anal. Calcd for $C_{34}H_{43}N_2O_2PPd$ (649.11 g mol^{-1}): C, 62.91; H, 6.68; N, 4.32. Found: C, 62.63; H, 6.78; N, 4.45.

Acetato(1,3-dimesitylimidazolin-2-ylidene)[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (5). Yield: 84%. ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ 7.06−6.99 (5H, m), 6.91−6.87 (5H, m), 6.83−6.54 (8H, m), 2.66 (2H, s, C*H*$_2$), 2.41 (3H, s, C*H*$_3$), 2.31 (3H, s, C*H*$_3$), 2.21−1.79 (15H), 2.12 (6H, s). ^{13}C-{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ 188.0 (N*C*N), 172.3 (s, *C*O$_2$CH$_3$), 162.4, 159.1, 143.2, 142.8, 138.4, 137.9, 137.2, 136.7, 136.4, 136.3, 136.1, 135.1, 134.9, 133.5, 133.0, 132.8, 132.4, 132.2, 131.7 (d, J = 2.6 Hz), 130.5 (d, J = 4.7 Hz), 129.7 (d, J = 2.4 Hz), 129.3, 129.1, 129.0, 128.9, 126.9, 126.6, 125.6, 125.4, 124.3 (C$_{Ar}$), 122.1 (N*CHCH*N), 46.5 (*C*H$_2$), 23.7 (d, J = 5.7 Hz), 22.1 (d, J = 4.1 Hz), 21.4, 21.2, 21.1, 21.0, 20.8 (d, J = 4.1 Hz), 18.9, 18.2 (*C*H$_3$). ^{31}P{^{1}H} NMR (161 MHz, 300 K, C_6D_6): δ 30.31. MS (FAB) *m/z* (%): 729.6 (2, [M − COCH$_3$]), 713.6 (30, [M$^+$]), 409.3 (4, [Pd + carbene]), 395.5 (11), 321.3 (17), 305.3 (100, [carbene]). Anal. Calcd for $C_{44}H_{47}N_2O_2PPd$ (773.25 g mol^{-1}): C, 68.34; H, 6.13; N, 3.62. Found: C, 68.03; H, 6.25; N, 3.34.

Acetato(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (6). Yield: 92%. ^{1}H NMR (270 MHz, 300 K, C_6D_6): δ 7.48 (2H, d, $^3J_{HH}$ = 7.2 Hz, Ar), 7.23 (6H, br, Ar), 7.19 (5H, d, $^3J_{HH}$ = 7.3 Hz, Ar), 7.12 (2H, d, $^3J_{HH}$ = 7.3 Hz, Ar), 7.08 (2H, d, $^3J_{HH}$ = 8.1 Hz, Ar), 7.00 (2H, d, $^3J_{HH}$ = 8.8 Hz, Ar), 6.95 (2H, d, $^3J_{HH}$ = 7.3 Hz, Ar), 6.90 (4H, t, $^3J_{HH}$ = 8.1 Hz, Ar), 6.75 (2H, d, $^3J_{HH}$ = 7.2 Hz, Ar), 2.98 (2H, br, C*H*$_2$), 2.75 (3H, br, CO$_2$C*H*$_3$), 2.18 (3H, s, C*H*$_3$), 2.00 (3H, s, C*H*$_3$). ^{13}C{^{1}H} NMR (67.9 MHz, 300 K, C_6D_6): δ 186.0 (d, $^2J_{PC}$ = 96.2 Hz, NCN), 174.0 (*C*O$_2$-CH$_3$), 142.1 (d, $^2J_{PC}$ = 14.7 Hz, *ipso*-C of P-*o*-tol), 142.0 (d, $^2J_{PC}$ = 15.3 Hz, *ipso*-C of P-*o*-tol), 139.3, 136.9 (*ipso*-C of N−Ph), 136.5 (*ipso*-C of C−Ph), 131.5 (d, $^2J_{PC}$ = 11.7 Hz, *ipso*-C of P-*o*-tolyl), 132.9, 132.6, 132.1, 131.9, 131.9, 130.9, 129.3, 128.9 (Aryl), 128.0 (d, $^4J_{PC}$ = 3.3 Hz, *p*-C of P-*o*-tolyl), 127.7, 127.6, 127.5, 127.5, 127.4 (Aryl), 127.1 (d, $^4J_{PC}$ = 2.3 Hz, *p*-C of P-*o*-tolyl), 126.5 (d, $^4J_{CP}$ = 2.8 Hz), 126.3, 126.1, 124.6, 124.5, 124.3, 124.1, 124.1, 123.8, 123.5, 122.6 (Aryl), 105.8 (N*C*PhNPh), 91.6 (*C*H$_2$), 23.3 (*C*H$_3$), 20.0 (*C*H$_3$). ^{31}P NMR (109.1 MHz, 300 K, $C_6H_5CH_3$): δ 29.8 (s). MS (FAB) *m/z* (%): 705.8 (14, [M$^+$ − OAc]), 408.8 (19, [Pd + phosphine]), 401.8 (6, [Pd + carbene]), 298.0 (100, [carbene]). Anal. Calcd for $C_{43}H_{38}N_3O_2PPd$ (766.15 g mol^{-1}): C, 67.41; H, 5.00; N, 5.48. Found: C, 66.16; H, 5.57; N, 7.10.

Acetato(dimesitylimidazolin-2-ylidene)[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]palladium(II) (7). Yield: 83%. ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ 7.28 (1H, d, $^3J_{HH}$ = 7.2 Hz), 7.18 (1H, t, $^3J_{HH}$ = 7.5 Hz), 7.11 (2H, d, $^3J_{HH}$ = 8.0 Hz), 7.04 (1H, d, $^3J_{HH}$ = 6.6 Hz), 7.01 (2H, s), 6.99 (1H, s), 6.83 (1H, t, $^3J_{HH}$ = 6.4 Hz), 6.80 (1H, s), 6.77 (1H, s), 6.62 (1H, m), 6.45 (1H, s), 6.27 (1H, s), 3.08 (2H, s, C*H*$_2$), 2.47 (3H, s,C*H*$_3$), 2.14 (6H, br s), 2.12−2.05 (12H, m), 1.94 (3H, s, CO$_2$C*H*$_3$), 1.34 (9H, m, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ 188.6 (N*C*N), 164.9 (d, *C*O$_2$CH$_3$, J_{PC} = 14.6 Hz), 148.7, 138.4, 138.1, 137.8, 137.3, 137.0, 136.1, 135.6, 135.4, 132.5, 132.1, 131.3, 129.8, 129.4, 129.3, 129.1, 128.8, 128.5, 125.6, 124.3, 123.2, 122.7, 121.8, 121.5 (*C*$_{Ar}$), 120.5 (N*CHCH*N), 35.4 (*C*(CH$_3$)$_3$), 35.2 (br), 28.8 (d, J_{PC} = 6.3 Hz, *C*H$_{3,t-Bu}$), 28.6 (d, J_{PC} = 6.2 Hz, *C*H$_{3,t-Bu}$), 28.1 (d, J_{PC} = 6.3 Hz, *C*H$_{3,t-Bu}$), 22.7 (br, *C*H$_{3,tolyl}$), 21.4, 20.9, 18.5, 17.9 (*C*H$_3$). ^{31}P{^{1}H} NMR (109 MHz, 300 K, C_6D_6): δ 51.55, 46.25 (*cis*/*trans* = 45/55). MS (FAB) *m/z* (%): 679.7 (37, [M$^+$ − OAc]), 395.5 (11), 303.3 (100, [carbene]). Anal. Calcd for $C_{41}H_{49}N_2O_2PPd$ (739.23 g mol^{-1}): C, 66.61; H, 6.68; N, 3.79. Found: C, 66.49; H, 6.63; N, 3.61.

Acetato(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]palladium(II) (8a). Yield: 93%. ^{1}H NMR (270 MHz, 300 K, (CD$_3$)$_2$SO): δ 8.59 (2H, m), 7.81 (2H, m), 7.56−7.03 (16H, m), 6.91 (2H, m), 6.70 (1H, t, $^3J_{HH}$ = 7.8 Hz), 3.34 (2H, s, C*H*$_2$), 2.23 (3H, br s), 2.04 (3H, s), 1.35 (9H, d, $^3J_{HH}$ = 14.6 Hz). ^{13}C-{^{1}H} NMR (67.9 MHz, 300 K, (CD$_3$)$_2$SO): δ 186.6 (N*C*N), 173.9 (s, *C*O$_2$CH$_3$), 156.9, 142.0, 139.0, 136.5, 131.8 (d, J_{PC} = 2.6 Hz), 131.2, 130.9 (d, J_{PC} = 3.1 Hz), 130.1, 129.3, 128.9, 128.7, 128.3, 128.1, 124.8 (d, J_{PC} = 6.7 Hz), 123.8, 123.1 (*C*$_{Ar}$), 41.3 (*C*(CH$_3$)$_3$), 33.7 (d, J_{PC} = 12.7 Hz, *C*H$_2$), 27.8 (m, *C*H$_3$), 25.3 (*C*H$_{3,tolyl}$), 22.2 (d, J_{PC} = 12.4 Hz, CO$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (109 MHz, 300 K, (CD$_3$)$_2$SO): δ 58.14 (s), 57.42 (s) (*I* = 59/41). ^{31}P{^{1}H} NMR (161 MHz, 300 K, $C_6H_5CH_3$): δ 57.09 (s), 56.40 (s). MS (FAB) *m/z* (%): 672.6 (62, [M$^+$ − OAc]), 402.3 (6), 388.4 (27), 375.3 (20), 298.3 (100, [carbene]). Anal. Calcd for $C_{40}H_{40}N_3O_2PPd$ (732.18 g mol^{-1}): C, 65.62; H, 5.51; N, 5.74. Found: C, 65.49; H, 5.43; N, 5.42.

Acetato(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)[*o*-(cyclohexyl-*o*-tolylphosphino)benzyl]palladium(II) (9). Yield: 82%. ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ 8.96 (2H, d, $^3J_{HH}$ = 7.6 Hz), 7.83 (3H, m), 7.39 (2H, t, $^3J_{HH}$ = 8.0 Hz), 7.28 (4H, t, $^3J_{HH}$ = 7.2 Hz), 7.11 (2H, m), 7.01−6.81 (10H, m), 2.95 (2H, m, C*H*$_2$), 2.61 (3H, s, C*H*$_{3,tolyl}$), 2.07 (3H, s,

CH_3), 1.92−1.1 (11H). ^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ 190.4 (d, J = 3.8 Hz, NCN), 175.3 (s, CO_2CH_3), 159.1 (d, J = 15.4 Hz, C_{Aryl}), 153.3 (s, CN), 143.4 (d, J = 11.6 Hz), 140.8 (d, J = 6.9 Hz), 138.0 (d, J = 8.4 Hz), 134.7, 134.3, 132.0−131.3 (m), 130.3, 130.0 (d, J = 9.2 Hz), 129.9, 129.3 (d, J = 3.0 Hz), 129.1, 128.9, 128.6, 125.9, 125.4 (d, J = 6.1 Hz), 124.7, 124.3, 36.7 (d, J = 8.4 Hz, CH_2), 29.6−26.4 (m, C_{Hexyl}), 24.7 (s, $CH_{3,tolyl}$), 23.2 (d, J = 13.0 Hz), 19.8 (s, CO_2CH_3). ^{31}P{^{1}H} NMR (109 MHz, 300 K, C_6D_6): δ 43.52 (s), 42.86 (s), (*cis*/*trans*). ^{31}P{^{1}H} NMR (161 MHz, 300 K, $(CD_3)_2SO$): δ 39.36 (s), 39.07 (s), (*cis*/*trans*). MS (FAB) *m/z* (%): 697.2 (39, [M$^+$]), 400.5 (15, [M$^+$ − (OAc + carbene)], 318.5 (5, [M$^+$ − (OAc + carbene + cyclohexyl)], 311.6 (3, [M$^+$ − (OAc + carbene + *o*-tolyl)], 297.7 (100, [carbene]). Anal. Calcd for $C_{42}H_{42}N_3O_2PPd$ (752.20 g mol^{-1}): C, 66.53; H, 5.58; N, 5.54. Found: C, 66.48; H, 5.40; N, 5.41.

Bromo(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)[*o*-(di-cyclohexylphosphino)benzyl]palladium-(II) (10). Yield: 77%. ^{1}H NMR (270 MHz, 300 K, $CDCl_3$): δ 8.71 (2H, d, $^3J_{HH}$ = 7.2 Hz, Ar), 7.79 (2H, d, $^3J_{HH}$ = 9.3 Hz, Ar), 7.47−6.96 (15H, m, Ar), 2.34 (2H, s, CH_2), 1.80−1.12 (22H, m, C_6H_{11}). ^{13}C{^{1}H} NMR (67.9 MHz, 300 K, $CDCl_3$): δ 190.0 (d, $^2J_{PC}$ = 130.0 Hz, NCN), 159.5 (d, $^2J_{PC}$ = 34.7 Hz, *ipso*-C of P-*o*-tolyl), 153.1 (d, J_{PC} = 5.7 Hz, P-*o*-tolyl), 139.9, 137.6, 132.9, 132.3, 130.7 (d, J_{PC} = 2.6 Hz, P-*o*-tolyl), 130.1, 129.3 (Ar), 129.1 (d, J_{PC} = 5.7 Hz, P-*o*-tolyl), 128.7, 128.6, 128.5 (Ar), 128.2 (d, J_{PC} = 5.2 Hz, P-*o*-tolyl), 125.2 (Ar), 124.7 (d, J_{PC} = 5.7 Hz, P-*o*-tolyl), 123.4 (Ar), 34.1 (CH_2), 29.0 (d, J_{PC} = 3.6 Hz, C_6H_{11}), 28.8 (d, J_{PC} = 3.6 Hz, C_6H_{11}), 28.7, 28.3, 27.0 26.8, 26.4, 26.2 (C_6H_{11}). ^{31}P{^{1}H} NMR (109.1 MHz, 300 K, $C_6H_5CH_3$): δ 63.6 (s). MS (FAB) *m/z* (%): 692.8 (18, [M$^+$ − Br]), 402.4 (3, [Pd + carbene]), 393.5 (15, [Pd + phosphine]), 298.4 (100, [carbene]), 287.4 (23, [phosphine]). Anal. Calcd for $C_{39}H_{43}BrN_3PPd$ (771.08 g mol^{-1}): C, 60.75, H, 5.62, N, 5.45. Found: C, 60.90, H, 5.67, N, 5.04.

Bromo(1,3-dimesitylimidazolin-2-ylidene)[*o*-(dimesitylphosphino)-3,5-dimethylbenzyl]palladium(II) (11). Yield: 74%. ^{1}H NMR (270 MHz, 300 K, C_6D_6): δ 6.81 (4H, d, $^3J_{HH}$ = 6.4 Hz), 6.68 (4H, br s), 6.45 (1H, s), 6.28 (1H, s), 6.25 (2H, s), 2.25−1.91 (29H, m), 1.68 (3H, m), 1.40 (12H, br s). ^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ 193.9 (NCN), 165.3 (d, J = 37.3 Hz), 142.7 (d, J = 10.6 Hz), 141.8 (d, J = 10.0 Hz), 139.1, 138.9, 138.5, 138.1, 137.8, 137.5, 137.4, 136.8, 136.6, 135.6, 135.4, 130.7, 130.6, 129.3, 129.0, 128.9, 126.4, 125.6, 121.7, 120.6 (NCHCHN), 35.4 (br, CH_2), 24.5 (d, J = 10.6 Hz), 24.1 (d, J = 9.3 Hz), 23.7 (d, J = 9.3 Hz), 23.2 (d, J = 11.2 Hz), 21.5, 21.3, 21.1, 21.0, 20.9, 18.5, 18.0 (CH_3). ^{31}P-{^{1}H} NMR (109 MHz, 300 K, C_6D_6): δ 25.14. MS (FAB) *m/z* (%): 797.8 (22, [M$^+$ − Br]), 407.4 (2), 303.3 (100, [carbene]). Anal. Calcd for $C_{48}H_{56}N_2BrPPd$ (878.27 g mol^{-1}): C, 65.64; H, 6.43; N, 3.19. Found: C, 65.49; H, 6.21; N, 3.31.

Acetato(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)[*o*-(dimesitylphosphino)-3,5-dimethylbenzyl]-palladium(II) (12). Yield: 65%. ^{1}H NMR (270 MHz, 300 K, $(CD_3)_2SO$): δ 8.42 (1H, d, $^3J_{HH}$ = 6.7 Hz), 7.69 (2H, d, $^3J_{HH}$ = 7.4 Hz), 7.57−7.25 (12H, m), 6.89 (2H, br s), 6.80 (4H, br s), 3.69 (2H, s, CH_2), 2.25−2.14 (12H, m), 2.07−1.94 (15H, m). ^{13}C{^{1}H} NMR (67.9 MHz, 300 K, $(CD_3)_2SO$): δ 190.6 (d, J = 6.8 Hz, NCN), 173.5 (s, CO_2CH_3), 153.1 (br), 141.9, 141.6, 141.4, 141.1, 140.7, 140.6, 139.3, 138.8 (d, J = 1.2 Hz), 138.7, 137.1, 130.6, 130.4, 130.3, 130.2, 129.6, 128.8, 128.6, 128.4 (br), 128.1, 127.8, 127.5, 122.7 (C_{Ar}), 24.4 (s, CH_2), 23.5, 23.4, 22.7 (d, J = 4.7 Hz), 22.5 (d, J = 4.8 Hz), 22.2, 22.0 (CH_3), 20.4 (s, CO_2CH_3). ^{31}P{^{1}H} NMR (109 MHz, 300 K, $(CD_3)_2SO$): δ 18.58 (s) (*cis*, I = 28%), 17.80 (s) (*trans*, I = 72%). MS (FAB) *m/z* (%): 790.8 (39, [M$^+$ − OAc]), 670.6 (3, [M$^+$ − (OAc + Mes)]), 493.4 (10, [Pd + phosphine]), 416 (27), 402.3 (9), 388.5 (29, [phosphine]), 373.5 (40), 357.3 (6), 298.3 (100, [carbene]), 269.3 (9), 252.2 (14), 234.2 (23). Anal. Calcd for $C_{49}H_{50}N_3O_2PPd$ (850.33 g mol^{-1}): C, 69.21; H, 5.93; N, 4.94. Found: C, 69.43; H, 5.63; N, 4.54.

Acetato[3-(*tert*-butyl)-1-(2-pyridyl)imidazolin-2-ylidene]-[*o*-(di-*o*-tolylphosphino)benzyl)palladium(II) (16). Yield: 90%.^{1}H NMR (270 MHz, 300 K, C_6D_6): δ 7.92−6.81 (16H, m, Ar), 3.10 (2H, br, CH_2), 2.83 (3H, br, CO_2CH_3), 2.22 (3H, s, PhCH_3), 2.13 (9H, s, C(CH_3)$_3$), 2.08 (PhCH_3). ^{13}C{^{1}H} NMR (67.9 MHz, 300 K, C_6D_6): δ 181.7 (d, $^2J_{PC}$ = 90.8 Hz, NCN), 171.5 ($COCH_3$) 141.6 (d, $^2J_{PC}$ = 14.0 Hz, *ipso*-C of P-*o*-tolyl), 141.2 (d, $^2J_{PC}$ = 14.8 Hz, *ipso*-C of P-*o*-tolyl), 135.1, (*ipso*-C of N-py), 131.7, 131.4, 131.1, 131.0, 129.9, 129.8 (d, $^2J_{PC}$ = 12.1 Hz, *ipso*-C of P-*o*-tolyl), 129.2, 128.5, 128.0, 126.2, 126.0, 125.8, 125.6, 125.3, 124.7, 123.8, (Aryl), 126.9 (d, $^4J_{PC}$ = 3.2 Hz, *p*-C of P-*o*-tolyl), 126.3 (d, $^4J_{PC}$ = 2.4 Hz, *p*-C of P-*o*-tolyl), 125.7 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C of P-*o*-tolyl), 118.8, 118.1 (NCHCHN), 66.8 (C(CH$_3$)$_3$), 64.3 (CH_2), 28.9 (C(CH$_3$)$_3$), 26.3 (C(CH$_3$)$_3$), 24.5 (CO_2CH_3). ^{31}P{^{1}H} NMR (109.1 MHz, 300 K, $C_6H_5CH_3$): δ 31.6 (s). MS (FAB) *m/z*: 610 [M$^+$ − OAc], 554 [M$^+$ − (OAc + *t*-Bu)], 409 [M$^+$ − (OAc + carbene)], 319 [M$^+$ − (OAc + carbene + *o*-tolyl)], 307 [M$^+$ − (OAc + P(*o*-tolyl)$_3$)], 202 [carbene], 146 [carbene − *t*-Bu]. Anal. Calcd for $C_{35}H_{38}N_3O_2PPd$ (670.07 g mol^{-1}): C, 62.73, H, 5.72, N, 6.27. Found: C, 63.01, H, 5.66, N, 6.50.

Acetato[5-(diphenylphosphino)-2-methylnaphthyl]-(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)-palladium(II) (19a). Yield: 73%. ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ 8.60 (2H, d, $^3J_{HH}$ = 8.4 Hz), 7.93−6.58 (28H, m), 2.50 (3H, s, C$H_{3(Aryl)}$), 1.72 (3H, s, CO_2CH_3). ^{1}H NMR (270 MHz, 300 K, $CDCl_3$): δ 8.19 (2H, d, $^3J_{HH}$ = 6.7 Hz), 7.70−6.85 (28H, m), 2.10 (3H, s, C$H_{3(Aryl)}$), 1.79 (3H, s, CO_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ 188.7 (d, J = 12.3 Hz, NCN), 175.7 (CO_2), 161.0, 153.6, 151.4, 151.0, 150.6 (d, J = 17.5 Hz), 140.8, 140.4, 140.2, 133.6, 133.5, 133.4, 133.3, 130.2, 129.3, 128.9, 128.6, 128.5, 127.4, 127.1, 126.3, 125.6, 123.7, 123.4 (C_{Ar}), 24.6 (CH_3), 21.5 (d, J = 50.4 Hz, CO_2CH_3). ^{31}P{^{1}H} NMR (109 MHz, 300 K, C_6D_6): δ 62.71 (s). ^{31}P{^{1}H} NMR (109 MHz, 300 K, $CDCl_3$): δ 62.93 (s). ^{31}P{^{1}H} NMR (109 MHz, 300 K, d_8-THF): δ 63.03 (s). MS (FAB) *m/z* (%): 728.8 (73, [M$^+$ − OAc]), 431.4 (64, [M$^+$ − (OAc + carbene)]), 353 (12), 298.4 (100, [carbene]). Anal. Calcd for $C_{45}H_{36}N_3O_2PPd$ (788.18 g mol^{-1}): C, 68.57; H, 4.60; N, 5.33. Found: C, 68.79; H, 4.43; N, 5.51.

Preparation of Complexes 8b, 13, 14, and 19b. The free carbene (1.1 mmol) and the palladacycle dimer (0.25 mmol) were each dissolved in dry toluene (10 mL) and cooled to −80 °C. The carbene solution was slowly added via a syringe to the palladacycle solution, slowly heated to room temperature, and stirred for 3 h. The solvent was removed in a vacuum, and the remaining solid was washed twice with anhydrous *n*-hexane.

Bis(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)[*o*-(*tert*-butyl-*o*-tolylphosphino)benzyl]palladium-(II) Acetate (8b). Yield: 86%. ^{1}H NMR (270 MHz, 300 K, $(CD_3)_2SO$): δ 8.64 (2H, d, $^3J_{HH}$ = 7.4 Hz), 7.81 (2H, m), 7.54−7.02 (30H, m), 6.91 (2H, m), 3.35 (2H, s, CH_2), 2.24 (3H, br s), 1.92 (3H, s), 1.45 (9H, d, $^3J_{HH}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (67.9 MHz, 300 K, $(CD_3)_2SO$): δ 188.8 (NCN), 186.5 (NCN), 173.8 (s, CO_2CH_3), 158.2 (d, J_{PC} = 17.9 Hz), 152.7, 142.5 (d, J_{PC} = 11.9 Hz), 139.6, 139.4, 136.9, 136.8, 133.4, 133.3, 132.7, 132.6, 131.8, 131.6, 131.4, 131.1, 130.7 (d, J_{PC} = 2.5 Hz), 129.9, 129.6, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.6, 128.3, 128.1, 128.0 (d, J_{PC} = 2.1 Hz), 124.9 (d, J_{PC} = 5.7 Hz), 124.7 (d, J_{PC} = 4.2 Hz), 123.8, 123.4, 41.2 (C(CH$_3$)$_3$), 33.7 (d, J_{PC} = 5.7 Hz, CH_2), 27.5 (d, J_{PC} = 6.2 Hz, CH_3), 22.2 (d, J_{PC} = 8.8 Hz, $CH_{3,tolyl}$), 19.2 (s, CO_2CH_3). ^{31}P{^{1}H} NMR (109 MHz, 300 K, $(CD_3)_2SO$): δ 53.04 (s), 51.35 (s) (I = 56/44). ^{31}P{^{1}H} NMR (161 MHz, 300 K, $C_6H_5CH_3$): δ 51.55 (s), 50.06 (s) (I = 62/38). Anal. Calcd for $C_{60}H_{55}N_6O_2PPd$ (1029.51 g mol^{-1}): C, 70.00; H, 5.38; N, 8.16. Found: C, 69.68; H, 5.40; N, 7.81.

Bis(1,3-dicyclohexylimidazolin-2-ylidene)[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) Acetate (13). Yield: 84%. ^{1}H NMR (270 MHz, 300 K, $CD_3)_2SO$): δ 7.75−7.52 (4H, m), 7.48−7.36 (4H, m), 7.36−7.20 (4H, m), 7.16 (2H, t, $^3J_{HH}$ = 7.4 Hz), 6.75 (2H, t, $^3J_{HH}$ = 8.2 Hz), 2.51 (2H, s, CH_2),

2.12 (3H, s, C$H_{3,tolyl}$), 2.09 (3H, s, C$H_{3,tolyl}$), 1.82−1.40 (28H, m), 1.14−0.96 (16H, m). $^{13}C\{^1H\}$ NMR (67.9 MHz, 300 K, $(CD_3)_2SO$): δ 177.4 (br, CO_2CH_3), 174.3 (d, NCN, $^2J_{PC}$ = 35.2 Hz), 172.4 (d, NCN, $^2J_{PC}$ = 35.8 Hz), 157.7 (d, C_{Ar}, J_{PC} = 33.7 Hz), 140.8 (d, C_{Ar}, J_{PC} = 13.0 Hz), 135.3, 134.6, 132.8, 132.1 (d, C_{Ar}, J_{PC} = 5.2 Hz), 131.1, 130.2 (br), 128.4, 128.1, 126.3, 125.9 (d, C_{Ar}, J_{PC} = 6.2 Hz), 119.5 (br), 58.5 (br s), 34.1, 32.4, 29.6 (CH_2), 23.8−24.9 (br), 21.7 (CO_2CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, 300 K, $(CD_3)_2SO$): δ 26.31 (s). MS (CI) *m/z* (%): 873.6 (34, [M^+ − OAc]), 641.3 (73, [M^+ − (carbene + OAc]), 570.3 (11, [Pd + 2*carbene]), 409.1 (3, [M^+ − (2*carbene + OAc]), 336.2 (7, [Pd + carbene]), 233.2 (100, [carbene]. Anal. Calcd for $C_{53}H_{71}N_4O_2PPd*C_6H_{12}O_2$ (1049.68 g mol^{-1}): C, 67.51; H, 7.97; N, 5.34. Found: C, 66.85; H, 7.86; N, 5.02.

Bis(1,3-dicyclohexylimidazolin-2-ylidene)[*o*-(dicyclohexylphosphino)benzyl]palladium(II) Bromide (14). Yield: 93%. ^1H NMR (270 MHz, 300 K, $(CD_3)_2SO$): δ 7.51 (4H, m), 7.24 (2H, m), 7.13 (2H, d, $^3J_{HH}$ = 5.7 Hz), 4.12 (6H, br s, CH), 3.59 (2H, s, CH_2), 2.69−2.28 (8H, m), 1.9−0.7 (52H, m, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, $(CD_3)_2SO$): δ 176.5 (NCN), 175.6 (NCN), 134.3, 130.9, 128.8, 128.1, 125.2, 123.8, 118.8 (m, NCH), 59.1 (br, CH_{Hexyl}), 58.1 (br, CH_{Hexyl}), 33.8, 33.3, 32.5, 32.1 (br), 31.2 (s, CH_2Pd), 27.2, 26.8, 26.4, 25.7, 25.4, 25.3, 24.8, 24.5, 24.2, 24.1, 23.9 (CH_2). $^{31}P\{^1H\}$ NMR (109 MHz, 300 K, $(CD_3)_2SO$): δ 48.05 (s). MS (FAB) *m/z* (%): 858.0 (18, [M^+ − Br]), 625.6 (61, [M^+ − (Br^- + carbene)]), 570.6 (6, [Pd + 2*carbene]), 393.3 (4), 336.3 (4), 287.4 (4), 233.3 (100, [carbene]). Anal. Calcd for $C_{49}H_{76}N_4BrPPd$ (938.45 g mol^{-1}): C, 62.71; H, 8.16; N, 5.97. Found: C, 62.32; H, 8.07; N, 5.63.

Bis(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)[5-(diphenylphosphino)-2-methylnaphthyl]palladium(II) Acetate (19b). Yield: 91%. ^1H NMR (400 MHz, 300 K, C_6D_6): δ 9.26 (2H, m), 8.95 (2H, d, $^3J_{HH}$ = 8.8 Hz), 7.98−6.62 (41H, m), 1.98 (3H, s, C$H_{3(Aryl)}$), 1.89 (3H, s, CO_2CH_3). ^1H NMR (270 MHz, 300 K, $CDCl_3$): δ 8.57 (2H, dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.0 Hz), 8.26 (2H, m), 7.69−6.79 (41H, m), 2.06 (3H, s, C$H_{3(Aryl)}$), 1.43 (3H, s, CO_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, C_6D_6): δ 191.9 (NCN), 190.6 (NCN), 175.1 (CO_2), 161.1, 153.3 (t, J = 15.5 Hz), 151.4, 151.0, 150.6 (d, J = 17.5 Hz), 138.6, 138.5, 138.2, 137.2, 132.2, 132.1, 131.9 (d, J = 2.3 Hz), 131.8, 130.3, 130.1 (d, J = 1.6 Hz), 129.9 (d, J = 1.6 Hz), 129.7 (d, J = 1.5 Hz), 129.5, 129.4, 128.8, 128.6 (m), 128.5, 128.4, 127.4, 127.1, 126.3, 126.1, 125.6, 123.9, 123.7, 123.4 (C_{Ar}), 25.7 (CH_3), 21.1 (CO_2CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, 300 K, C_6D_6): δ 51.45 (s). $^{31}P\{^1H\}$ NMR (109 MHz, 300 K, $CDCl_3$): δ 51.49 (s). $^{31}P\{^1H\}$ NMR (109 MHz, 300 K, d_8-THF): δ 51.82 (s). MS (FAB) *m/z* (%): 1026.2 (3, [M^+ − OAc]), 728.8 (69, [M^+ − (OAc + carbene)]), 431.4 (61, [M^+ − (OAc + 2 carbene)]), 353 (11), 298.4 (100, [carbene]). Anal. Calcd for $C_{65}H_{51}N_6O_2PPd$ (1086.48 g mol^{-1}): C, 71.92; H, 4.74; N, 7.74. Found: C, 71.48; H, 4.33; N, 7.62.

Preparation of Tris(1,3-dimethylimidazolin-2-ylidene)[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) Acetate (15). The free carbene 1,3-dimethylimidazolin-2-ylidene (150 mg, 1.55 mmol) and *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (234 mg, 0.25 mmol) were each dissolved in dry toluene (10 mL) and cooled to −80 °C. The carbene solution was slowly added via a syringe to the palladacycle solution, slowly heated to room temperature, and stirred for 3 h. The solvent was removed in a vacuum, and the remaining light yellow solid was washed twice with anhydrous *n*-hexane.

Yield: 67%. ^1H NMR (400 MHz, 300 K, C_6D_6): δ 7.15−6.80 (18H, m), 3.15 (2H, s, CH_2), 2.40 (6H, s, C$H_{3,tolyl}$), 1.51 (18H, s, CH_3), 1.34 (3H, br s, CO_2CH_3). ^1H NMR (270 MHz, 300 K, $(CD_3)_2SO$): δ 7.28 (9H, d, $^3J_{HH}$ = 4.5 Hz), 7.13 (6H, m), 6.60 (3H, m), 3.50 (2H, s, CH_2), 2.29 (6H, s, C$H_{3,tolyl}$), 1.10 (18H, s, CH_3). $^{13}C\{^1H\}$ NMR (67.9 MHz, 300 K, C_6D_6): δ 180.5 (s, NCN), 177.7 (s, CO_2CH_3), 158.7 (d, C_{Ar}, J_{PC} = 23.8 Hz), 143.0 (d, C_{Ar}, J_{PC} = 26.5 Hz), 135.0 (d, C_{Ar}, J_{PC} = 11.4 Hz), 133.5, 132.8, 130.5 (d, C_{Ar}, J_{PC} = 4.6 Hz), 130.1 (d, C_{Ar}, J_{PC} = 4.2 Hz), 129.1, 128.8, 126.6, 122.4 (NCH$(CH_3)_2$), 37.0 (s, CH_2), 33.4 (br s, CH_3), 30.1 (s, CO_2CH_3), 21.4 ($CH_{3,tolyl}$), 21.1 ($CH_{3,tolyl}$). $^{31}P\{^1H\}$ NMR (161 MHz, 300 K, C_6D_6): δ −26.31 (s). $^{31}P\{^1H\}$ NMR (161 MHz, 300 K, $C_6H_5CH_3$): δ −27.38 (s). MS (FAB) *m/z* (%): 697.4 (11, [M^+ − OAc]), 601.3 (42, [M^+ − (OAc + carbene)]), 505.1 (78, [M^+ − (OAc + (carbene)$_2$)]), 409.1 (5, [M^+ − (OAc + (carbene)$_3$)]), 393.2 (3, [Pd + (carbene)$_3$]), 298.1 (20), 215.0 (6), 204.1 (5, [Pd + carbene]). Anal. Calcd for $C_{38}H_{47}N_6O_2PPd$ (757.21 g mol^{-1}): C, 60.27; H, 6.26; N, 11.10. Found: C, 59.86; H, 6.32; N, 10.93.

Preparation of [*o*-(Di-*o*-tolylphosphino)benzyl][1-*tert*-butyl-3-(2′C)-pyridyl imidazolin-2-ylidenato,2-*C*,1′-*N*]palladium(II) Tetrafluoroborate (17). Acetato[3-(*tert*-butyl)-1-(2-pyridyl)imidazolin-2-ylidene][*o*-(di-*o*-tolylphosphino)benzyl)palladium(II) (**16**) (100 mg, 0.15 mmol) and tetrabutylammonium bromide (1000 mg, 3.11 mmol) were dissolved in dichlormethane (10 mL) and stirred for 1.5 h at room temperature. After removal of the solvent in vacuo, the residue was washed with methanol (three times with 6 mL) and hexane (twice with 6 mL). The white solid was suspended in acetone, and silver tetrafluoroborate (50 mg, 0.26 mmol) was added. The mixture was stirred for 2 h at room temperature and filtered. The solution was reduced in vacuo to 1 mL, and 15 mL diethyl ether was added. The precipitate was filtered off and dissolved in dichloromethane. Insoluble silver salts were removed by filtration, and the solution was reduced in vacuo to 1 mL. After the addition of 15 mL of diethyl ether a white solid was collected by filtration.

Yield: 96%. ^1H NMR (270 MHz, 300 K, C_6D_6): δ 8.15 (1H, t, $^3J_{HH}$ = 8.2 Hz, pyridine), 8.09 (1H, t, $^3J_{HH}$ = 8.2 Hz, pyridine), 7.53−6.97 (14H, m, Ar), 3.69 (2H, br, CH_2), 2.39 (3H, s, PhCH_3), 1.80 (9H, s, C(CH_3)$_3$), 1.67 (PhCH_3). $^{13}C\{^1H\}$ NMR (67.9 MHz, 300 K, C_6D_6): δ 178.5 (s, NCN), 144.7 (d, $^2J_{PC}$ = 14.6 Hz, *ipso*-C of P-*o*-tolyl), 142.5 (d, $^2J_{PC}$ = 14.3 Hz, *ipso*-C of P-*o*-tolyl), 133.7 (*ipso*-C of N-py), 131.3 (d, $^2J_{PC}$ = 13.1 Hz, *ipso*-C of P-*o*-tolyl), 131.2, 131.1, 127.0, 126.9, 126.7, 126.1, 126.0, 124.5, 124.4, 124.1, 123.8, 123.7, 123.6, 122.9, 122.6, (Aryl), 126.0 (d, $^4J_{PC}$ = 2.4 Hz, *p*-C of P-*o*-tolyl), 125.4 (d, $^4J_{PC}$ = 2.1 Hz, *p*-C of P-*o*-tolyl), 124.8 (d, $^4J_{PC}$ = 2.7 Hz, *p*-C of P-*o*-tolyl), 121.7, 117.6 (NCHCHN), 65.8 (C(CH$_3$)$_3$), 59.7 (CH_2), 31.6 (C(CH_3)$_3$), 29.8 (C(CH_3)$_3$). ^{31}P NMR (109.1 MHz, 300 K, $CDCl_3$): δ 32.4 (s). Anal. Calcd for $C_{33}H_{35}N_3PPdBF_4$ (697.84 g mol^{-1}): C, 56.80; H, 5.06; N, 6.02. Found: C, 56.80; H, 5.29; N, 5.72.

Preparation of μ-Chloro-(2-(dimethylaminomethyl)-phenyl-*C*^{1},*N*)(1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)palladium(II) (21). The free carbene 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene (165 mg, 0.55 mmol) and di-μ-chlorobis(2-(dimethylaminomethyl)phenyl-*C*^{1},*N*)dipalladium(II) (138 mg, 0.25 mmol) were each dissolved in dry toluene (10 mL) and cooled to −80 °C. The carbene solution was slowly added via a syringe to the palladacycle solution, slowly heated to room temperature, and stirred for 3 h. The solvent was removed in a vacuum, and the remaining solid was washed twice with anhydrous *n*-hexane.

Yield: 86%. ^1H NMR (400 MHz, 300 K, $(CD_3)_2SO$): δ 8.82 (2H, d, $^3J_{HH}$ = 8.0 Hz), 7.96 (2H, d, $^3J_{HH}$ = 6.8 Hz), 7.67 (2H, t, $^3J_{HH}$ = 6.8 Hz), 7.41−7.56 (8H,m), 6.80 (4H,br s), 6.20 (1H, d, $^3J_{HH}$ = 7.2 Hz), 3.75 (1H, d, $^2J_{HH}$ = 14.8 Hz, CH_2), 3.59 (1H, d, ^2J = 14.8 Hz, CH_2), 2.63 (s, 3H, CH_3), 2.44 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, 300 K, $(CD_3)_2SO$): δ 180.0 (NCN), 153.5, 148.3, 148.0, 139.2, 136.7, 134.9, 131.0, 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, 128.1, 127.9, 125.3, 123.4, 123.2, 121.7 (CN), 74.2 (CH_2), 53.1 (CH_3), 52.1 (CH_3). MS (FAB) *m/z* (%): 572.2 (10, [M + H^+]), 537.2 (61, [M^+ − Cl^-]), 402.1 (26, [Pd + carbene]), 298.2 (100, [carbene]). Anal. Calcd for $C_{29}H_{27}N_4PdCl$ (573.42 g mol^{-1}): C, 60.74; H, 4.75; N, 9.77. Found: C, 61.16; H, 4.70; N, 9.53.

Single-Crystal X-ray Structure Determination of Compounds 6, (13·($C_6H_{12}O_2$), and 16). Crystal data and details of the structure determination are presented in Table 6.

Suitable single crystals for the X-ray diffraction study were grown from dichloromethane/*n*-pentane (acetone/4-hydroxy-4-methyl-2-pentanone, dichloromethane/*n*-pentane). A clear colorless fragment (pale yellow fragment, colorless needle) was 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, FR951) and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 6529 (7938, 6210) reflections. Data collection was performed at 123 (123, 173) K (Oxford Cryosystems) within a θ-range of $1.90° < \theta < 25.33°$ ($1.60° < \theta < 25.34°$, $4.10° < \theta < 25.37°$). Each was measured with nine data sets in rotation scan mode with $\Delta\varphi/\Delta\omega = 1.0°$ (0.5°, 1.0°). A total number of 40 884 (83 297, 136 328) intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay and absorption effects. After merging [$R_{int} = 0.036$ (0.039, 0.058)] a sum of 6532 (9981, 5611) (all data) and 5888 (7779, 4793) [$I > 2\sigma(I)$], respectively, remained, and all data were used. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. **6** and **16**: All hydrogen atoms were found and refined with individual isotropic displacement parameters. **13**·($C_6H_{12}C_2$): Methyl hydrogen atoms and the hydrogen atom at the hydroxyl group of the solvent molecule were located from difference Fourier syntheses and refined as part of rigid rotating groups, with C−H = 0.98 Å and $U_{iso(H)} = 1.5U_{eq(C)}$ and $U_{iso(H)} = 1.2U_{eq(O)}$, respectively. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C−H distances of (1.00, 0.99 Å) and 0.95 Å, respectively, and $U_{iso(H)} = 1.2U_{eq(C)}$. Full-matrix least-squares refinements with 603 (630, 531) parameters 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 < 0.001 (0.001, 0.001). 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 II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97.[33] **13**·($C_6H_{12}C_2$): In the solid state a hydrogen bridge between the anion CH_3COO^- and the hydroxyl group of the solvent molecule is observed, O2−H2···O4, with O2−H2 = 1.05 Å; H2···O4 = 1.67 Å, O2···O4 = 2.714(3) Å, and ∠O2−H2···O4 = 167.72°. **16**: The allocation of the nitrogen atom N16 in the pyridyl ring could be proved clearly. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-278797 (**6**), CCDC-278796 [**13**·($C_6H_{12}O_2$)], and CCDC-278795 (**16**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for **6**, **13**, and **16** are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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