Synthesis of Monocarbenepalladium(0) Complexes and Their Catalytic Behavior in Cross-Coupling Reactions of Aryldiazonium Salts

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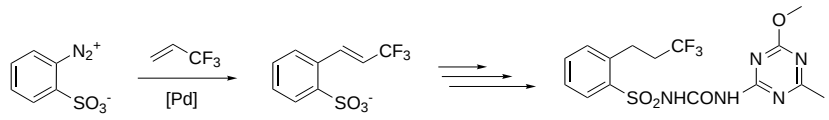
Dedicated to Professor Wolfgang Beck on the occasion of his 70th birthday

Abstract: The first monocarbenepalladium(0) complexes with benzoquinone and naphthoquinone as additional ligands have been prepared. As demonstrated by NMR spectroscopy and X-ray analysis, the complexes show a unique coordination mode giving quinone-bridged dimers. The monocarbenepalladium(0) complexes allow efficient cross-coupling reactions of aryldiazonium salts with olefins (Heck reaction) and arylboronic acids (Suzuki reaction).

Keywords: carbenes · Heck reaction · homogeneous catalysis · palladium · Suzuki reaction

Introduction

Palladium-catalyzed coupling reactions of aryl–X derivatives are among the most powerful tools for organic synthesis. These processes offer opportunities for an environmentally more friendly production of fine chemicals and possibilities to reduce the number of steps in the synthesis of pharmaceuticals and agrochemicals. Hence, the development of new catalysts has been a major goal in organometallic chemistry and catalysis. Most of the developed complexes have been applied on laboratory-scale. In addition, some industrial applications of this methodology have emerged.[1] One of the earliest examples of a palladium-catalyzed coupling reaction realized on an industrial scale is the Matsuda–Heck reaction of an aryldiazonium salt with 1,1,1-trifluoropropene in the presence of a dibenzylidenacetonepalladium(0) complex (Scheme 1). The reaction sequence was developed elegantly by Baumeister, Blaser, and co-workers from Ciba–Geigy and is performed, nowadays, on a multi-ton scale by Syngenta for the synthesis of the herbicide Prosulfuron.[2]



Scheme 1. Synthesis of Prosulfuron.

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Apart from the industrial synthesis of Prosulfuron, various palladium-catalyzed Heck reactions of diazonium salts have also been studied.[3] Compared to similar reactions of aryl iodides and bromides, the Heck coupling of aryldiazonium salts proceeds with comparably low catalyst efficiency. Critical for the success of this coupling reaction is the easy formation of low-coordinate palladium(0) complexes at ambient conditions. For such reactions, ideally a palladium(0) precatalyst would be used which generates a defined highly reactive 12e or 14e palladium complex at low temperature ($< 50\,^{\circ}C$). We[4] and others[5] have studied palladium-catalyzed Heck and Suzuki reactions of aryl halides with defined low-coordinate palladium phosphine complexes. Unfortunately, diazonium salts often undergo side reactions in the presence of phosphine ligands. Thus, we were interested in the synthesis of other defined low-coordinate palladium(0) complexes without phosphine ligands. We thought that monocarbenepalladium(0) complexes might be suitable catalysts for coupling reactions of aryldiazonium salts. In the last five years palladium–carbene complexes have become increasingly important as catalysts for Heck, Suzuki, and Sonogashira coupling reactions, copolymerizations, and amination of aryl halides.[6] Most recently, the use of in situ generated palladium–carbene complexes for coupling reactions of aryldiazonium salts has been demonstrated by Andrus and Song.[7] This prompted us to disclose our results on this topic. Herein we report the synthesis of new monocarbenepalladium(0) complexes, their unusual coordination chemistry, and their catalytic performance in various coupling reactions of aryldiazonium salts.

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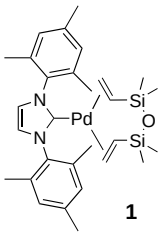
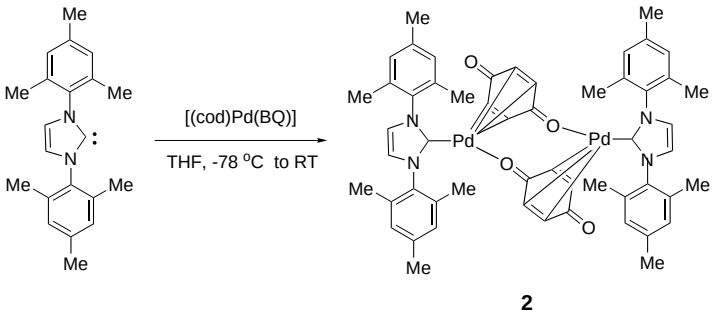
Results and Discussion

Synthesis and characterization of monocarbenepalladium complexes: Despite the increasing interest in palladium–carbene complexes, there are only few examples of palladium(0)–carbene complexes known.[8] So far only one phosphine-free monocarbenepalladium(0) complex, 1,3-dimesitylimidazol-2-ylidenepalladium(0)-η^2,η^2-1,1,3,3-tetramethyl-1,3-divinyldisiloxane (**1**; [(IMes)Pd^0(dvds)] has been synthesized and characterized by us.[9] Complex **1** was prepared by reacting the palladium(0) diallylether complex [$(Pd_2(dae)_3$][10] with 1,3-dimesitylimidazol-2-ylidene carbene (IMes)[11] in the presence of excess of 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (dvds) at $-30\,^{\circ}C$. In this complex, the central palladium atom is coordinated by two olefin units from $H_2C{=}CHSiMe_2OSiMe_2HC{=}CH_2$ and the carbene ligand in a trigonal-planar coordination. Complex **1** has already been proved to be an outstanding catalyst for telomerization reactions. Having been successful with telomerization reactions, we tested this complex for other coupling reactions such as Heck and Suzuki reactions. Initial studies on the Heck reaction of aryldiazonium salts with acrylic acid derivatives using catalyst **1** gave good yields of the desired coupling products, but the catalyst decomposed during catalysis leaving palladium black (see section Catalysis below). Hence, we focused on the preparation of other defined stable monocarbenepalladium complexes as precursors for active palladium catalysts for Heck and Suzuki reactions.



1

Initial attempts to prepare monocarbenepalladium(0)monoolefin complexes from [$Pd_2(dae)_3$] similar to complex **1** using *p*-quinones as monoolefins were not successful. Thus, we tried to perform a selective exchange of a cyclooctadiene ligand (COD) from known [(cod)Pd(quinone)] (quinone = *p*-benzoquinone (BQ), 1,4-naphthoquinone (NQ)) complexes[12] by one equivalent of free carbene. Indeed, facile exchange of COD takes place upon the addition of one equivalent of free carbene to [(cod)Pd(quinone)] in tetrahydrofuran as solvent. During the course of the reaction the initial yellow color changes to dark red, showing the formation of a new complex (Scheme 2 and Scheme 3). We initially believed that the complexes **2** and **3** were monomeric 14e monocarbenepalladium(0)quinone complexes; however, the detailed NMR and X-ray analysis of complexes **2** and **3** showed that they exist as dimeric palladium species in which quinones are coordinated in a novel coordination mode. In complex **2**, both the olefinic bonds of benzoquinone are coordinated with one palladium atom, and one of the carbonyl groups of benzoquinone is coordinated with the other palladium atom thereby producing



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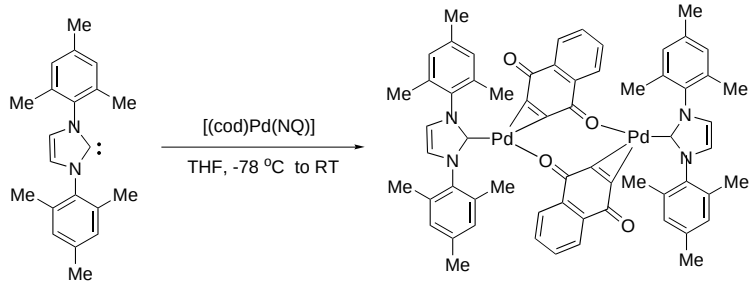
Scheme 2. Synthesis of complex **2**.

a benzoquinone-bridged dimer (Scheme 2). Similarly in complex **3**, the olefinic bond of naphthoquinone is coordinated with one palladium atom, and one of the carbonyl groups is coordinateded with the other palladium atom to produce a naphthoquinone-bridged dimer (Scheme 3).

The olefinic protons of quinones coordinated to the palladium centers in complexes **2** and **3** show a shift of 2.02–3.22 ppm toward lower frequency in the ^{1}H NMR spectra, which is in accordance with observations for [$Pd(L_2)(\eta^2$-alkene)] complexes.[13] The ^{1}H NMR spectrum of



3

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

complex **2** shows two doublets at $\delta = 4.55$ and 4.76 ppm clearly indicating the presence of two kinds of olefinic protons. Of the three peaks in the low-field region of the ^{13}C NMR spectrum, one can be assigned to a carbene-carbon atom bound to a palladium center, and the other two to the nonequivalent carbonyl groups of benzoquinone. The ^{1}H NMR spectrum of complex **3** shows the same pattern as **2** in the coordinated olefinic region. There are two doublets at $\delta = 3.88$ and 3.94 ppm, indicating two nonequivalent olefinic protons. Similar to the ^{13}C NMR spectrum of complex **2**, that of complex **3** shows peaks in the low-field region, one for a carbene-carbon atom bound to a palladium center and two for the nonequivalent carbonyl groups of naphthoquinone.

Suitable crystals of complex **3** for X-ray crystal structure analysis were obtained by slow diffusion of diethyl ether into a solution of **3** in dichloromethane. The molecular structure of **3** (Figure 1) shows its dimeric form and a distorted trigonal-planar coordination geometry at the palladium centers. Each palladium atom is coordinated by one carbene ligand. The distances Pd1–C7 (2.025(5) Å) and Pd2–C14 (2.028(5) Å) are in the expected range.[14] The angles between the plane of the naphthoquinone residue and the coordination plane (94.7°

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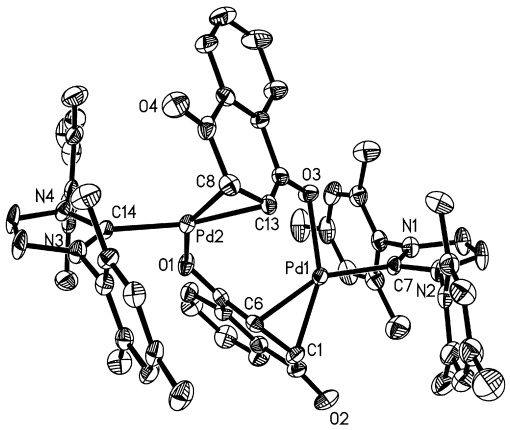


Figure 1. Crystal structure of **3** (30% probability ellipsoids). For clarity hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Pd1–C1 2.100(5), Pd1–C6 2.128(5), Pd1–C7 2.025(5), Pd1–O3 2.170(4), Pd2–C8 2.098(5), Pd2–C13 2.152(5), Pd2–C14 2.028(5), Pd2–O1 2.154(4); C7-Pd1-O3 92.5(2), O3-Pd1-CE(C1/C6) 132.4, C7-Pd1-CE(C1/C6) 134.7, C14-Pd2-O1 96.3(2), O1-Pd2-CE(C8/C13) 132.4, C14-Pd2-CE(C8/C13) 131.0; CE = midpoints of the coordinated C=C bonds.

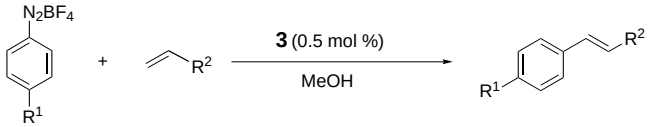
and 92.5°) show that the metal–alkene bond is approximately perpendicular to the plane of the napthoquinone ligand. The bond lengths of both the alkene and the carbonyl groups are longer than those in free quinone.[15] The bond lengths of the coordinated olefinic bonds C1–C6 (1.405(7) Å) and C8–C13 (1.406(8) Å) are comparable with such bonds in other quinone complexes of palladium.[13] The crystal structure shows two kinds of carbonyl groups. The bond lengths of C=O bonds coordinated to a palladium atom are longer (C5–O1 1.280(6), C12–O3 1.266(7) Å) than those of the noncoordinated C=O groups (C2–O2 1.233(6), C9–O4 1.220(7) Å). The Pd1–O3 (2.170(4) Å) and Pd2–O1 (2.154(4) Å) bond lengths are in the expected range.[16]

The IR spectra of the complexes **2** and **3** show a bathochromic shift of the stretching frequency ν(C=O) of the coordinated as well as noncoordinated carbonyl groups. The shift is small for noncoordinated carbonyl groups ($\Delta\nu =$ 14 cm^{-1} for **2** and 28 cm^{-1} for **3**)[13c] compared to that for the coordinated carbonyl groups ($\Delta\nu = 127\ cm^{-1}$ for **2** and 130 cm^{-1} for **3**).

Quinones are commonly used as ligands for the synthesis of palladium(0) and platinum(0) complexes due to their strong π-acceptor properties which stabilize the metal(0) center in these complexes. Interestingly, the coordination of quinone to the palladium center occurs through both olefinic and carbonyl functionalities in complexes **2** and **3**. To the best of our knowledge, such a bonding mode has not been described earlier.

Catalysis: With suitable monocarbenepalladium(0) complexes in hand we tested the Heck reaction[17] of different diazonium salts with styrene and acrylic acid esters. All reactions were run in methanol as solvent with a catalyst concentration of 1 mol% Pd. Initially, we compared the three defined monocarbene complexes **1**, **2**, and **3** in the reaction of 4-methoxybenzenediazonium tetrafluoroborate with 2-ethylhexyl acrylate to give 2-ethylhexyl 4-methoxycinnamate, which is a commercially important sun-screen agent. The Heck reaction with these substrates using catalyst **1** gave the desired product in 92% yield. However, **1** decomposed to a palladium mirror during the course of the reaction. The catalysts **2** and **3** performed well in this reaction and the yields were 96 and 91%, respectively. Fortunately, no palladium black formation was observed.

After the initial comparison of catalysts, we continued the coupling reactions with **3** as catalyst. Diazonium salts such as 4-methoxybenzenediazonium tetrafluoroborate, 4-(*N*,*N*-diethylamino)benzenediazonium tetrafluoroborate, 4-nitrobenzenediazonium tetrafluoroborate and 4-bromobenzenediazonium tetrafluoroborate were used for this catalysis with ethyl acrylate, 2-ethylhexyl acrylate, and styrene as olefins (Scheme 4; Table 1). The reactions proceed smoothly at 50–65 °C within 1-3 h yielding the corresponding stilbenes and cinnamic esters in good to excellent yield (87–96%).



Scheme 4. Heck reaction of aryldiazonium salts with various olefins.

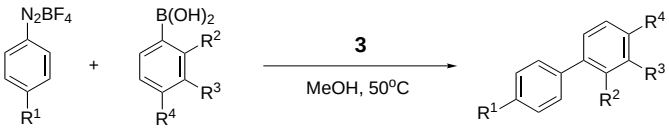
Table 1. Heck reaction of aryldiazonium salts.

Entry	Catalyst	R^1	R^2	Temperature [°C]	Time [h]	Yield [%]
1	**1**	OMe	$CO_2CH_2CH(Et)(CH_2)_3CH_3$	50	1	92
2	**2**	OMe	$CO_2CH_2CH(Et)(CH_2)_3CH_3$	50	1	96
3	**3**	OMe	Ph	50	3	87
4	**3**	OMe	CO_2Et	50	1	91
5	**3**	OMe	$CO_2CH_2CH(Et)(CH_2)_3CH_3$	50	1	91
6[a]	**3**	NEt_2	Ph	75	1	88
7	**3**	NEt_2	CO_2Et	50	1	88
8	**3**	NEt_2	$CO_2CH_2CH(Et)(CH_2)_3CH_3$	50	1	99
9	**3**	NO_2	Ph	65	2	97
10	**3**	NO_2	CO_2Et	65	1	61
11	**3**	NO_2	$CO_2CH_2CH(Et)(CH_2)_3CH_3$	65	1	96
12	**3**	Br	Ph	50	2	51
13	**3**	Br	$CO_2CH_2CH(Et)(CH_2)_3CH_3$	50	2	89

[a] Ethanol is used as solvent.

Apparently there is no significant difference in reactivity between aryldiazonium salts with electron-donating or electron-withdrawing groups. In the case of the bromo derivative, a selective activation of the diazonium group by the carbenepalladium complex is observed. Nevertheless, activation of the C–Br and even C–Cl bonds is possible at higher temperatures.[18]

In addition to Heck reactions, the cross-coupling reactions of aryl–X and arylboronic acids (Suzuki reaction) are of general interest to organic synthesis. The Suzuki reaction is the most versatile and important method for the synthesis of unsymmetrically substituted biaryl compounds.[19] So far only a few studies of Suzuki reactions with aryldiazonium salts have appeared.[20] Here, we performed the reactions of different aryldiazonium salts with different arylboronic acids in the presence of **3** (Scheme 5; Table 2). The reactions of aryldiazo-



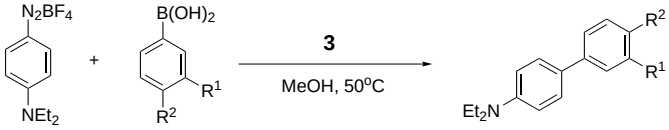
Scheme 5. Suzuki reaction of aryldiazonium salts with various arylboronic acids.

Table 2. Suzuki reaction of aryldiazonium salts using catalyst **3**.

Entry	R^1	R^2	R^3	R^4	Yield [%]
1	NEt_2	H	H	H	97
2	NEt_2	Me	H	H	100
3	NEt_2	H	OEt	H	99
4	NEt_2	H	H	Br	99
5	NEt_2		1-naphthyl		87
6	NEt_2		3-thiophenyl		94
7	OMe	H	H	H	62
8	NO_2	H	H	H	87
9	Br	H	H	H	75

nium salts with arylboronic acids were smooth at 50 °C. Similar to the Heck reaction, no pronounced effect of substituents on the yield of the biaryl is observed. In all cases, the coupling products (even with 3-thiophenylboronic acid) were obtained in good to excellent yields (62 – 100 %).

While most of the catalyst tests were performed in the presence of 0.5 mol % of **3**, we were also interested in reactions with lower catalyst loading due to the high price of palladium (Scheme 6). As shown in Table 3, the coupling of



Scheme 6. Suzuki reaction at lower catalyst loadings.

Table 3. Suzuki reaction at lower catalyst loadings.

Entry	R^1	R^2	Catalyst **3** [mol %]	Time [h]	Yield [%]	TON
1	H	H	0.05	6	41	410
2	H	H	0.10	6	76	380
3	H	H	0.15	5	99	330
4	H	H	0.20	3	99	195
5	OEt	H	0.05	6	45	450
6	OEt	H	0.10	6	99	495

4-(*N*,*N*-diethylamino)benzenediazonium tetrafluoroborate with phenylboronic acid and 3-ethoxyphenylboronic acid proceeds efficiently even in the presence of 0.1 mol % of **3**. Hence, turnover numbers (TON) up to 495 with respect to Pd can be achieved at high product yields. Further decrease of the amount of catalyst leads to lower yields due to unspecific side reactions of the aryldiazonium salts.

After having shown that diazonium salts can be coupled with high yield in the presence of monocarbenepalladium complexes, we focused on similar coupling reactions of anilines in the presence of a diazotization reagent. This one-pot procedure has the advantage that isolation of the diazonium salt can be omitted. Indeed, the coupling of 4-nitroaniline with phenylboronic acid proceeds in methanol as solvent in the presence of one equivalent of *tert*-butylnitrite. Without optimization 4-nitrobiphenyl is obtained in 52 % yield within 1 h. Also a similar yield is obtained when the coupling was carried out in water, demonstrating the stability of the complex.

Conclusion

We have prepared the first monocarbenepalladium(0) monoolefin complexes **2** and **3**. These quinone complexes are air- and moisture-stable. NMR spectroscopy and X-ray analysis of the complexes reveal a remarkable bidentate bonding mode of the quinone. The catalytic activity of the defined monocarbenepalladium(0) complexes is promising and yields of more than 90 % in Heck and Suzuki coupling reactions with different aryldiazonium salts have been achieved.

Experimental Section

General: All chemicals were commercially available (Fluka or Aldrich) and used without further purification. Carbenes[11] and [(cod)Pd(quinone)][12] were synthesized according to the literature. The complexes were characterized by elemental analysis, IR, ^{1}H, and ^{13}C NMR spectroscopy, and MS. Coupling products were identified by GC-MS, and ^{1}H and ^{13}C NMR spectroscopy. The data of non commercially available coupling products are given below.

X-ray crystallographic study of complex 3: X-ray data of **3** were collected on a STOE-IPDS diffractometer by using graphite-monochromated $Mo_{K\alpha}$ radiation. The structure was solved by direct methods (SHELXS-86)[21] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions and refined by using the riding model. XP (BRUKER axs) was used for the structure representation. Crystal data for **3**: crystal size $0.3 \times 0.3 \times 0.2$ mm, red prism, space group $P2_1/n$, monoclinic, $a = 11.635(2)$, $b = 25.521(5)$, $c = 18.391(4)$ Å, $\beta = 98.87(3)^\circ$, $V = 5396(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.401$ g cm^{-3}, 12 784 reflections measured, 7030 were independent of symmetry and 4968 were observed ($I > 2\sigma(I)$), $RI = 0.044$, wR^2 (all data) $= 0.112$, 649 parameters, residual electron density (max.) 0.514 e Å^{-3}. CCDC-183538 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk)).

Synthesis of [(1,3-dimesitylimidazol-2-ylidene)(benzoquinone)palladium(0)]$_2$ (2): 1,3-Dimesitylimidazol-2-ylidene (304 mg, 1.0 mmol) dissolved in tetrahydrofuran (20 mL) was added slowly to a pale yellow solution of (1,5-cyclooctadiene)(benzoquinone)palladium(0) (322.5 mg, 1.0 mmol) in tetrahydrofuran (40 mL) at −78 °C with stirring. The solution became dark red after the complete addition. The reaction mixture was allowed to warm slowly to room temperature. Then stirring was continued for 2 h at room temperature. The solvent was evaporated until a volume of approximately 3 mL remained. Subsequently, diethyl ether (30 mL) was added slowly. Dark brown crystals obtained were separated and washed with diethyl ether (2×10 mL) and dried under vacuo. Yield: 452 mg, 87 %; ^{1}H NMR (400 MHz, [D$_8$]THF, 23 °C): $\delta = 1.99$ (s, 24 H; *o*-CH$_3$), 2.34 (s, 12 H; *p*-CH$_3$), 4.55 (d, ^3J(H,H) = 8.1 Hz, 4 H; bq-CH), 4.76 (d, ^3J(H,H) = 8.3 Hz, 4 H; bq-CH), 6.95 (s, 8 H; aryl-CH), 7.22 ppm (s, 4 H; imidazole-CH); ^{13}C NMR (100 MHz, [D$_8$]THF, 23 °C): $\delta = 18.1$ (CH$_3$), 21.2 (CH$_3$), 95.9 (bq-CH), 107.9 (bq-CH), 123.8 (CH), 129.5 (CH), 136.9, 138.1, 138.9, 171.3, 183.6, 190.8 ppm; IR (KBr): $\tilde{\nu} = 3441$, 1632, 1587, 1519, 1488, 1401, 1322, 845,

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740, 691 cm^{-1}; MS (FAB): *m/z* (%): 1038 (5) $[M]^+$, 822 (100), 714 (62); elemental analysis calcd (%) for $C_{54}H_{56}N_4O_4Pd_2$ (1037.9): C 62.49, H 5.44, N 5.39; found: C 62.75, H 5.42, N 5.30.

Synthesis of [(1,3-dimesitylimidazol-2-ylidene)(naphthoquinone)palladium(0)]$_2$ (3): Complex **3** was prepared similar to **2** from (1,5-cyclooctadiene)(naphthoquinone)palladium(0) (372.5 mg, 1 mmol). Yield: 480 mg, 84%; ^{1}H NMR (400 MHz, [D$_8$]THF, 23 °C): $\delta = 1.85$ (s, 12H; CH$_3$), 2.09 (s, 12H; CH$_3$), 3.34 (s, 12H; CH$_3$), 3.88 (d, ^3J(H,H) = 6.5 Hz, 2H; nq-CH), 3.94 (d, ^3J(H,H) = 6.5 Hz, 2H; nq-CH), 6.84 (s, 8H; aryl-CH), 7.15 (m, 4H; aryl-CH), 7.17 (s, 4H; imidazole-CH), 7.34 (d, ^3J(H,H) = 7.3 Hz, 2H; aryl-CH), 7.37 ppm (d, ^3J(H,H) = 7.5 Hz, 2H; aryl-CH); ^{13}C NMR (100 MHz, [D$_8$]THF, 23 °C): $\delta = 19.0$ (CH$_3$), 19.1 (CH$_3$), 19.5 (CH$_3$), 56.2 (nq-CH), 72.1 (nq-CH), 124.7 (CH), 125.9 (CH), 126.9 (CH), 130.1 (CH), 130.3 (CH), 130.9 (CH), 131.6 (CH), 136.0, 137.8, 138.1, 139.1, 139.8, 140.9, 170.4, 184.3, 192.9 ppm; IR (KBr): $\tilde{\nu} = 3448$, 1632, 1577, 1530, 1488, 1319, 1298, 1009, 850, 783 cm^{-1}; MS (FAB): *m/z* (%): 1138 (3) $[M]^+$, 821 (100), 714 (30); elemental analysis calcd (%) for $C_{62}H_{60}N_4O_4Pd_2$ (1137.6): C 65.44, H 5.31, N 4.92; found: C 65.79, H 5.48, N 4.80.

General procedure for Heck and Suzuki reactions: Aryldiazonium salts (1.0 mmol), olefin (1.5 mmol) or arylboronic acid (1.5 mmol), and **3** (5.7 mg, 0.005 mmol, 1 mol% Pd) were charged in a Schlenk tube under argon. Methanol (5 mL) was syringed in and the solution was stirred at 50 °C for 1 h. Diethyleneglycol di-*n*-butyl ether (200 μL) was added as internal standard and the yield was determined by GC. After the organic phase had been washed with water and brine, the solvent was evaporated. The product was isolated by column chromatography (silica gel, hexane/ethyl acetate mixtures).

Analytical data of coupling products

2′-Ethylhexyl 4-methoxycinnamate: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 0.91$ (m, 6H), 1.32–1.58 (m, 9H), 3.84 (s, 3H), 4.11 (m, 2H), 6.31 (d, ^3J(H,H) = 15.9 Hz, 1H), 6.89 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.47 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.62 ppm (d, ^3J(H,H) = 16.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 11.5$, 14.5, 23.4, 24.3, 29.4, 30.9, 39.3, 55.8, 67.2, 114.7, 116.2, 127.6, 130.1, 144.6, 161.7, 168.0 ppm; MS (70 eV): *m/z* (%): 290 (23) $[M]^+$, 178 (100).

2′-Ethylhexyl 4-*N,N*-diethylaminocinnamate: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 0.82$ (m, 6H), 1.11 (t, ^3J(H,H) = 6.9 Hz, 6H), 1.15–1.58 (m, 9H), 3.32 (q, ^3J(H,H) = 6.9 Hz, 4H), 4.02 (m, 2H), 6.12 (d, ^3J(H,H) = 15.9 Hz, 1H), 6.55 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.32 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.52 ppm (d, ^3J(H,H) = 15.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 11.5$, 13.0, 14.5, 23.4, 24.3, 29.4, 30.9, 39.3, 44.9, 67.0, 111.6, 112.4, 121.8, 130.4, 145.5, 149.7, 168.7 ppm; MS (70 eV): *m/z* (%): 331 (60) $[M]^+$, 316 (100).

2′-Ethylhexyl 4-nitrocinnamate: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta =$ 0.85 (m, 6H), 1.25–1.60 (m, 9H), 4.08 (m, 2H), 6.50 (d, ^3J(H,H) = 16.0 Hz, 1H), 7.61 (m, 3H), 8.18 ppm (d, ^3J(H,H) = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 11.4$, 14.5, 23.4, 24.2, 29.4, 30.8, 39.2, 67.8, 123.1, 124.6, 129.1, 141.0, 141.9, 148.9, 166.6 ppm; MS (70 eV): *m/z* (%): 305 (28) $[M]^+$, 176 (35), 70 (100).

2′-Ethylhexyl 4-bromocinnamate: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta =$ 0.84 (m, 6H), 1.24–1.36 (m, 8H), 1.57 (m, 1H), 4.05 (m, 2H), 6.36 (d, ^3J(H,H) = 16.1 Hz, 1H), 7.34 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.44 (d, ^3J(H,H) = 8.3 Hz, 2H), 7.55 ppm (d, ^3J(H,H) = 16.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 11.5$, 14.5, 23.4, 24.3, 29.4, 30.9, 67.5, 119.5, 124.9, 129.9, 132.5, 133.8, 143.5, 167.4 ppm; MS (70 eV): *m/z* (%): 340 (4) $[M]^+$, 338 (4), 228 (84), 226 (74), 70 (100).

Ethyl 4-methoxycinnamate: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.32$ (t, ^3J(H,H) = 7.1 Hz, 3H), 3.83 (s, 3H), 4.24 (q, ^3J(H,H) = 7.2 Hz, 2H), 6.30 (d, ^3J(H,H) = 15.8 Hz, 1H), 6.89 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.46 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.63 ppm (d, ^3J(H,H) = 15.9 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 14.8$, 55.7, 60.7, 114.7, 116.1, 127.6, 130.1, 144.6, 161.7, 167.7 ppm; MS (70 eV): *m/z* (%): 206 (60) $[M]^+$, 161 (100).

Ethyl 4-*N,N*-diethylaminocinnamate: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.32$ (t, ^3J(H,H) = 7.1 Hz, 6H), 1.45 (t, ^3J(H,H) = 7.1 Hz, 3H), 3.55 (q, ^3J(H,H) = 6.9 Hz, 4H), 4.39 (q, ^3J(H,H) = 7.1 Hz, 2H), 6.35 (d, ^3J(H,H) = 15.9 Hz, 1H), 6.79 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.55 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.75 ppm (d, ^3J(H,H) = 15.9 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 13.0$, 14.9, 44.9, 60.4, 111.6, 112.2, 121.8, 130.5, 145.6, 149.7, 168.4 ppm; MS (70 eV): *m/z* (%): 247 (58) $[M]^+$, 232 (100).

4-Methoxystilbene: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 3.83$ (s, 3H), 6.90 (d, ^3J(H,H) = 8.5 Hz, 2H), 6.97 (d, ^3J(H,H) = 16.2 Hz, 1H), 7.06 (d, ^3J(H,H) = 16.2 Hz, 1H), 7.23–7.36 (m, 3H), 7.45 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.48 ppm (d, ^3J(H,H) = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 55.8$, 114.6, 126.7, 127.0, 127.6, 128.1, 128.6, 129.1, 130.6, 138.1, 159.7 ppm; MS (70 eV): *m/z* (%): 210 (100) $[M]^+$.

4-*N,N*-Diethylaminostilbene: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.09$ (m, 6H), 3.29 (m, 4H), 6.59 (d, ^3J(H,H) = 8.5 Hz, 2H), 6.81 (d, ^3J(H,H) = 16.3 Hz, 1H), 6.36 (d, ^3J(H,H) = 16.3 Hz, 1H), 6.99–7.19 (m, 3H), 7.24 (m, 2H), 7.31 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.39 ppm (m, 2H); MS (70 eV): *m/z* (%): 251 (66) $[M]^+$, 236 (100).

4-Nitrostilbene: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 7.14$ (d, ^3J(H,H) = 16.2 Hz, 1H), 7.25–7.42 (m, 4H), 7.55 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.63 (d, ^3J(H,H) = 8.7 Hz, 2H), 8.22 ppm (d, ^3J(H,H) = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 123.1$, 125.2, 125.8, 126.0, 127.8, 127.9, 132.3, 135.1, 142.8, 145.7 ppm; MS (70 eV): *m/z* (%): 225 (100) $[M]^+$.

4-Bromostilbene: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 6.96$ (d, ^3J(H,H) = 16.3 Hz, 1H), 7.03 (d, ^3J(H,H) = 16.3 Hz, 1H), 7.20 (m, 1H), 7.28 (m, 4H), 7.42 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta =$ 121.8, 127.0, 127.8, 128.3, 128.4, 129.2, 129.9, 132.2, 136.7, 137.8 ppm; MS (70 eV): *m/z* (%): 260 (56) $[M]^+$, 258 (54), 179 (93), 178 (100).

4-*N,N*-Diethylaminobiphenyl: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.20$ (t, ^3J(H,H) = 6.9 Hz, 6H), 3.40 (q, ^3J(H,H) = 6.9 Hz, 4H), 6.75 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.24 (m, 1H), 7.39 (t, ^3J(H,H) = 7.5 Hz, 2H), 7.48 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.55 ppm (d, ^3J(H,H) = 7.7, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 13.1$, 44.9, 112.4, 126.2, 126.6, 128.4, 128.5, 129.1, 141.8, 147.6 ppm; MS (70 eV): *m/z* (%): 225 (59) $[M]^+$, 210 (100).

4-*N,N*-Diethylamino-2′-methylbiphenyl: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.13$ (t, ^3J(H,H) = 6.9 Hz, 6H), 2.25 (s, 3H), 3.31 (q, ^3J(H,H) = 7.1 Hz, 4H), 6.64 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.11–7.18 ppm (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 13.1$, 21.2, 44.8, 111.6, 126.2, 126.8, 129.2, 130.4, 130.6, 130.7, 135.9, 142.5, 147.1 ppm; MS (70 eV): *m/z* (%): 239 (56) $[M]^+$, 224 (100).

4-*N,N*-Diethylamino-3′-ethoxybiphenyl: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.12$ (t, ^3J(H,H) = 6.9 Hz, 6H), 1.36 (t, ^3J(H,H) = 6.9 Hz, 3H), 3.31 (q, ^3J(H,H) = 6.9 Hz, 4H), 4.00 (q, ^3J(H,H) = 6.9 Hz, 2H), 6.65 (d, ^3J(H,H) = 8.9 Hz, 2H), 6.70 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.2 Hz, 1H), 7.02 (d, ^4J(H,H) = 1.9 Hz, 1H), 7.05 (d, ^3J(H,H) = 7.7 Hz, 1H), 7.20 (dd, ^3J(H,H) = 5.9 Hz, ^3J(H,H) = 6.5 Hz, 1H), 7.40 ppm (d, ^3J(H,H) = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 13.1$, 15.4, 44.8, 63.8, 112.2, 112.3, 112.9, 119.1, 128.3, 128.4, 130.0, 143.3, 147.7, 159.7 ppm; MS (70 eV): *m/z* (%): 269 (61) $[M]^+$, 254 (100).

4-*N,N*-Diethylamino-4′-bromobiphenyl: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.20$ (t, ^3J(H,H) = 7.2 Hz, 6H), 3.33 (q, ^3J(H,H) = 6.9 Hz, 4H), 6.66 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.33 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.36 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.41 ppm (d, ^3J(H,H) = 8.52H, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 13.0$, 44.8, 112.3, 120.1, 127.0, 128.1, 128.2, 132.1, 140.6, 147.8 ppm; MS (70 eV): *m/z* (%): 305 (62) $[M]^+$, 303 (56), 290 (100).

1-(4′-*N,N*-Diethylaminophenyl)naphthalene: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.16$ (t, ^3J(H,H) = 7.1 Hz, 6H), 3.36 (q, ^3J(H,H) = 7.2 Hz, 4H), 6.72 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.23–7.44 (m, 6H), 7.71 (d, ^3J(H,H) = 8.1 Hz, 1H), 7.81 (d, ^3J(H,H) = 7.9 Hz, 1H), 7.99 ppm (d, ^3J(H,H) = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 13.2$, 44.9, 111.8, 117.0, 126.0, 126.1, 126.2, 126.9, 127.2, 128.0, 128.7, 131.5, 132.4, 134.4, 141.1, 147.5 ppm; MS (70 eV): *m/z* (%): 275 (50) $[M]^+$, 260 (100).

3-(4′-*N,N*-Diethylaminophenyl)thiophene: ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = 1.11$ (t, ^3J(H,H) = 7.1 Hz, 6H), 3.30 (q, ^3J(H,H) = 7.2 Hz, 4H), 6.63 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.18 (s, 1H), 7.26 (d, ^3J(H,H) = 2.0 Hz, 2H), 7.38 ppm (d, ^3J(H,H) = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 23 °C): $\delta = 13.1$, 44.8, 112.3, 117.6, 126.1, 126.6, 127.9, 136.1, 143.1, 147.4 ppm; MS (70 eV): *m/z*(%): 231 (65) $[M]^+$, 216 (100).

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