APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 595–601
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.745

Palladium(II) complexes with P,N- and C,N-ligands as catalysts for the Heck reaction

Thomas Schultz, Norbert Schmees and Andreas Pfaltz*

Department of Chemistry, University of Basel, St Johanns-Ring 19, CH-4056 Basel, Switzerland

Received 25 November 2003; Accepted 31 January 2004

A series of palladium(II) complexes with different Schiff base ligands were synthesized. Phosphine-free Schiff bases derived from benzaldehyde formed cyclometallated complexes, which are air- and moisture-stable and have dimeric, acetate-bridged structures. Monomeric, air- and moisture-stable complexes were obtained with phosphine-containing Schiff bases. The chelating iminophosphine ligands coordinate to palladium via the phosphorus and the nitrogen atom. These complexes were applied as catalysts for the Heck reaction with bromobenzene and styrene. Excellent yields of *trans*-stilbene were obtained with catalyst loadings of 0.01 mol%. The influence of water on the performance of the catalysts was investigated. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: homogeneous catalysis; Heck reaction; palladium complexes; palladacycles; iminophosphines

INTRODUCTION

The Heck reaction is a versatile method for the formation of C–C bonds in organic synthesis,[1,2] giving access to a wide range of olefinic products. Many examples have been reported exploiting this reaction for the synthesis of pharmaceuticals,[3] fine chemicals[4] and polymers.[5] For industrial applications it is necessary to develop highly active catalysts, which allow the use of low catalyst loadings and inexpensive starting materials with low reactivity.

Phosphine-containing palladacycles,[6] phosphine-free palladacycles[7–9] and bulky monodentate alkyl phosphines[10–12] were found to be highly efficient catalysts for the Heck reaction with aryl bromides. Recently, palladium acetate was also reported to be a highly efficient catalyst under optimized conditions.[13,14] Palladium iminophosphine complexes have been rarely used as catalyst for the Heck reaction,[15] although such complexes are known to be versatile catalysts for many different reactions, such as the copolymerization of carbon monoxide and ethylene,[16] the hydrosilylation of ketones,[17] and Suzuki[17] and Stille coupling.[18]

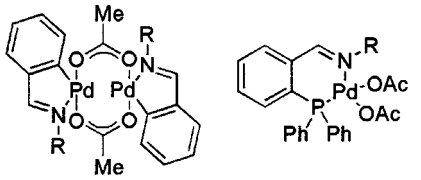
In connection with our studies of the kinetics and mechanism of Heck reactions,[19–21] we have prepared a series of palladium(II) complexes from simple benzaldimines and related *ortho*-(diphenylphosphino)benzaldimines. As the reaction conditions can have a significant influence on the catalyst performance, it is necessary to compare different palladium complexes under identical conditions. In our study, we focused on the phosphine-free palladacycles **1**[22] and **2** and the structurally related iminophosphine complexes **3** and **4** (Fig. 1) as catalysts for the reaction of bromobenzene with styrene. Here, we report the synthesis and crystal structures of these complexes (**1**–**4**) and their application as catalysts for the Heck reaction.

*Correspondence to: Andreas Pfaltz, Department of Chemistry, University of Basel, St Johanns-Ring 19, CH-4056 Basel, Switzerland.
E-mail: andreas.pfaltz@unibas.ch
Contract/grant sponsor: Swiss National Science Foundation.

RESULTS AND DISCUSSION

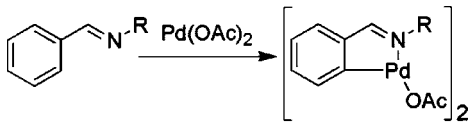
Starting from the commercially available Schiff bases benzylideneaniline (**5**) and benzylidenebenzylamine (**6**) two air- and moisture-stable cyclometallated imine complexes (**1** and **2**) were synthesized (Scheme 1). Although acetic acid is a common solvent for the preparation of palladacycles, it is not essential for the formation of cyclometallated complexes. The synthesis of palladacycle **2** was performed in tetrahydrofuran (THF), whereas acetic acid was used for palladacycle **1**. With benzylidenebenzylamine (**6**) the formation of endo- and exo-metallated complexes should be possible (endo- or exo-cyclic imine double bond). Nevertheless, two-dimensional NMR studies showed, that the endo-palladacycle **2** was formed exclusively. The reason for the strong tendency of Schiff bases to form endo-metallacycles was proposed to be the aromatic character of the conjugated π-system, formed by the

Copyright © 2004 John Wiley & Sons, Ltd.



1 R = Ph, **2** R = Bn **3** R = Ph, **4** R = Bn

Figure 1. Structures of the palladium(II) complexes **1**–**4**.



5 R = Ph
6 R = Bn

1 R = Ph
2 R = Bn

Scheme 1.

aryl ring, the imine double bond and a filled d orbital of the metal with appropriate symmetry.[23]

For complexes **1** and **2**, crystals suitable for X-ray analysis were obtained. Both palladacycles (**1** and **2**) were found to form dimeric, acetate-bridged, nearly C_2-symmetric complexes (Figs 2 and 3). The palladium atoms are coordinated in a square planar arrangement by one cyclometallated imine ligand and two bridging acetate moieties. In both complexes (**1** and **2**), the two cyclopalladated imine subunits of the dimers are arranged in an anti fashion. The palladium–carbon bonds are significantly shorter and, therefore, stronger than the palladium–nitrogen bonds (Δd = 0.05–0.08 Å). In the trans position to the nitrogen atoms, the palladium–oxygen bonds were found to be shorter than trans to the palladium–carbon bonds. A comparison of complexes **1** and **2** shows that the bond lengths and angles of the ($PdCNO_2$) core are almost identical.

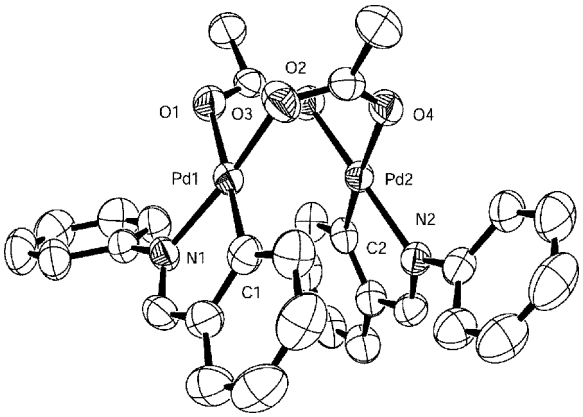


Figure 2. X-ray structure of complex **1**. ORTEP representation with 50% elipsoid probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 = 1.959, Pd2–C2 = 1.962, Pd1–N1 = 2.040, Pd2–N2 = 2.037, Pd1–O3 = 2.033, Pd2–O2 = 2.040, Pd1–O1 = 2.136, Pd2–O4 = 2.137, N1–Pd1–C1 = 81.24, N2–Pd2–C2 = 81.02, O1–Pd1–O3 = 88.81, O2–Pd2–O4 = 90.68.

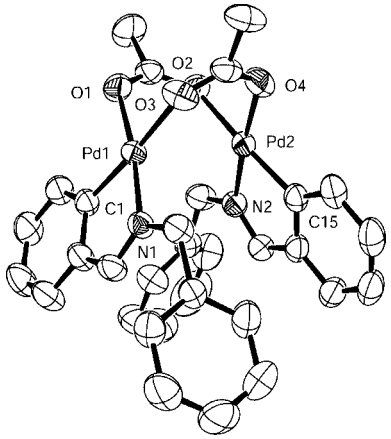
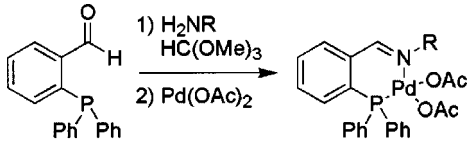


Figure 3. X-ray structure of complex **2**. ORTEP representation with 50% elipsoid probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 = 1.964, Pd2–C15 = 1.958, Pd1–N1 = 2.021, Pd2–N2 = 2.008, Pd1–O1 = 2.053, Pd2–O4 = 2.038, Pd1–O3 = 2.152, Pd2–O2 = 2.136, N1–Pd1–C1 = 81.33, N2–Pd2–C15 = 81.41, O1–Pd1–O3 = 89.43, O2–Pd2–O4 = 88.58.

The iminophosphine ligands have been easily accessible by condensation of the commercially available *ortho*-(diphenylphosphino)benzaldehyde (**7**) with aniline or benzylamine. In contrast to the phosphine-free Schiff bases **5** and **6**, monomeric complexes were formed with palladium acetate, containing one iminophosphine ligand and two acetate moieties (Scheme 2). As expected, the iminophosphines act as bidentate ligands, coordinating to the palladium via the nitrogen and the phosphorus atoms.

Crystals suitable for X-ray analysis were obtained for complexes **4** and **5**. The palladium atoms are coordinated in a square planar arrangement by one iminophosphine ligand and two acetate moieties (Figs 4 and 5). For both iminophosphine complexes (**3** and **4**), comparable bond lengths and angles were found for the ($PdNO_2P$) core. The bond lengths of the palladium–nitrogen and the



7 **3** R = Ph, **4** R = Bn

Scheme 2.

Copyright © 2004 John Wiley & Sons, Ltd.

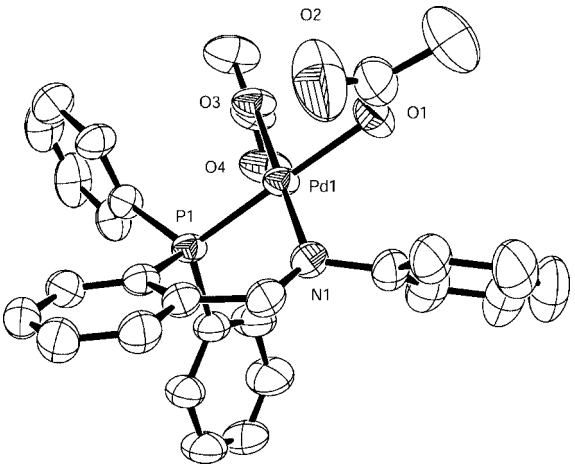


Figure 4. X-ray structure of complex **3**. ORTEP representation with 50% elipsoid probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–P1 = 2.196, Pd1–N1 = 2.011, Pd1–O1 = 2.103, Pd1–O3 = 1.996, N1–Pd1–P1 = 87.86, O1–Pd1–O3 = 86.14.

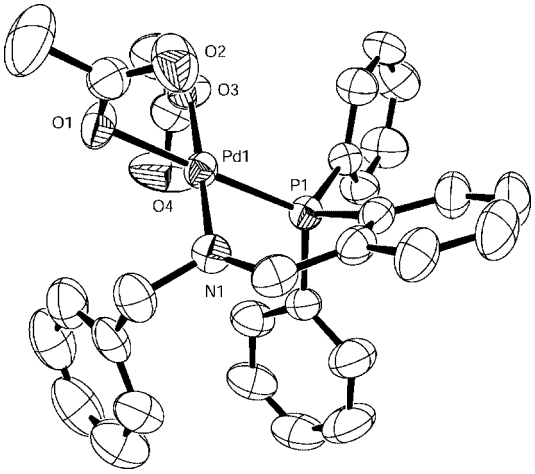


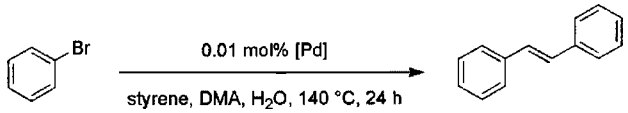
Figure 5. X-ray structure of complex **4**. ORTEP representation with 50% elipsoid probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–P1 = 2.201, Pd1–N1 = 2.021, Pd1–O1 = 2.097, Pd1–O3 = 2.019, N1–Pd1–P1 = 86.51, O1–Pd1–O3 = 87.13.

palladium–oxygen bonds are comparable to the distances found for the palladacycles (**1** and **2**). As expected, the palladium–oxygen bonds in trans position to the nitrogen atoms are shorter than the palladium–oxygen bonds trans to the phosphorus atoms. The formation of a more flexible six-membered chelate ring by the iminophosphine ligands enables larger bite angles, which are closer to an ideal square planar coordination, than in the five-membered chelate rings of the palladacycles **1** and **2**.

The palladium complexes **1**–**4** have been used as catalysts for the Heck reaction with bromobenzene and styrene (Scheme 3). The reactions were performed under an inert atmosphere in the presence of sodium acetate using anhydrous dimethylacetamide (DMA) as solvent. The reaction mixture was equilibrated to 140 °C, prior to the addition of a catalyst solution. After 24 h at 140 °C, the conversion and the yield were determined by gas chromatography (GC) using tridecane as an internal standard. Under anhydrous reaction conditions, essentially full conversions and very high yields of *trans*-stilbene were obtained with 0.01 mol% of the palladacycles **1** and **2** (Table 1), whereas the iminophosphine complexes **3** and **4** gave slightly lower conversions and yields under these conditions.

It has been observed that the addition of water can have an accelerating effect on the reaction of bromobenzene and butyl acrylate using palladacycle **1**.[19–21] However, in this case, the addition of 2.5 mol l^{-1} water to the reaction mixture led to a significant loss of activity for the iminophosphine complexes **3** and **4**, whereas no influence on the performance of the palladacycles **1** and **2** was observed (Table 1). Upon the addition of water, essentially full conversions and very high yields of *trans*-stilbene were obtained with the palladacycles (**1** and **2**).

In summary, the phosphine-free palladacycles **1** and **2** were found to be efficient catalysts for the Heck reaction of bromobenzene with styrene, exhibiting similar activity to the best catalysts reported in literature.[24] The iminophosphine complexes **3** and **4** were less reactive and more sensitive to water than complexes **1** and **2**, which gave the same conversions and yields in the presence and absence of water.



Scheme 3.

Table 1. Heck reaction of bromobenzene and styrene

Catalyst	H_2O (mol l^{-1})	Conversion (%)	Yield (%) 1,1-Diphenylethene	Yield (%) *trans*-Stilbene
1	—	97	7	90
1	2.5	97	8	89
2	—	97	8	90
2	2.5	99	7	90
3	—	89	6	74
3	2.5	26	1	17
4	—	97	7	88
4	2.5	84	6	75

Copyright © 2004 John Wiley & Sons, Ltd.

Table 2. Crystallographic data for complexes **1** and **2**

Complex	**1**	**2**
Molecular formula	$C_{30}H_{26}N_2O_4Pd_2$	$C_{32}H_{30}N_2O_4Pd_2{\cdot}CHCl_3$
Formula weight	691.35	838.78
Colour	Orange	Yellow
Temperature (K)	293	293
Crystal size (mm^3)	$0.09 \times 0.13 \times 0.19$	$0.10 \times 0.11 \times 0.43$
Crystal system	Monoclinic	Triclinic
Space group	$P21/n$	$P\bar{1}$
a (Å)	8.7287(1)	11.1099(2)
b (Å)	23.2933(3)	11.6845(2)
c (Å)	13.3603(1)	13.8027(2)
α (°)	90	77.2719(11)
β (°)	94.6862(8)	80.771(1)
γ (°)	90	80.6952(9)
Volume ($Å^3$)	2707.3	1710.2
Z	4	2
Density (calc.) ($g\ cm^{-3}$)	1.696	1.629
μ(Mo Kα) (mm^{-1})	1.367	1.324
Scan type	φ and ω scans	φ and ω scans
$F(000)$	1367.067	832.449
θ range for data collection (°)	4.54–30.01	4.48–30.03
Completeness to θ max (%)	98.8	99.2
Reflections measured	14 595	13 819
Independent reflections	7810	9922
Reflections used	5531	7469
Number of parameters	344	398
R ($I > 2\sigma(I)$)	0.0245	0.0295
wR ($I > 2\sigma(I)$)	0.0289	0.0372
Goodness of fit on F	1.0311	1.0520
Residual density ($e^-\ Å^{-3}$)	0.39; −0.48	0.65; −0.61
CCDC deposition code	225 297	225 296

EXPERIMENTAL

General

All reactions were conducted under an inert atmosphere using standard Schlenk and dry-box techniques. The reagents and solvents were dried following standard procedures and stored under argon prior to use.

trans-Di-(μ-acetato)-bis-(benzylideneanilino)-dipalladium(II) (1)

Palladium acetate (303 mg, 1.35 mmol) and benzylideneaniline (298 mg, 1.64 mmol) was dissolved in 15 ml of degassed acetic acid. The solution was heated to 100 °C for 30 min. After cooling to room temperature, the solution was concentrated to 3 ml and layered with diethyl ether. The crystals, formed within 24 h at room temperature, were filtered off and recrystallized from chloroform–heptane, yielding complex **1** as a red solid (331 mg, 0.48 mmol, 71%).

^{1}H NMR (400.1 MHz, $CDCl_3$), δ ppm: 1.81 (s, 6H, CH_3), 6.65 (m, 2H, CH, arom.), 6.85 (m, 4H, CH, arom.), 6.96 (m, 2H, CH, arom.), 7.06 (m, 2H, CH, arom.), 7.18–7.24 (m, 8H, CH, arom.), 7.64 (s, 2H, N=CH). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$), δ ppm: 24.41 (CH_3), 123.65 (CH, arom.), 124.32 (CH, arom.), 127.76 (CH, arom.), 127.88 (CH, arom.), 128.41 (CH, arom.), 130.75 (CH, arom.), 133.02 (CH, arom.), 146.08 (C, arom.), 147.78 (C, arom.), 155.74 (C, arom.), 173.07 (CH, CH=N), 180.87 (C, CO). IR (KBr, cm^{-1}): 3053.6w, 2992.5w, 1576.3s, 1515.6s, 1485.5m, 1406.0s, 1352.0m, 1296.3w, 1233.8w, 1198.3m, 1114.7w, 1077.2w, 1046.8w, 1024.7w, 957.2w, 921.2w, 901.4w, 764.1s, 717.6m, 690.6s, 621.4w, 579.5w, 549.9w, 432.3w. MS (FAB, NBA), m/z (%): 692 (8) $[M + H]^+$, 633 (20), 286 (30), 180 (100), 77 (18). M.p.: 223 °C decomposition. Anal. Found: C, 52.05; H, 3.77; N, 3.99. Calc. for $C_{30}H_{26}N_2O_4Pd_2$: C, 52.12; H, 3.79; N, 4.05%.

trans-Di-(μ-acetato)-bis-(benzylidenebenzylamino)dipalladium(II) (2)

Palladium acetate (207 mg, 0.92 mmol) and benzylidenebenzylamine (150 mg, 0.77 mmol) was dissolved in 10 ml of THF. The solution was refluxed for 2 h. Subsequently, the

Copyright © 2004 John Wiley & Sons, Ltd.

Table 3. Crystallographic data for complexes **3** and **4**

Complex	**3**	**4**
Molecular formula	$C_{29}H_{26}NO_4PPd\cdot(CHCl_3)_2$	$C_{30}H_{28}NO_4PPd$
Formula weight	826.66	603.93
Colour	Yellow	Yellow
Temperature (K)	173	293
Crystal size (mm^3)	$0.20 \times 0.28 \times 0.42$	$0.02 \times 0.20 \times 0.40$
Crystal system	Trigonal	Monoclinic
Space group	$R\bar{3}$	$P21/n$
a (Å)	37.2673(3)	10.2308(12)
b (Å)	37.2673(3)	11.022(1)
c (Å)	13.9228(1)	24.605(3)
α (°)	90	90
β (°)	90	91.855(15)
γ (°)	120	90
Volume ($Å^3$)	16 746.1(2)	2773.0
Z	18	4
Density (calc.) ($g\ cm^{-3}$)	1.479	1.446
μ(Mo Kα) (mm^{-1})	1.006	0.762
Scan type	φ and ω scans	φ and ω scans
$F(000)$	7486.716	1228.118
θ range for data collection (°)	4.66–27.50	4.49–27.52
Completeness to θ max (%)	100	99.5
Reflections measured	100 772	16 836
Independent reflections	8543	6352
Reflections used	5472	3764
Number of parameters	463	334
R	0.0532 ($I > 3\sigma(I)$)	0.0433 ($I > 2\sigma(I)$)
wR	0.0588 ($I > 3\sigma(I)$)	0.0338 ($I > 2\sigma(I)$)
Goodness of fit on F	1.0676	1.1458
Residual density ($e^-\ Å^{-3}$)	1.88; −0.76	0.64; −0.44
CCDC deposition code	225 298	225 299

solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane, 1 : 1, $R_f = 0.22$). The resulting solid was crystallized from chloroform–hexane, yielding complex **2** as a yellow, crystalline solid (189 mg, 0.26 mmol, 68%).

^{1}H NMR (500.1 MHz, $CDCl_3$), δ ppm: 2.18 (s, 6H, CH_3), 4.01 (dd, $^2J = 16.1$ Hz, $^4J = 1.5$ Hz, 2H, CH_2), 4.57 (dd, $^2J = 16.1$ Hz, $^4J = 1.5$ Hz, 2H, CH_2), 6.84 (m, 4H, CH, arom.), 7.06 (m, 6H, CH, arom.), 7.08 (t, $^4J = 1.6$ Hz, 2H, CH, N=CH), 7.17 (m, 2H, CH, arom.), 7.26 (m, 6H, CH, arom.). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$), δ ppm: 24.52 (CH_3), 61.46 (CH_2), 124.05 (CH, arom.), 126.71 (CH, arom.), 128.13 (CH, arom.), 128.80 (CH, arom.), 129.56 (CH, arom.), 129.83 (CH, arom.), 132.17 (CH, arom.), 134.56 (C, arom.), 146.22 (C, arom.), 155.16 (C, arom.), 171.81 (C, CH=N), 181.18 (C, CO). IR (KBr, cm^{-1}): 3055.5w, 2990.6m, 1612.6s, 1584.0s, 1568.0s, 1493.7m, 1417.9s, 1373.2m, 1340.5w, 1310.7w, 1225.5m, 1216.8m, 1114.2w, 1044.5w, 1020.6m, 970.3w, 757.5s, 716.3w, 702.1m, 686.5m, 662.2w, 622.0w, 492.1w, 430.2m. MS (FAB, NBA), m/z (%): 720 (12) $[M + H]^+$, 661 (21), 300 (56), 194 (58), 91 (100). M.p.: 196 °C decomposition. Anal. Found: C, 53.52; H, 4.34; N, 3.82. Calc. for $C_{32}H_{30}N_2O_4Pd_2$: C, 53.42; H, 4.20; N, 3.89%.

Di-(acetato)-[*o*-(diphenylphosphino)-benzylideneaniline]palladium(II) (3)

Aniline (401 mg, 4.31 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (240 mg, 0.83 mmol) in 3 ml of degassed trimethyl orthoformate. The reaction mixture was stirred for 16 h at room temperature, before the volatiles were removed under reduced pressure. The residue was dissolved in 1 ml of dichloromethane, and a solution of palladium acetate (193 mg, 0.86 mmol) in 2 ml of dichloromethane was added. After 24 h at room temperature, the solution was added slowly to 10 ml of pentane. The precipitate was filtered off and washed three times with pentane. Complex **3** was isolated as a yellow solid (286 mg, 0.48 mmol, 58%).

^{1}H NMR (400.1 MHz, $CDCl_3$), δ ppm: 1.25 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 7.14 (m, 1H, CH, arom.), 7.30 (m, 1H, CH, arom.), 7.37 (m, 2H, CH, arom.), 7.47 (m, 4H, CH,

Copyright © 2004 John Wiley & Sons, Ltd.

arom.), 7.53–7.58 (m, 5H, CH, arom.), 7.70 (m, 2H, CH, arom.), 7.84 (m, 4H, CH, arom.), 7.92 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$), δ ppm: 21.71 (s, CH_3), 23.35 (s, CH_3), 122.86 (s, CH, arom.), 125.00 (d, $^1J_{C-P} = 45.6$ Hz, C, arom.), 125.06 (d, $^1J_{C-P} = 59.0$ Hz, C, arom.), 128.28 (s, CH, arom.), 128.81 (s, CH, arom.), 128.91 (s, C, arom.), 132.06 (d, $^4J_{C-P} = 2.9$ Hz, CH, arom.), 132.32 (d, $^4J_{C-P} = 1.9$ Hz, CH, arom.), 132.77 (d, $^4J_{C-P} = 2.4$ Hz, CH, arom.), 133.74 (d, $^3J_{C-P} = 7.2$ Hz, CH, arom.), 134.58 (d, $^2J_{C-P} = 11.5$ Hz, CH, arom.), 136.63 (d, $^3J_{C-P} = 8.6$ Hz, CH, arom.), 136.85 (d, $^2J_{C-P} = 15.4$ Hz, CH, arom.), 150.25 (s, CO), 164.97 (d, $^3J_{C-P} = 8.4$ Hz, N=CH), 176.52 (s, CO) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$), δ ppm: 22.83. IR (KBr, cm^{-1}): 3058.7w, 2923.6w, 1619.8s, 1610.0s, 1493.0m, 1437.8m, 1364.0s, 1312.7s, 1241.3w, 1198.0w, 1102.9m, 1012.0w, 783.2m, 766.5m, 702.7s, 576.3m, 552.1m, 533.4m, 514.2w, 495.3w. MS (FAB, NBA), m/z (%): 530 (14) $[M - OAc]^+$, 471 (21), 288 (100), 192 (48), 136 (34), 77 (29). M.p.: 193 °C decomposition. Anal. Found: C, 58.73; H, 4.38; N, 2.16. Calc. for $C_{29}H_{26}NO_4PPd$: C, 59.04; H, 4.44; N, 2.37%.

Di-(acetato)-[*o*-(diphenylphosphino)-benzylidenebenzylamine]palladium(II) (4)

Benzylamine (78 mg, 0.73 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (169 mg, 0.58 mmol) in 3 ml of degassed trimethyl orthoformate. After stirring the reaction mixture for 16 h at room temperature, the volatiles were removed under reduced pressure. The residue was dissolved in 1 ml of dichloromethane, and a solution of palladium acetate (126 mg, 0.56 mmol) in 2 ml of dichloromethane was added. After 3 h at room temperature, the solution was concentrated to 1 ml and added to 5 ml of pentane. The precipitate was filtered off and washed three times with pentane. Complex **4** was obtained as a yellow solid (208 mg, 0.34 mmol, 61%).

^1H NMR (500.1 MHz, $CDCl_3$), δ ppm: 1.34 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 5.07 (bs, 2H, CH_2), 7.05 (m, 1H, CH, arom.), 7.23–7.35 (m, 9H, CH, arom.), 7.42–7.53 (m, 7H, arom.), 7.61 (m, 2H, CH, arom.), 7.88 (bs, 1H, N=CH). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$), δ ppm: 21.78 (s, CH_3), 24.27 (s, CH_3), 67.50 (s, CH_2), 124.68 (d, $^1J_{C-P} = 59.5$ Hz, C, arom.), 124.77 (d, $^1J_{C-P} = 48.9$ Hz, C, arom.), 128.65 (d, $^3J_{C-P} = 11.8$ Hz, CH, arom.), 128.70 (s, CH, arom.), 129.27 (s, CH, arom.), 129.97 (s, CH, arom.), 131.58 (d, $^4J_{C-P} = 2.9$ Hz, CH, arom.), 132.09 (d, $^4J_{C-P} = 2.1$ Hz, CH, arom.), 132.49 (d, $^2J_{C-P} = 2.4$ Hz, CH, arom.), 133.33 (d, $^3J_{C-P} = 7.7$ Hz, CH, arom.), 134. 32 (d, $^2J_{C-P} = 11.7$ Hz, CH, arom.), 134.38 (s, C, arom.), 135.76 (d, $^3J_{C-P} = 8.7$ Hz, CH, arom.), 136.84 (d, $^2J_{C-P} = 15.7$ Hz, C, arom.), 163.94 (d, $^3J_{C-P} = 8.7$ Hz, CH, N=CH), 176.54 (s, C, CO), 177.79 (s, C, CO). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$), δ ppm: 26.71. IR (KBr, cm^{-1}): 3044.4w, 2922.2w, 1633.3s, 1627.8s, 1605.6s, 1483.3w, 1438.9m, 1377.8s, 1322.3m, 1310.2s, 1233.3w, 1100.0m, 1016.7w, 750.0m, 694.4s, 616.7w, 544.4m, 483.2w. MS (FAB, NBA), m/z (%): 544 (12) $[M - OAc]^+$, 484 (75), 393 (16), 317 (15), 302 (32), 288 (84), 183 (26), 91 (100). M.p.: 195 °C decomposition. Anal. Found: C, 59.41; H, 4.73; N, 2.20. Calc. for $C_{30}H_{28}NO_4PPd$: C, 59.66; H, 4.67; N, 2.32%.

General procedure for the Heck reaction

A glass ampoule equipped with a Teflon screw cap (Young valve) was charged with sodium acetate (154 mg, 1.88 mmol), bromobenzene (196 mg, 1.25 mmol), styrene (196 mg, 1.88 mmol), tridecane (150 mg, 0.81 mmol), and 5 ml of DMA. The reaction mixture was equilibrated to 140 °C for 5 min, before a solution of the catalyst in DMA (0.10 ml, 1.25 μmol ml^{-1}) was added. After 24 h at 140 °C, the reaction mixture was cooled to 0 °C, diluted with 50 ml of cyclohexane, and washed three times with water. The organic phase was dried over magnesium sulfate and analysed directly. Conversion and yield were determined from the solution by GC.

Single crystal X-ray structure determination

Crystals, suitable for single crystal X-ray structure determination, were obtained by dissolving the complexes (**1**–**4**) in chloroform and layering the solutions with pentane. Data collection was carried out on a Nonius KappaCCD diffractometer using the COLLECT software suite.[25] The usual corrections were applied. No absorption correction was determined. The structures were solved by direct methods using the program SIR92.[26] Anisotropic least-squares refinement was carried out on all non-hydrogen atoms using the program CRYSTALS.[27] Hydrogen atoms are in calculated positions. Crystallographic data of complexes (**1**–**4**): see Tables 2 and 3.

Acknowledgements

We thank M. Neuburger, Dr S. Schaffner, B. Bulic, Dr P. Mukherjee and St. Kaiser for the determination and refinement of the X-ray structures, Dr K. Kulicke for the performance of several NMR experiments, and M. Langer for his assistance in the synthesis of complex **3**. Financial support by the Swiss National Science Foundation is gratefully acknowledged.

REFERENCES

1. Mizoroki T, Mori K, Ozaki A. *Bull. Chem. Soc. Jpn.* 1971; **44**: 581.
2. Heck RF, Nolley JP Jr. *J. Org. Chem.* 1972; **37**: 2320.
3. King AO, Corley EG, Anderson RK, Larsen RD, Verhoeven TR, Reider PJ, Xiang YB, Belley M, Leblanc Y, Labelle M, Parsit P, Zamboni RJ. *J. Org. Chem.* 1993; **58**: 3731.
4. Zapf A, Beller M. *Top. Catal.* 2002; **19**: 101 (and references cited therein).
5. Greiner A, Heitz W. *Makromol. Chem. Rapid Commun.* 1988; **9**: 581.
6. Hermann WA, Brossmer C, Reisinger CP, Riermeier TH, Öfele K, Beller M. *Chem. Eur. J.* 1997; **3**: 1357.
7. Ohff M, Ohff A, Milstein D. *Chem. Commun.* 1999; 357.
8. Schmees N. Heck-Reaktionen und Palladium-katalysierte Substitutionen. Dissertation, University of Cologne, 1998.
9. Loiseleur O. Enantioselective allylic substitution and Heck reactions. Dissertation, University of Basel, 1996.
10. Littke AF, Fu GC. *J. Am. Chem. Soc.* 2001; **123**: 6989.
11. Stambuli JP, Stauffer SR, Shaughnessy KH, Hartwig JF. *J. Am. Chem. Soc.* 2001; **123**: 2677.

Copyright © 2004 John Wiley & Sons, Ltd.

12. Shaughnessy KH, Kim P, Hartwig JF. *J. Am. Chem. Soc.* 1999; **121**: 2123.
13. De Vries AHM, Mulders JMCA, Mommers JHM, Henderickx HJW, de Vries JG. *Org. Lett.* 2003; **5**: 3285.
14. Yao Q, Kinney EP, Yang Z. *J. Org. Chem.* 2003; **68**: 7528.
15. Reddy KR, Surekha K, Lee GH, Peng SM, Liu ST. *Organometallics* 2000; **19**: 2637.
16. Reddy KR, Chen CL, Liu YH, Peng SM, Chen JT, Liu ST. *Organometallics* 1999; **18**: 2574.
17. Doherty S, Knight JG, Scanlan TH, Elsegood MRJ, Clegg W. *J. Organometal. Chem.* 2002; **650**: 231.
18. Shirakawa E, Yoshida H, Takaya H. *Tetrahedron Lett.* 1997; **38**: 3759.
19. Rosner T, Pfaltz A, Blackmond DG. *J. Am. Chem. Soc.* 2001; **123**: 4621.
20. Rosner T, Le Bars J, Pfaltz A, Blackmond DG. *J. Am. Chem. Soc.* 2001; **123**: 1848.
21. Blackmond DG, Rosner T, Pfaltz A. *Org. Proc. Res. Dev.* 1999; **3**: 275.
22. Granell J, Sainz D, Sales J. *J. Chem. Soc. Dalton Trans.* 1986; 1785.
23. Navarro-Ranninger C, Lopez-Solera I, Alvarez-Valdes A, Rodriguez-Ramos JH, Masaguer JR, Garcia-Ruano JL, Solans X. *Organometallics* 1993; **12**: 4104.
24. Beletskaya IP, Cheprakov AV. *Chem. Rev.* 2000; **100**: 3009.
25. *COLLECT* Software, Nonius BV, 1997–2001.
26. Altomare A, Cascarano G, Giacovazzo G, Guagliardi A, Burla MC, Polidori G, Camalli M. *J. Appl. Crystallogr.* 1994; **27**: 435.
27. Watkin DJ, Prout CK, Carruthers JR, Betteridge PW, Cooper RI. *CRYSTALS*, Issue 11. Chemical Crystallography Laboratory: Oxford, 2001.

Copyright © 2004 John Wiley & Sons, Ltd.