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Synthesis and characterization of phospha-palladacycles and their catalytic properties in the olefination of chloro- and bromoarenes

Guido D. Frey [a], Claus-Peter Reisinger [b], Eberhardt Herdtweck [a], Wolfgang A. Herrmann [a,*]

[a] Department Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstraße4, D-85747 Garching, Germany
[b] EXATEC GmbH & Co. KG, Friedrich-Ebert-Straße, D-51429 Bergisch Gladbach, Germany

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Abstract

Acetylacetonates of phospha-palladacycles are new catalysts in the Heck coupling of aryl chlorides and bromides with styrene. Turnover numbers (TON) of much higher than 300,000 and product yields up to 99% are obtained.

Keywords: Catalysis; CC-coupling; Heck reaction; Palladacycles; Palladium; Chloroarenes

1. Introduction

Most of our work on palladacycle catalytic systems has been focused on the arylation of olefines with aryl halides – generally referred as the Mizoroki–Heck reaction [1]. Because of its enormous synthetic potential for generating carbon–carbon bonds and its tolerance towards a wide range of functional groups, this reaction has received considerable attention [2]. Catalysts based upon cyclopalladated tris(*o*-tolyl)phosphine were first characterized by Shaw [3], Aleya [4], and Heck [5], and were intensely investigated in our group [6]. They promised to become excellent catalysts in organic synthesis.

It was repeatedly mentioned that acetylacetonate substituted palladacycles (**1**, **2**) (Fig. 1) show very high TON in the Heck coupling reaction of iodobenzene with styrene [7,8]. However, iodobenzene is very expensive and not at all a candidate in industry as a chemical feedstock. We logically developed routes to catalytically activate the industrially relevant bromo- and particularly chloroarenes.

2. Synthesis and properties of the catalysts

The new acetylacetonate palladacycles were prepared by treatment of the acetate bridged palladacycles **3** [6] with 2,4-pentandione (Hacac) in dichloromethane to afford the acetylacetonate products **5a**–**5e** in nearly quantitative yield according to Scheme 1.

Another possibility to achieve the catalysts **5a**–**5e**, is to start from the halide-bridged palladacycles **4a**–**4e** in a sodiumhydroxide/toluene/water mixture.

By reaction of phosphane **6** with $Pd(OAc)_2$ at room temperature in toluene for 12 h, the expected dinuclear

* Corresponding author. Tel.: +49 89 289 13080; fax: +49 89 289 13473.
E-mail address: lit@arthur.anorg.chemie.tu-muenchen.de (W.A. Herrmann).

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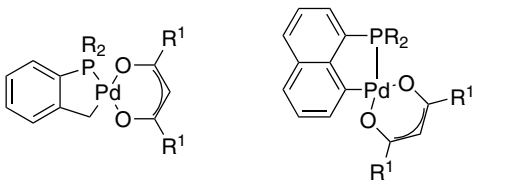


1a R = *o*-tolyl, $R^1 = CH_3$ **2a** R = naphthyl, $R^1 = CH_3$
1b R = *o*-tolyl, $R^1 = CF_3$ **2b** R = naphthyl, $R^1 = CF_3$

Fig. 1. Acetylacetonate catalysts.

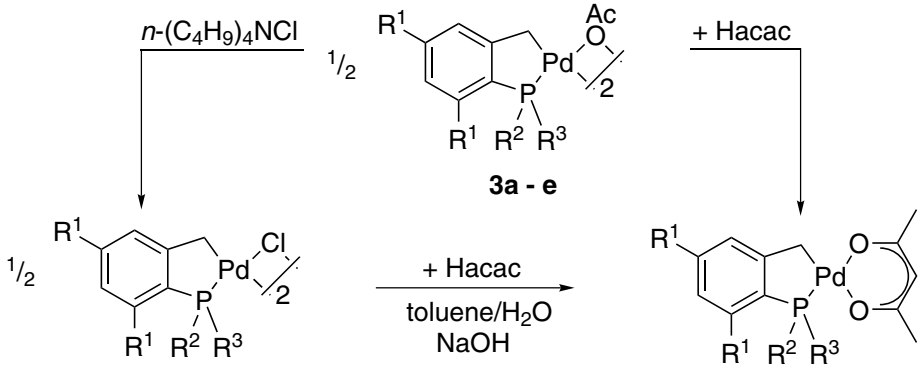
metallacycle **7** can be obtained in 88% yield. Compound **7** shows broad ^1H NMR signals at 25 °C. By treating **7** with 2,4-pentandione in dichlormethane we received the mononuclear acetylacetonato complex **8** (see Scheme 2). This product shows very sharp NMR signals at 25 °C. Such broad and sharp NMR spectra were similarly found at other palladacycles [7,8b].

3. Catalysis

The formation of CC-bonds between arenes and olefines is an important reaction in modern synthetic arene chemistry [9]. In particular, palladium-catalyzed reactions have proven to be most versatile in this reaction. Aryl olefines are commonly employed building blocks in natural products as well as in fine chemicals synthesis making the Mizoroki–Heck reaction one of the most important modern synthetic methods [2b].

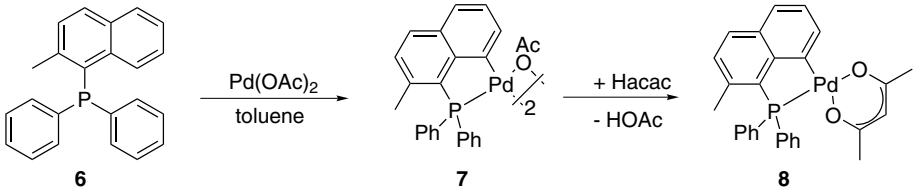
The catalysts **5a**–**5e** and **8** are quite equal for the Heck coupling of bromoaryls with styrene to stilbenes (Table 1). A lower reactivity is observed for catalyst **8** in comparison to the other catalysts for the reaction of chloroaryls with styrene. The lower reactivity of naphthyl-substituted palladacycles was also observed by Shaw et al. [7] at the example of iodobenzene/styrene. The TONs of the catalysts (**5a**–**5e**) in these reactions are as high as the reported ones [7]. However, it is now possible with the new acetylacetonato-palladacycles to couple the relatively little reactive, cheaper bromo- and chloroaryls with styrene.

Screening for the optimum base showed most inorganic bases are equally capable of furnishing stilbene. Differences in TON were generally small. The very cheap NaOAc showed very good results. Palladium black precipitation was not detected when the bases NaOAc, Na_2CO_3, Cs_2CO_3, K_2CO_3 were used. Stronger



5a $R^1 = CH_3$ R^2 = mesityl R^3 = mesityl
5b R^1 = H R^2 = *o*-tolyl R^3 = cyclohexyl
5c R^1 = H R^2 = *o*-tolyl R^3 = *t*-butyl
5d R^1 = H R^2 = *t*-butyl R^3 = *t*-butyl
5e R^1 = H R^2 = cyclohexyl R^3 = cyclohexyl

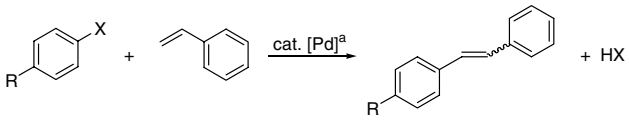
Scheme 1. Synthesis of acetylacetonate-palladacycles (**5a**–**5e**).



6 **7** **8**

Scheme 2. Preparation of complexes **7** and **8**.

Table 1
Comparison of the catalysts **5a**–**5e** and **8** in Heck olefination of aryl halides with styrene



Entry	R	X	Catalyst	mol% Catalyst	*t* (h)	Conversion (%)	Yield [%][b]	TON[c]
1	$COCH_3$	Br	**5a**	0.1	18	100	91	910
2	$COCH_3$	Br	**5b**	0.1	18	100	95	950
3	$COCH_3$	Br	**5c**	0.1	18	100	95	950
4	$COCH_3$	Br	**5d**	0.1	18	100	>99	990
5	$COCH_3$	Br	**5e**	0.1	18	100	>99	990
6	$COCH_3$	Br	**8**	0.1	18	100	98	980
7	H	Br	**5a**	1	18	84	80	80
8	H	Br	**5b**	1	18	95	94	95
9	H	Br	**5c**	1	18	90	86	86
10	H	Br	**5d**	1	18	96	94	94
11	H	Br	**5e**	1	18	93	90	90
12	H	Br	**8**	0.1	19	81	79	790
13	OCH_3	Br	**5c**	0.1	18	82	81	810
14	OCH_3	Br	**5d**	0.033	23	59	55	1410
15	$COCH_3$	Cl	**5a**	0.1	18	56	51	510
16	$COCH_3$	Cl	**5b**	0.1	18	9	8	80
17	$COCH_3$	Cl	**5c**	0.1	18	53	50	510
18	$COCH_3$	Cl	**5d**	0.1	18	39	34	340
19	$COCH_3$	Cl	**5e**	0.1	18	41	38	380
20	$COCH_3$	Cl	**8**	0.1	18	8	6	60

[a] One equivalent of aryl halide, 1.5 equivalents of styrene, 1.5 equivalents of NaOAc, dimethylacetamide (DMAc), $T = 130$ °C.
[b] GC – yields using diethyleneglycol-di-*n*-butyl ether as the internal standard.
[c] (mol product)/(mol Pd).

bases like $Ca(OH)_2$ and especially KOH rendered useless as they lead to small decomposition of the catalyst and additionally of NBu_4Br in a Hofmann-type elimination and less yield [10]. We ascribe the indifference in TON towards the nature of the base to the good solubility of all bases in presence of NBu_4Br at 130 °C and by using the very polar solvent dimethylacetamide (DMAc). Thus, any base which is capable of reductively eliminating HX from the hydrido palladium species $HPd(L)_2X$ can be used. As a result for coupling of chloroarenes with styrene, Cs_2CO_3 can be replaced by much more active and economic bases like NaOAc or Na_2CO_3. The addition of the co-catalyst NBu_4Br performs a higher TON of the catalysts. This result has been reported for palladacycles like **3** in our group [6].

It has long been known that in the Heck reaction very polar solvents such as dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) perform the best results. NMP gives better results for deactivated aryl halides than the cheaper DMAc (Table 3). The highly polar solvent sulfolane results in no product and in the decomposition of the palladacycle. Hexamethylphosphoramide (HMPA) gave acceptable results in the catalysis, but is highly toxic and expensive and therefore not the first choice for a solvent.

In Fig. 2 the 4-bromoacetophenone was converted completely after 420 min to the according product [(*E*/*Z*)-4-acetylstilbene], with a TOF over the whole time of 430 [mol product per mol **5d** per hour]. Using bromoanisole as a reactant a decreased yield was obtained by changing the solvent from NMP (65% yield) to DMAc (55% yield).

With the new palladacycles it is also possible to couple non activated chloroarenes with styrene (see Table 4).

The acetylacetonato-palladacycle **5d** shows a very high TON of up to 329,000 [mol product per mol **5d**] with the activated bromoacetophenone, even with the non activated bromobenzene turn over numbers of up to 265,000 could be achieved. With chlorobenzene a dramatic decrease of the TON was recognized but a TON of 3500 for a non activated chloroaryl is still one of the best results ever published in literature for phospha-palladacycles (see Table 5). The range of the catalytic turn over frequencies (TOF) lies in the range of 4700–50 [mol product per mol **5d** per hour]. All determinations were carried out without the co-catalyst NBu_4Br; adding this co-catalyst even higher TON and TOF can be expected (cf. Table 2).

4. Single crystal X-ray structure determination of compounds 5e and 7

Crystal data and details of the structure determination are presented in Table 6. Suitable single crystals for the

Table 2
The influence of base and co-catalyst in the Heck reaction[a]

Entry	R	X	Base	Co-catalyst	Catalyst	mol% Catalyst	t (h)	Conversion (%)	Yield (%)[b]	TON[c]
21	$C(O)CH_3$	Br	NaOAc	NBu_4 Br	**7**	0.1	14	100	>99	990
22	$C(O)CH_3$	Br	NaOAc	–	**7**	0.1	14	100	85	850
23	$C(O)CH_3$	Br	Cs_2CO_3	–	**7**	0.1	14	20	10	100
24	H	Br	Na_2CO_3	NBu_4Br	**5d**	0.1	19	99	98	980
25	H	Br	$Ca(OH)_2$	NBu_4Br	**5d**	0.1	19	97	96	960
26	H	Br	K_2CO_3	NBu_4Br	**5d**	0.1	19	96	95	950
27	H	Br	NaOAc	NBu_4Br	**5d**	0.1	19	93	92	920
28	H	Br	KOH	NBu_4Br	**5d**	0.1	19	82	82	820
29	H	Br	$CsCO_3$	NBu_4Br	**5d**	0.1	19	77	75	750
30	H	Br	NaOAc	–	**5d**	1	18	96	94	94
31	H	Br	K_2CO_3	–	**8**	0.1	19	98	97	970
32	H	Br	Na_2CO_3	–	**8**	0.1	19	96	95	950
33	H	Br	KOH	–	**8**	0.1	19	93	91	910
34	H	Br	$Ca(OH)_2$	–	**8**	0.1	19	95	88	880
35	H	Br	NaOAc	–	**8**	0.1	19	81	80	800
36	H	Br	$CsCO_3$	–	**8**	0.1	19	34	34	340
37	OCH_3	Br	NaOAc	–	**5c**	0.1	18	82	81	810
38	OCH_3	Br	K_2CO_3	–	**5c**	0.1	18	57	53	530
39	OCH_3	Br	$CsCO_3$	–	**5c**	0.1	18	13	9	88
40	OCH_3	Br	NaOAc	NBu_4Br	**7**	0.1	18	85	84	840
41	OCH_3	Br	NaOAc	NBu_4Br	**7**	0.01	18	69	53	5300
42	OCH_3	Br	NaOAc	–	**7**	0.1	18	68	67	670
43	$COCH_3$	Cl	NaOAc	–	**5d**	0.1	18	39	34	340
44	$COCH_3$	Cl	$Ca(OH)_2$	–	**5d**	0.033	23	2	1.8	54
45	$COCH_3$	Cl	Cs_2CO_3	–	**7**	0.1	14	31	29	290
46	H	Cl	NaOAc	NBu_4Br	**7**	0.1	14	25	19	190
47	H	Cl	Cs_2CO_3	NBu_4Br	**7**	0.1	14	2	1	10

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

Table 3
Influence of the solvent in the Heck coupling reaction of aryl halides with styrene[a]

Entry	R	X	Base	Solvent	Catalyst	mol% Catalyst	t (h)	Conversion (%)	Yield (%)[b]	TON[c]
48	$COCH_3$	Br	NaOAc	DMAc	**5d**	0.1	18	100	>99	990
49	$COCH_3$	Br	NaOAc	NMP	**5d**	0.033	23	100	>99	3030
50	OCH_3	Br	NaOAc	HMPA	**5c**	0.1	18	85	85	850
51	OCH_3	Br	NaOAc	NMP	**5c**	0.1	18	86	84	840
52	OCH_3	Br	NaOAc	DMAc	**5c**	0.1	18	82	81	810
53	OCH_3	Br	K_2CO_3	DMAc	**5c**	0.1	18	58	53	530
54	OCH_3	Br	$CsCO_3$	DMAc	**5c**	0.1	18	14	9	88
55	OCH_3	Br	NaOAc	sulfolane	**5c**	0.1	18	0	0	0
56	OCH_3	Br	NaOAc	NMP	**5d**	0.033	23	74	65	1970
57	OCH_3	Br	NaOAc	DMAc	**5d**	0.033	23	59	55	1660

[a] One equivalent of aryl halide, 1.5 equivalents of styrene, 1.5 equivalents of base, $T = 130$ °C.
[b] GC – yields using diethyleneglycol-di-*n*-butyl ether as the internal standard.
[c] (mol product)/(mol Pd).

X-ray diffraction study were grown from dichlormethane by slow evaporation of the solvent at ambient temperature. A clear colorless fragment (light yellow prism) 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 4435 (9918) reflections. Data collection were performed at 123 (123) K (OXFORD CRYOSYSTEMS) within a θ-range of $1.89° < \theta < 25.36°$ ($1.95° < \theta < 25.34°$). Measured with nine (four) data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0°$ (1.0°). A total number of 51,741 (67,268) intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging [$R_{int} = 0.038$ (0.040)] a sum of 4234 (9680) (all data) and 3961 (7912) [$I > 2\sigma(I)$],

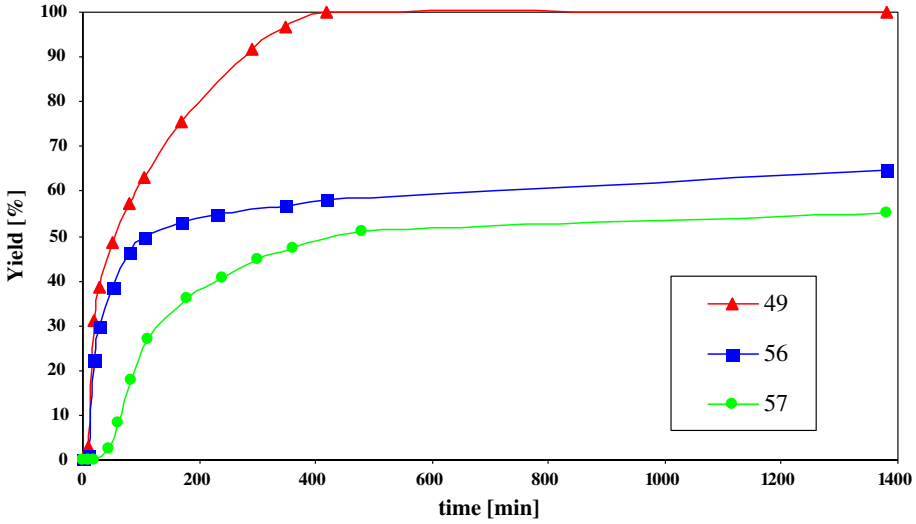
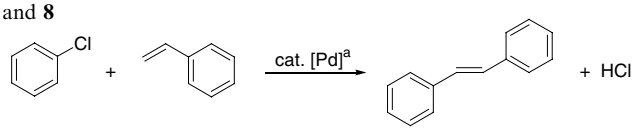


Fig. 2. Comparison of different reaction conditions and dependence of the solvent in the Heck reaction: yield of the product against time. Reaction conditions: aryl halide (1 mmol), styrene (1.5 mmol), NaOAc (1.5 mmol), $T = 130$ °C, catalyst **5d** (numbers see entry in Table 4).

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. **5e**: All hydrogen atoms were found and refined with individual isotropic displacement parameters. **7**: All hydrogen atoms were placed in ideal positions (riding model).

Table 4
Heck olefination of chlorobenzene with styrene and the catalysts **5a**–**5e** and **8**



Entry	Catalyst	mol% Catalyst	Conversion (%)	Yield (%)[b]	TON[c]
58	**5a**	0.1	17	2	20
59	**5b**	0.1	14	2	20
60	**5c**	0.1	2	1.8	18
61	**5d**	0.1	16	1.5	15
62	**5e**	0.1	14	1	10
63	**8**	0.1	9	1	10

[a] One equivalent of chlorobenzene, 1.5 equivalents of styrene, 1.5 equivalents of $Ca(OH)_2$, *N*-methylpyrrolidone, $T = 130$ °C, $t = 22$ h.
[b] GC – yields using diethyleneglycol-di-*n*-butyl ether as the internal standard.
[c] (mol product)/(mol Pd).

Table 5
Determination of turn over numbers in the Heck olefination of different aryl halides with styrene and palladacycle **5d** as catalyst[a]

Entry	R	X	mol% Catalyst	Yield (%)[b]	TON[c]
64	4-$COCH_3$	Br	0.000161	53	329000
65	4-H	Br	0.000242	64	265000
66	4-H	Cl	0.00241	8	3500

[a] One equivalent of aryl halide, 1.5 equivalents of styrene, 1.5 equivalents of NaOAc, DMAc, $T = 130$ °C, $t = 70$ h.
[b] GC – yields using diethyleneglycol-di-*n*-butyl ether as the internal standard.
[c] (mol product)/(mol Pd).

Table 6
Crystallographic data for complex **5e** and **7**

	5e	**7**
Formula	$C_{24}H_{35}O_2PPd$	$C_{50}H_{42}O_4P_2Pd_2$
F_w	492.91	981.62
Color/habit	Colorless/fragment	Light yellow/prism
Crystal dimensions (mm^3)	$0.36 \times 0.51 \times 0.56$	$0.38 \times 0.43 \times 0.76$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	9.6461(1)	11.4471(1)
b (Å)	13.6063(1)	23.1637(1)
c (Å)	17.6048(1)	20.1354(2)
β (°)	90.1833(4)	97.2331(3)
V ($Å^3$)	2310.58(3)	5296.56(7)
Z	4	4
T (K)	123	123
D_{calc} (g cm^{-3})	1.417	1.231
μ (mm^{-1})	0.889	0.776
$F(000)$	1024	1984
θ Range (°)	1.89–25.36	1.95–25.34
Index ranges (h,k,l)	±11, ±16, ±21	±13, ±27, ±24
No. of reflections collected	51,741	67,268
No. of independent reflections/R_{int}	4234/0.038	9680/0.040
No. of observed reflections ($I > 2\sigma(I)$)	3961	7912
No. of data/restraints/parameters	4234/0/394	9680/0/527
$R1/wR2$ ($I > 2\sigma(I)$)[a]	0.0204/0.0468	0.0334/0.0887
$R1/wR2$ (all data)[a]	0.0228/0.0477	0.0420/0.0919
GOF (on F^2)[a]	1.088	1.074
Largest differential peak and hole (e $Å^{-3}$)	+0.62/−0.39	+1.15/−0.65

[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 $= \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

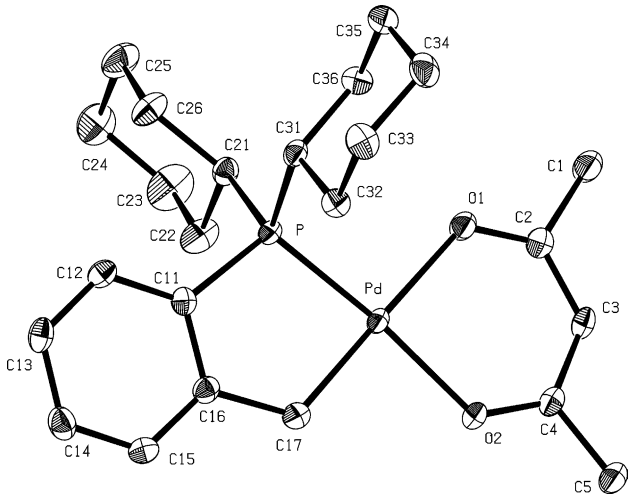


Fig. 3. ORTEP style plot of the solid state structure of compound **5e**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd–P 2.1983(4), Pd–O1 2.116(1), Pd–O2 2.081(1), Pd–C17 2.030(2); P–Pd–O1 97.69(4), P–Pd–O2 170.78(4), P–Pd–C17 84.06(6), O1–Pd–O2 89.96(5), O1–Pd–C17 176.24(7), O2–Pd–C17 88.61(7), Pd–P–C11 106.01(6), Pd–P–C21 113.72(6), Pd–P–C31 114.71(6), C11–P–C21 107.86(8), C11–P–C31 105.99(8), C21–P–C31 108.05(8).

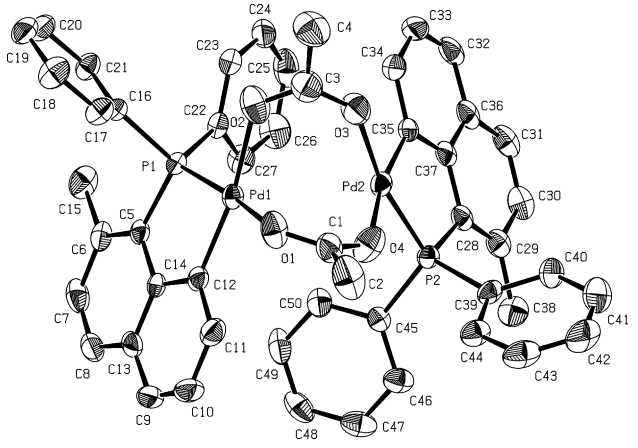


Fig. 4. ORTEP style plot of the solid state structure of compound **7**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd1–P1 2.1937(7), Pd1–O1 2.107(2), Pd1–O2 2.149(2), Pd1–C12 1.989(3), Pd2–P2 2.1960(7), Pd2–O3 2.104(2), Pd2–O4 2.125(2), Pd2–C35 1.986(3); P1–Pd1–O1 171.53(6), P1–Pd1–O2 93.90(6), P1–Pd1–C12 83.45(7), O1–Pd1–O2 87.13(9), O1–Pd1–C12 94.2(1), O2–Pd1–C12 170.5(1), P2–Pd2–O3 167.81(7), P2–Pd2–O4 91.83(7), P2–Pd2–C35 83.48(8), O3–Pd2–O4 89.02(9), O3–Pd2–C35 93.7(1), O4–Pd2–C35 170.1(1), Pd1–P1–C5 105.80(8), Pd1–P1–C16 111.01(9), Pd1–P1–C22 116.11(9), C5–P1–C16 109.6(1), C5–P1–C22 107.4(1), C16–P1–C22 106.8(1), Pd2–P2–C28 105.62(8), Pd2–P2–C39 110.75(9), Pd2–P2–C45 115.65(9), C28–P2–C39 108.9(1), C28–P2–C45 108.5(1), C39–P2–C45 107.2(1).

Full-matrix least-squares refinements with 394 (527) 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). 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, SIR-92, and SHELXL-97 [11]. **5e**: Small extinction effects were corrected with the SHELXL-97 procedure [$\varepsilon = 0.0015(1)$]. **7**: An unresolvable disorder of solvent molecules was cured effectively with the PLATON CALC SQUEEZE procedure. Complexes **5e** and **7** are shown in Figs. 3 and 4.

In the solid state of complex **5e** the two oxygen atoms of the acetylacetonate group do not have equal bond lengths to the palladium. The oxygen coordinated *trans* to the carbon shows a longer bond length (211.6(1) pm) than the oxygen coordinated *trans* to the phosphine (208.1(1) pm), because of the donating effect of this carbanion. This behaviour was first observed in complex **1a** (211.2, 207.8 pm) for these complexes in our group [8a]. Also results of a crystallographic analysis of complex **5d** showed the same characteristics 211.1(4) and 208.9(4) pm [12].

5. Conclusion

Acetylacetonate complexes of palladacycles show excellent air and thermal stability even at elevated temperatures. They are very active catalysts for the Mizoroki–Heck reaction. The structural identity was settled by single crystal X-ray diffraction studies. Both activity and stability of the catalytically active species can be triggered by the new catalysts in the Mizoroki–Heck reaction. It is now proven that these catalysts are successfully applicable to arylbromides and -chlorides in the coupling with styrene.

6. Experimental

6.1. General comments

(2-Methylnaphthyl)diphenylphosphane **6** [13] and the dimeric palladacycle-precursors (**3a**–**3e**) were prepared according to reported procedures [6b].

^{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 Hertz. GC–MS spectra were measured on a Hewlett–Packard gas chromatograph GC 5890 A equipped with a mass selective detector MS 5970 B. 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.

6.2. Preparation of acetylacetonato-[o-(dimesitylphosphino)-3,5-dimethylbenzyl]palladium(II) (**5a**)

To a solution of 1.23 g (1.11 mmol) $Pd_2(OAc)_2[o\text{-}CH_2C_6H_2(CH)_2P(Mes)_2]_2$ in 20 ml dichloromethane 300 mg (3 mmol) acetylacetone were added and stirred for 1 h at room temperature. The solvent was removed and the residue was washed with cold diethylether. The product was recrystallized from dichloromethane as a white solid in 99.9% (658 mg) yield.

^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 7.2 (1H, s, H_{Aryl}), 6.8 (4H, s, $H_{Mesityl}$), 6.4 (1H, s, H_{Aryl}), 5.15 (1H, s, CH_{acac}), 3.20 (2H, s, PdCH_2), 2.20 (3H, s, C$H_{3,Aryl}$), 2.15 (12H, s, C$H_{3,Mesityl}$), 2.12 (3H, s, C$H_{3,Aryl}$), 1.98 (3H, s, C$H_{3,acac}$), 1.84 (3H, s, C$H_{3,acac}$), 1.65 (6H, s, C$H_{3,Mesityl}$); ^{13}C {^{1}H} NMR(100 MHz, 300 K, $CDCl_3$): δ = 187.7 (s, *C*O$_{acac}$), 186.2 (s, *C*O$_{acac}$), 159.7 (d, C_{Aryl}, J_{PC} = 30 Hz), 142.3 (d, C_{Aryl}, J_{PC} = 10 Hz), 141.7 (m, C_{Aryl}), 140.0 (d, C_{Aryl}, J_{PC} = 2 Hz), 133.8 (s, C_{Aryl}), 133.3 (s, C_{Aryl}), 131.4 (d, C_{Aryl}, J_{PC} = 9 Hz), 129.5 (d, C_{Aryl}, J_{PC} = 8 Hz), 126.4 (d, C_{Aryl}, J_{PC} = 40 Hz), 125.3–124.5 (m, C_{Aryl}), 99.3 (s, *C*H$_{acac}$), 28.7 (s, *C*H$_{3,acac}$), 28.3 (s, *C*H$_{3,acac}$), 26.2 (s, *C*H$_2$), 25.2 (s, *C*H$_3$), 24.0 (s, *C*H$_3$), 21.3 (s, *C*H$_3$), 20.9 (s, *C*H$_3$); ^{31}P {^{1}H} NMR (161 MHz, 300 K, $CDCl_3$): δ = 24.7 (s). MS(FAB): *m*/*z* (%) = 592.6 (5, [M$^+$]), 492.7 (100, [M$^+$ − Acac]), 478.5 (10, [M$^+$ − Mes]). Anal. Calc. for $C_{32}H_{39}O_2PPd$ (593.04): C 64.81; H 6.63; Found: C 64.80; H 6.50%.

6.3. Preparation of acetylacetonato-[o-(cyclohexyl-o-tolylphosphino)-benzyl]palladium(II) (**5b**)

To a solution of 461 mg (0.5 mmol) $Pd_2(OAc)_2[o\text{-}CH_2C_6H_4P(Cy)(o\text{-}Tol)]_2$ in 20 ml dichloromethane 150 mg (1.5 mmol) acetylacetone were added and stirred for 1 h at room temperature. The solvent was removed and the residue was washed with diethylether. The product was recrystallized from DCM as a white solid in 99.8% (500 mg) yield.

^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 7.56 (1H, td, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.8 Hz, H_{Aryl}), 7.33 (1H, tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, H_{Aryl}), 7.30 (1H, dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, H_{Aryl}), 7.26–7.18 (3H, m, H_{Aryl}), 7.08–7.06 (2H, m, H_{Aryl}), 5.26 (1H, s, CH_{acac}), 3.45 (2H, m, $^3J_{HH}$ = 3.6 Hz, PdCH_2), 2.69 (3H, s, C$H_{3,Aryl}$), 2.00 (3H, s, C$H_{3,acac}$), 1.81 (3H, s, C$H_{3,acac}$), 2.6–1.2 (11H, m). ^{13}C {^{1}H} NMR(100 MHz, 300 K, $CDCl_3$): δ = 188.2 (s, *C*O$_{acac}$), 186.6 (s, *C*O$_{acac}$), 158.9 (d, C_{Aryl}, J_{PC} = 29 Hz), 143.6 (d, C_{Aryl}, J_{PC} = 12 Hz), 134.9 (s, C_{Aryl}), 134.4 (s, C_{Aryl}), 132.5 (d, C_{Aryl}, J_{PC} = 9 Hz), 131.8 (d, C_{Aryl}, J_{PC} = 5 Hz), 131.2 (d, C_{Aryl}, J_{PC} = 2 Hz), 131.0 (s, C_{Aryl}), 130.8 (d, C_{Aryl}, J_{PC} = 2 Hz), 129.3 (s, C_{Aryl}), 128.7 (d, C_{Aryl}, J_{PC} = 9 Hz), 125.9 (d, C_{Aryl}, J_{PC} = 7 Hz), 99.7 (s, *C*H$_{acac}$), 37.2 (s, *C*H$_{3,acac}$), 36.9 (s, *C*H$_{3,acac}$), 31.4 (s, *C*H$_{Hexyl}$), 29.5–26.8 (m, *C*H$_{2,Hexyl}$), 25.6 (s, *C*H$_2$), 23.8 (s, *C*H$_{3,Tolyl}$). ^{31}P {^{1}H} NMR(161 MHz, 300 K, $CDCl_3$): δ = 47.1 (s). MS(FAB): *m*/*z* (%) = 500.6 (7, [M$^+$]), 400.7 (100, [M$^+$ − Acac]), 318.6 (28, [M$^+$ − (Acac + cyclohexyl)]). Anal. Calc. for $C_{25}H_{31}O_2PPd$ (500.90): C 59.95; H 6.24; P 6.18; Pd 21.24; Found: C 59.80; H 6.30; P 6.10; Pd 21.20%.

6.4. Preparation of acetylacetonato-[o-(t-butyl-o-tolylphosphino)-benzyl]palladium(II) (**5c**)

To a solution of 448 mg (0.5 mmol) $Pd_2(OAc)_2[o\text{-}CH_2C_6H_4P(t\text{-}Bu)(o\text{-}Tol)]_2$ in 20 ml dichloromethane 150 mg (1.5 mmol) acetylacetone were added and stirred for 1 h at room temperature. The solvent was removed and the residue was washed with diethylether. The product was recrystallized from dichloromethane as a white solid in 99.0% (470 mg) yield.

^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 7.84 (1H, td, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.8 Hz, H_{Aryl}), 7.32 (1H, tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, H_{Aryl}), 7.29 (1H, d, $^3J_{HH}$ = 7.2 Hz, H_{Aryl}), 7.26–7.15 (4H, m, H_{Aryl}), 7.05 (1H, t, $^3J_{HH}$ = 7.6 Hz, H_{Aryl}), 5.24 (1H, s, CH_{acac}), 3.47 (2H, d, $^3J_{HH}$ = 3.6 Hz, PdCH_2), 2.54 (3H, s, C$H_{3,Tolyl}$), 1.99 (3H, s, C$H_{3,acac}$), 1.78 (3H, s, C$H_{3,acac}$), 1.50 (9H, d, $^3J_{HH}$ = 14.8 Hz, C$H_{3,t\text{-}Bu}$). ^{13}C {^{1}H} NMR(100 MHz, 300 K, $CDCl_3$): δ = 188.0 (s, *C*O$_{acac}$), 186.3 (s, *C*O$_{acac}$), 158.7 (d, C_{Aryl}, J_{PC} = 27 Hz), 143.7 (d, C_{Aryl}, J_{PC} = 12 Hz), 135.9 (s, C_{Aryl}), 135.4 (s, C_{Aryl}), 132.7 (d, C_{Aryl}, J_{PC} = 8 Hz), 132.5 (d, C_{Aryl}, J_{PC} = 4 Hz), 131.6 (s, C_{Aryl}), 131.0 (d, C_{Aryl}, J_{PC} = 2 Hz), 130.4 (d, C_{Aryl}, J_{PC} = 2 Hz), 129.2 (d, C_{Aryl}, J_{PC} = 35 Hz), 128.6 (d, C_{Aryl}, J_{PC} = 21 Hz), 125.2 (m, C_{Aryl}), 99.5 (s, *C*H$_{acac}$), 46.8 (s, *C* (CH$_3$)$_3$), 35.5 (s, *C*H$_{3,acac}$), 35.3 (s, *C*H$_{3,acac}$), 28.6 (m, *C*H$_{3,t\text{-}Bu}$), 23.8 (s, *C*H$_{3,Tolyl}$). ^{31}P {^{1}H} NMR(161 MHz, 300 K, $CDCl_3$): δ = 58.1 (s). MS(FAB): *m*/*z* (%) = 473.7 (6, [M$^+$]), 374.7 (100, [M$^+$ − Acac]), 318.6 (19, [M$^+$ − (Acac + *t*-Bu)]), 284.7 (7, [M$^+$ − (Acac + *o*-Tol)]), 226.6 (44, [M$^+$ − (Acac + *t*-Bu + *o*-Tol)]). Anal. Calc. for $C_{23}H_{29}O_2PPd$ (474.86): C 58.18; H 6.16; P 6.52; Pd 22.41; Found: C 58.80; H 6.20; P 6.55; Pd 22.70%.

6.5. Preparation of acetylacetonato-[o-(di-t-butylphosphino)-benzyl]palladium(II) (**5d**)

To a solution of 401 mg (0.5 mmol) $Pd_2(OAc)_2[o\text{-}CH_2C_6H_4P(t\text{-}Bu)_2]_2$ in 20 ml dichloromethane 150 mg

(1.5 mmol) acetylacetone were added and stirred for 1 h at room temperature. The solvent was removed and the residue was washed with diethylether. The product was recrystallized from dichloromethane as a white solid in 99.8% (440 mg) yield.

^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 7.43 (1H, t, $^3J_{HH}$ = 7.1 Hz, H_{Aryl}), 7.3–7.2 (2H, m, H_{Aryl}), 7.1 (1H, t, $^3J_{HH}$ = 6.7 Hz, H_{Aryl}), 5.23 (1H, s, CH_{acac}), 3.30 (2H, d, $^3J_{HH}$ = 4 Hz, PdCH_2), 1.93 (3H, s, C$H_{3,acac}$), 1.84 (3H, s, C$H_{3,acac}$), 1.36 (18H, d, $^3J_{HH}$ = 14 Hz, C$H_{3,t\text{-}Bu}$). ^{13}C {^{1}H} NMR(100 MHz, 300 K, $CDCl_3$): δ = 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, 300 K, $CDCl_3$): δ = 89.3 (s). MS(FAB): *m*/*z* (%) = 439.7 (12, [M^+]), 340.7 (100, [M^+ – Acac]), 284.7 (17, [M^+ – (Acac + *t*-Bu)]), 340.7 (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%.

6.6. Preparation of acetylacetonato-[*o*-(dicyclohexylphosphino)-benzyl]palladium(II) (**5e**)

To a solution of 517 mg (0.5 mmol) $Pd_2(Br)_2$[*o*-$CH_2C_6H_4P(Cy)_2]_2$ in 20 ml dichloromethane 150 mg (1.5 mmol) acetylacetone and 10 ml 2*N* NaOH were added and stirred for 1 h at room temperature. The solvent was removed and the residue was washed with diethylether. The product was recrystallized from dichloromethane as a white solid in 99.8% (492 mg) yield.

^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 7.2–7.0 (4H, m, H_{Aryl}), 5.22 (1H, s, CH_{acac}), 3.20 (2H, d, *J* = 3.5 Hz, PdCH_2), 1.99 (3H, s, C$H_{3,acac}$), 1.90 (3H, s, C$H_{3,acac}$), 2.2–1.1 (22H, m). ^{13}C {^{1}H} NMR(100 MHz, 300 K, $CDCl_3$): δ = 187.9 (s, *C* O_{acac}), 186.6 (s, *C* O_{acac}), 159.8 (d, C_{Aryl}, J_{PC} = 27 Hz), 132.6 (d, C_{Aryl}, J_{PC} = 47 Hz), 130.9 (s, C_{Aryl}), 130.2 (d, C_{Aryl}, J_{PC} = 18 Hz), 128.4 (d, C_{Aryl}, J_{PC} = 21 Hz), 125.2 (d, C_{Aryl}, J_{PC} = 7 Hz), 99.5 (s, *C*H$_{acac}$), 34.8 (s, *C*H$_{3,acac}$), 34.5 (s, *C*H$_{3,acac}$), 27.9 (*C*H$_2$), 28.8–26.5 (C_{Hexyl}). ^{31}P {^{1}H} NMR (161 MHz, 300 K, $CDCl_3$): δ = 66.7 (s). Anal. Calc. for $C_{24}H_{35}O_2PPd$ (492.91): C 58.48; H 7.16; P 6.28; Pd 21.59; Found: C 58.50; H 7.20; P 6.30; Pd 22.00%.

6.7. Preparation of trans-di(μ-acetato)-bis[5-(diphenylphosphino)-2-methylnaphthyl]dipalladium(II) (7)

The phosphine [(2-methylnaphthyl)diphenylphosphane] (**6**) (5.50 mmol) and $Pd(OAc)_2$ (5.43 mmol) were each dissolved in dry toluene (10 ml) and cooled to −80 °C. The phosphine solution was slowly added via a syringe to the palladiumacetate solution and slowly heated up to room temperature and stirred for 12 h. The solvent was removed via a syringe and the white solid was washed two times with toluene. Yield: 88% (2350 mg).

^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 7.80 (1H, s), 7.61–7.59 (5H, m), 7.44 (1H, s), 6.89–6.62 (9H, m), 2.15 (3H, s, CH_3), 1.79 (3H, s, CO_2CH_3). ^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 7.77 (1H, s), 7.57–7.41 (4H, m), 7.25 (4H, d, $^3J_{HH}$ = 7.6 Hz), 7.16 (4H, d, $^3J_{HH}$ = 7.2 Hz), 7.02 (2H, m), 2.34 (3H, s, CH_3), 1.77 (3H, s, CO_2CH_3). ^{1}H NMR (400 MHz, 300 K, $(CD_3)_2SO$): δ = 7.89 (1H, d, $^3J_{HH}$ = 6.7 Hz), 7.67–7.05 (14H, m), 1.97 (3H, s, CH_3), 1.86 (3H, s, CO_2CH_3). ^{13}C {^{1}H} NMR(100 MHz, 300 K, $(CD_3)_2SO$): δ = 179.2 (s, *C* O_2CH_3), 150.1, 148.6, 139.8, 132.2, 132.1, 131.8, 131.6, 130.9, 130.8, 129.2 (d, J_{PC} = 7.0 Hz), 128.8 (d, J_{PC} = 7.7 Hz), 128.1, 125.6, 125.2, 123.0, 25.1 (CO_2CH_3), 20.6 (CH_3). ^{31}P {^{1}H} NMR(109 MHz, 300 K, $(CD_3)_2SO$): δ = 62.1 (s). ^{31}P {^{1}H} NMR(161 MHz, 300 K, $CDCl_3$): δ = 62.6 (s). MS (FAB): *m*/*z* (%): 923.6 (23, [M^+ – OAc]), 864.6 (5, [M^+ – (2*OAc)]), 490.3 (13, [1/2 $(M)^+$]), 431.3 (100, [1/2 $(M – OAc)^+$]), 353.2 (19), 325.3 (41), 247.2 (98). Anal. Calc. for $C_{50}H_{42}O_4P_2Pd_2$ (981.62): C 61.18; H 4.31; Found: C 60.70; H 4.53%.

6.8. Preparation of acetylacetonato-[5-(diphenylphosphino)-2-methylnaphthyl]palladium(II) (8)

To a solution of 290 mg (0.29 mmol) *trans*-di(μ-acetato)-bis[5-(diphenylphosphino)-2-methylnaphthyl]dipalladium(II) (**7**) dissolved in 20 ml dichloromethane 90 mg (0.9 mmol) acetylacetone were added and stirred for 2 h at room temperature. The solvent was removed and the residue was washed with diethylether. The product was recrystallized from dichloromethane as a white solid in 99.8% (313 mg) yield.

^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 8.28 (1H, d, $^3J_{HH}$ = 3.6 Hz), 7.82–7.77 (5H, m), 7.57 (1H, d, $^3J_{HH}$ = 7.2 Hz), 7.45–7.39 (7H, m), 7.25 (1H, d, $^3J_{HH}$ = 2.4 Hz), 5.31 (1H, s CH_{acac}), 2.16 (3H, s, C$H_{3,acac}$), 2.11 (3H, s, C$H_{3,acac}$), 1.85 (3H, s, CH_3). ^{13}C {^{1}H} NMR(100 MHz, 300 K, $CDCl_3$): δ = 187.7 (s, *C*O_{acac}), 187.1 (s, *C*O_{acac}), 151.9, 151.2, 149.4 (d, $^2J_{PC}$ = 5.1 Hz), 140.1, 133.0, 132.8, 132.2, 132.1, 130.6, 130.1, 129.7, 129.2, 128.9, 128.8, 128.6, 128.5, 125.9, 123.3 (C_{Ar}), 99.6 (s, *C*H$_{acac}$), 28.3 (*C*H$_{3,acac}$), 28.1 (*C*H$_{3,acac}$), 21.8 (d, $^3J_{PC}$ = 3.9 Hz, *C*H$_3$). ^{31}P {^{1}H} NMR(161 MHz, 300 K, $CDCl_3$): δ = 61.7 (s). MS(FAB): *m*/*z* (%): 430.4 (M – Acac). Anal. Calc. for $C_{28}H_{25}O_2PPd_2 \cdot 1/4DCM$ (552.12): C 61.45; H 4.66; Cl 3.21; Found: C 61.26; H 4.64; Cl 2.85%.

6.9. General method for the Heck–Mizoroki coupling of arylhalides with styrene

The base (1.5 mmol) and tetrabutylammoniumbromid (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*-butylether and 2 ml of degassed solvent were added. After thermostating at 130 °C for 10 min the catalyst was added against a positive stream of argon. To 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 analyzed on a gas chromatograph.

7. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-270649 (**5e**) and CCDC-270648 (**7**). 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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