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Ligand effects in palladium-catalyzed Suzuki and Heck coupling reactions

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A range of sterically hindered diimine ligands and their palladium (II) complexes were synthesized. These compounds were fully characterized by elemental analysis, ^{1}H and ^{13}C-NMR spectroscopy. The use of the palladium complexes as catalysts for Suzuki and Heck coupling has been studied in an attempt to demonstrate the effect of side groups on catalytic activity. It was clearly seen that the location of side $-CH_3$ groups which bound to benzene ring had little effect on catalytic activity. Interestingly when we changed these $-CH_3$ groups with $-Cl$ groups the activity of the complexes increased. On the other hand, side groups which bound to imine nitrogen also had a large effect on catalytic activity. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: Suzuki coupling; Heck coupling; palladium (II)

Introduction

The coupling of aryl halides with aryl boronic acids, the Suzuki reaction is one of the most powerful and adaptable methods for the synthesis of biaryls.[1] The use of aryl chloride substrates in such reactions is attractive because they tend to be cheaper and more widely available than their bromide or iodide counterparts. Unfortunately the relatively high C–Cl bond strength retards the rate of oxidative addition and thus makes their activation more difficult than for heavier congeners.[2] On the other hand Suzuki coupling reaction with aryl, vinyl halides/triflates and boronic acids is very significant because it has been applied industrially to the production of losartan, which is a Merck antihypertensive drug.[3]

Palladium complexes which contain sterically hindered α-diimine ligands are highly efficacious for olefin polymerization[1,2] and also for Suzuki cross-coupling reactions.[4] We are interested in Pd-catalyzed carbon–carbon coupling reactions of the Heck and Suzuki type, which are also used in fine chemical synthesis, even though currently heterogeneous catalysts are preferred.[5,6]

In this work we wish to report on the synthesis and characterization of a series of palladium complexes which contain different side groups and to attempt to correlate the disparity of catalytic activity with these groups. We used our catalysts in the catalytic cross-coupling of various aryl halides with aryl boronic acids (Suzuki reaction)[7] and methyl acrylate (Heck reaction).[8,9]

Results and Discussion

Ligand synthesis

The diimines **1–12** were synthesized using Dean–Stark apparatus according to Fig. 1. Condensation of diverse amines in the presence of ketones finally afforded the desired diimines **1–12** in good yields. Characterization of α-diimines was accomplished by a combination of elemental analysis, ^{1}H and ^{13}C NMR spectroscopy. Elemental analyses of compounds fully fitted with theoretical results. The ^{1}H-NMR spectra of **1–3**, acidic protons which were seen between 7.5–7.6 as singlets, are an important point of characterization. On the other hand, because of the rotation of side $-CH_3$ groups, the ^{1}H-NMR spectrum shows differences between 2.00 and 2.50 ppm. For compound **3**, only one singlet was seen at 2.28 ppm (6H) because of molecular symmetry. For other compounds, R groups were easily characterized using ^{1}H and ^{13}C-NMR.

Synthesis of Pd–diimine Complexes

Treatment of $PdCl_2(CH_3CN)_2$ with ligands **1–12** (Fig. 1) in boiling CH_3CN for 2 h afforded complexes **13–24** cleanly in good isolated yields. All complexes were yellow solids that were air-stable both in the solid state and in solution (Fig. 2).

The identity of the compounds was established absolutely by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy. Elemental analyses of compounds fully fitted with experimental analysis. Diagnostic of chelating ligand coordination in these complexes is an overall downfield shift of signals in the ^{1}N-NMR spectra by about 5–15 ppm. Similar resonance shifts have been observed in related complexes.[9] All complexes are stable in air and readily soluble in polar organic compounds such as methanol, DMSO and DMF.

Suzuki coupling

Palladium complexes containing diimine ligands are excellent catalysts for Suzuki coupling. On the basis of these findings we think that our complexes should exhibit similar reactivities in C–C bond coupling reactions. Accordingly we investigated the activity of complexes **13–24** for the coupling of various aryl halides with aryl boronic acids. The results of this study are summarized in

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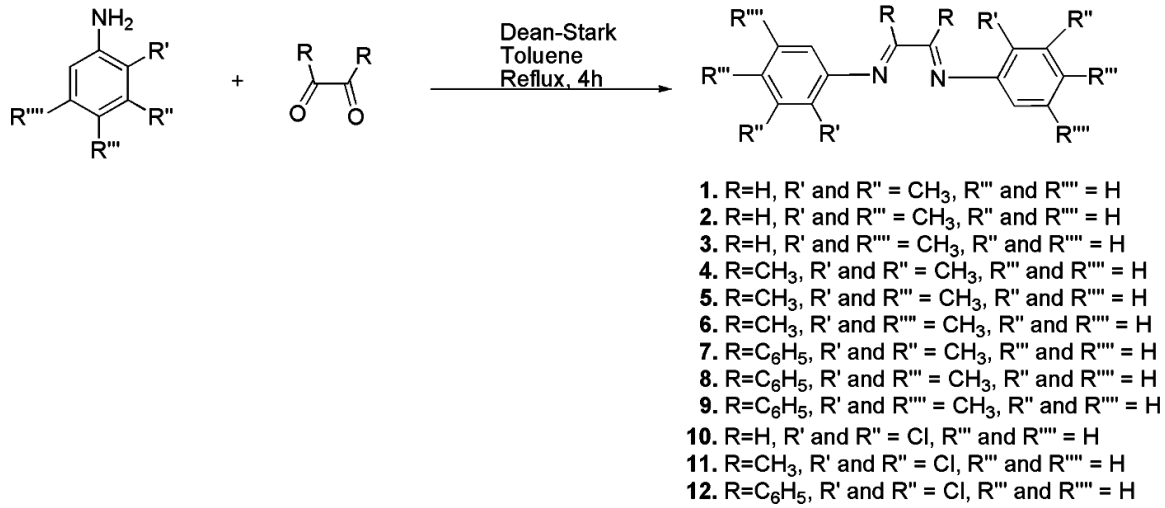
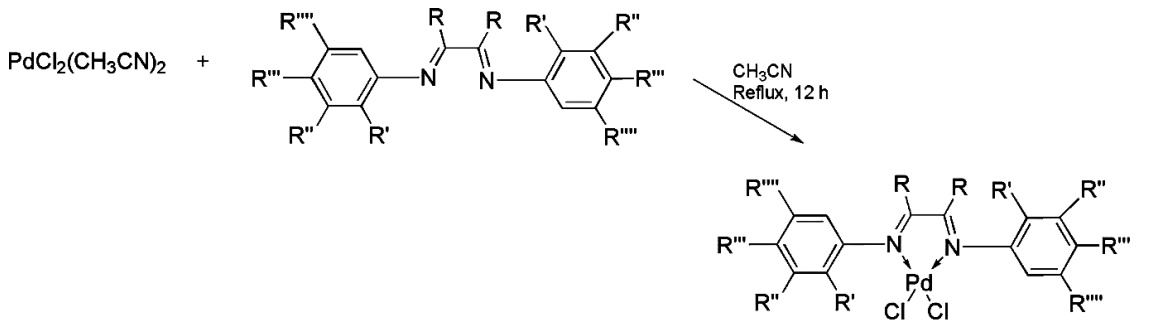


1. R=H, R' and R'' = CH_3, R''' and R'''' = H
2. R=H, R' and R''' = CH_3, R'' and R'''' = H
3. R=H, R' and R'''' = CH_3, R'' and R''' = H
4. R=CH_3, R' and R'' = CH_3, R''' and R'''' = H
5. R=CH_3, R' and R''' = CH_3, R'' and R'''' = H
6. R=CH_3, R' and R'''' = CH_3, R'' and R''' = H
7. R=C_6H_5, R' and R'' = CH_3, R''' and R'''' = H
8. R=C_6H_5, R' and R''' = CH_3, R'' and R'''' = H
9. R=C_6H_5, R' and R'''' = CH_3, R'' and R''' = H
10. R=H, R' and R'' = Cl, R''' and R'''' = H
11. R=CH_3, R' and R'' = Cl, R''' and R'''' = H
12. R=C_6H_5, R' and R'' = Cl, R''' and R'''' = H

Figure 1. Synthetic route of ligands.



13. R=H, R' and R'' = CH_3, R''' and R'''' = H
14. R=H, R' and R''' = CH_3, R'' and R'''' = H
15. R=H, R' and R'''' = CH_3, R'' and R''' = H
16. R=CH_3, R' and R'' = CH_3, R''' and R'''' = H
17. R=CH_3, R' and R''' = CH_3, R'' and R'''' = H
18. R=CH_3, R' and R'''' = CH_3, R'' and R''' = H
19. R=C_6H_5, R' and R'' = CH_3, R''' and R'''' = H
20. R=C_6H_5, R' and R''' = CH_3, R'' and R'''' = H
21. R=C_6H_5, R' and R'''' = CH_3, R'' and R''' = H
22. R=H, R' and R'' = Cl, R''' and R'''' = H
23. R=CH_3, R' and R'' = Cl, R''' and R'''' = H
24. R=C_6H_5, R' and R'' = Cl, R''' and R'''' = H

Figure 2. Synthetic route of complexes.

Table 1. In all cases the reactions were performed with 3 mol% of catalysts in dioxane at 80 °C with Cs_2CO_3 acting as base. These conditions have not been optimized.

In general, between the complexes with $-CH_3$ side groups, the coupling reaction is more efficient if complex **13–15** are used. On the other hand, it is difficult to establish any clear trends in the catalytic activity of complexes **19–21**. However, as seen from Table 1, complexes **16–18** display less activity than the others. This reactivity trend suggests that the stronger electron-donating ability of alkyl substituents, making the ligand more electron rich, renders the catalyst less active (Fig. 3). At that point, in order to attest these results, we changed side $-CH_3$ groups with electronegative $-Cl$ groups (**22–24**). Eventually as seen in Tables 1 and 2, when we used complex **22–24**, the activity of catalytic reaction increased as expected.

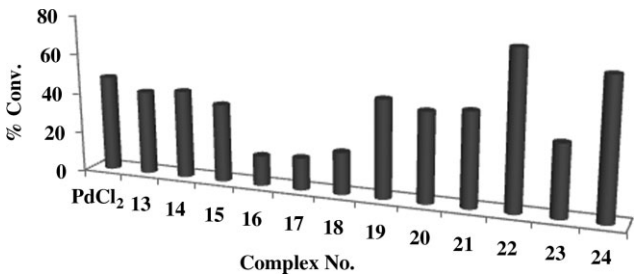
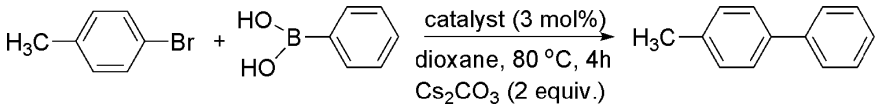


Figure 3. Comparison of complexes for Suzuki coupling reactions.

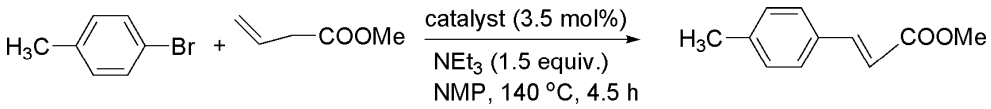
We observed that the coupling of 4-bromoacetophenone and 4-bromotoluene with phenylboronic acid proceeded smoothly to give 4-acetylphenyl in good yields. Finally, the catalytic effect was

Table 1. Suzuki cross-coupling of aryl halides with arylboronic acids[a]

Entry	Catalyst	Isolated yield (%)
		
1	**$PdCl_2$**	14[b]
2	**13**	65[b]
3	**14**	57[b]
4	**15**	62[b]
5	**16**	28[b]
6	**17**	35[b]
7	**18**	38[b]
8	**19**	51[b]
9	**20**	59[b]
10	**21**	49[b]
11	**22**	89[b]
12	**23**	59[b]
13	**24**	71[b]

[a] Reaction conditions: aryl halide (1.0 mmol), boronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol) and catalyst (3 mol%).
[b] Determined by GC.

Table 2. Heck cross-coupling of aryl halides with olefins[a]

Entry	Catalyst	Isolated yield (%)
		
1	**$PdCl_2$**	48[b]
2	**13**	77[b]
3	**14**	79[b]
4	**15**	66[b]
5	**16**	52[b]
6	**17**	50[b]
7	**18**	53[b]
8	**19**	68[b]
9	**20**	65[b]
10	**21**	65[b]
11	**22**	92[b]
12	**23**	79[b]
13	**24**	88[b]

[a] Reaction conditions: aryl halide (1.0 mmol), methyl acrylate (1.2 mmol), NEt_3 (1.5 mmol) and catalyst (3.5 mol%).
[b] Determined by GC.

confirmed by running the standard reaction on 4-bromotoluene without ligand (entry 1). The reaction proceeded, but led to only low yields.

Heck coupling

The Heck reaction between aryl bromides and methyl acrylate has been studied using complexes **12–24** as catalysts (Fig. 4). The results are summarized in Table 2. All of the reactions are performed with 3.5 mol% of catalysts in NMP as solvent at 140 °C with NEt_3 acting as base. Conditions were not optimized.

For catalysts, the Suzuki reaction is more efficient than the Heck coupling reaction. On the other hand, all complexes had moderate activity on the Heck coupling reaction and there was no clear trend in the catalytic activity of complexes **12–24**.

Conclusion

In summary, it was clearly seen that coupling reactions with aryl bromides show that the location of side $-CH_3$ groups which bound to benzene ring, had a considerable effect on catalytic activity. On the other hand, side groups which bound to imine nitrogen had a

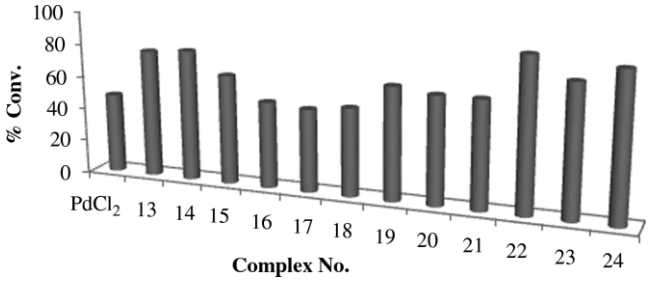


Figure 4. Comparision of complexes for Heck coupling reactions.

great effect on catalytic activity. When we changed $-CH_3$ groups for –Cl groups, the activity of complexes increased conspicuously. All of the complexes which were synthesized showed activity in both the Suzuki and Heck reactions. Despite their high catalytic activity, the overall efficiency of these complexes suffered due to a lack of stability, especially at high reaction temperatures. On the other hand, for a Heck reaction we saw a stronger electron donating ability of alkyl substituents, making the ligand more electron-rich and rendering the catalyst less active.

Experimental

All reactions were performed under a dry, oxygen-free, argon atmosphere. ^{1}H NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker X-WIN spectrometer operating at 400 MHz or Bruker/Biospin NMR 300 MHz with $SiMe_4$ (0.0 ppm) as internal reference. Element analysis were performed on a Leco CHNS 932. Melting points were measured on a Büchi Melting Point B-540 apparatus and are uncorrected. Atmospheric pressure chemical ionization (APCI) mass spectra were recorded with an Agilent 1100 MSD LC-MS mass spectrometer. All chemicals were standard reagent grade and used without further purification. $PdCl_2(CH_3CN)_2$ were prepared according to the literature.[9]

(*E*)-*N*-[(*E*)-2-(2,3-dimethylphenylimino)ethylidene]-2, 3-dimethylbenzenamine (1)

Glyoxal (0.01 mol, 0.58 g) was dissolved in a minimum amount of freshly distilled EtOH. To that solution 2,3-dimethylanilne (0.02 mol, 2.42 g) and benzene (30 ml) were added and refluxed with Dean–Stark apparatus for 4 h. The resulting solution was cooled to room temperature and the pale yellow solid was precipitated. After filtering the solution, crystals was washed with diethyl ether and dried under vacuum. Yield: 1.58 g (60%). Found: C 81.55, H 7.59, N 10.73, M^+ 263.21. Calcd for $C_{18}H_{20}N_2$: C 81.78, H 7.63, N 10.60. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 6H), 2.43 (s, 6H), 6.58–7.23 (m, 5H), 7.61 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 13.72, 19.97, 118.78, 119.07, 124.47, 126.63, 139.44, 145.12, 147.42.

(*E*)-*N*-[(*E*)-2-(2,4-dimethylphenylimino)ethylidene]-2, 4-dimethylbenzenamine (2)

Glyoxal (0.01 mol, 0.58 g) and 2,4-dimethylanilne (0.02 mol, 2.42 g) gave similarly to the procedure described for **1** a pale yellow solid. Yield: 1.92 (72%). Found: C 81.63, H 7.42, N 10.31, M^+ 261.72. Calcd for $C_{18}H_{20}N_2$: C 81.78, H 7.63, N 10.60. ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 6H), 2.45 (s, 6H), 6.44–7.02 (m, 6H), 7.63 (2H). ^{13}C NMR ($CDCl_3$): δ 18.6, 20.65, 124.20, 127.84, 128.40, 129.34, 133.72, 145.12, 151.04.

(*E*)-*N*-[(*E*)-2-(2,5-dimethylphenylimino)ethylidene]-2, 5-dimethylbenzenamine (3)

Glyoxal (0.01 mol, 0.58 g) and 2,5-dimethylaniline (0.02 mol, 2.42 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 1.88 (71%). Found: C 81.51, H 7.56, N 10.44, M^+ 262.89. Calcd for $C_{18}H_{20}N_2$: C 81.78, H 7.63, N 10.60. ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 12H), 6.62–7.34 (m, 6H), 7.71 (2H). ^{13}C NMR ($CDCl_3$): δ 18.17, 21.4, 124.55, 127.77, 128.44, 131.53, 136.14, 145.12, 148.74.

(*E*)-*N*-[(*E*)-3-(2,3-dimethylphenylimino)butan-2-ylidene]-2, 3-dimethylbenzenamine (4)

Butane-2,3-dione (0.01 mol, 0.86 g) and 2,3-dimethylanilne (0.02 mol, 2.42 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 2.13 (72%). Found: C 82.11, H 7.98, N 9.73, M^+ 292.89. Calcd for $C_{20}H_{24}N_2$: C 82.15, H 8.27, N 9.58. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 6H), 2.36 (s, 6H), 2.44 (s, 6H), 6.54–7.24 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 13.72, 15.15, 19.97, 118.63, 118.92, 124.43, 126.25, 138.59, 147.65, 162.52.

(*E*)-*N*-[(*E*)-3-(2,4-dimethylphenylimino)butan-2-ylidene]-2, 4-dimethylbenzenamine (5)

Butane-2,3-dione (0.01 mol, 0.86 g) and 2,4-dimethylanilne (0.02 mol, 2.42 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 2.48 (84%). Found: C 82.39, H 8.51, N 9.63, M^+ 291.10. Calcd for $C_{20}H_{24}N_2$: C 82.15, H 8.27, N 9.58. ^{1}H NMR ($CDCl_3$): δ 2.02 (s, 6H), 2.09 (s, 6H), 2.45 (s, 6H), 6.39–7.08 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 15.15, 18.64, 20.65, 124.04, 127.46, 128.25, 128.97, 133.67, 151.27, 160.52.

(*E*)-*N*-[(*E*)-3-(2,5-dimethylphenylimino)butan-2-ylidene]-2, 5-dimethylbenzenamine (6)

Butane-2,3-dione (0.01 mol, 0.86 g) and 2,5-dimethylanilne (0.02 mol, 2.42 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 1.84 (63%). Found: C 82.45, H 8.24, N 9.41, M^+ 292.25. Calcd for $C_{20}H_{24}N_2$: C 82.15, H 8.27, N 9.58. ^{1}H NMR ($CDCl_3$): δ 2.02 (s, 6H), 2.28 (s, 6H), 6.57–7.34 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 15.18, 18.24, 22.48, 126.51, 127.61, 128.29, 131.24, 135.62, 148.97, 161.52.

(*E*)-*N*-[(*E*)-2-(2,3-dimethylphenylimino)-1, 2-diphenylethylidene]-2,3-dimethylbenzen-amine (7)

Benzil (0.01 mol, 2.1 g) and 2,3-dimethylanilne (0.02 mol, 2.42 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 2.98 (71%). Found: C 86.21, H 6.63, N 6.71, M^+ 415.87. Calcd for $C_{30}H_{28}N_2$: C 86.50, H 6.78, N 6.72. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 6H), 2.43 (s, 6H), 6.63 (d,2H), 7.24–7.28 (m, 4H), 7.41–7.48 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 13.72, 19.97, 119.21, 119.49, 124.04, 126.22, 127.09, 127.85, 130.25, 133.84, 138.56, 147.98, 160.04.

(*E*)-*N*-[(*E*)-2-(2,4-dimethylphenylimino)-1, 2-diphenylethylidene]-2,4-dimethylbenzen-amine (8)

Benzil (0.01 mol, 2.1 g) and 2,4-dimethylanilne (0.02 mol, 2.42 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 2.81 (67%). Found: C 86.48, H 6.94, N 6.51, M^+ 415.88. Calcd for $C_{30}H_{28}N_2$ C 86.50, H 6.78, N 6.72. ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 6H), 2.51 (s, 6H), 6.49 (m, 2H), 6.92 (m, 4H), 7.43–7.49 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 18.60, 20.65, 124.62, 127.09, 127.43, 127.85, 128.82, 128.93, 130.25, 133.29, 133.57, 151.59, 161.04.

(*E*)-*N*-[(*E*)-2-(2,5-dimethylphenylimino)-1, 2-diphenylethylidene]-2,5-dimethylbenzen-amine (9)

Benzil (0.01 mol, 2.1 g) and 2,4-dimethylanilne (0.02 mol, 2.42 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 3.09 (79%). Found: C 86.21, H 6.41, N 6.39, M^+ 416.83. Calcd for $C_{30}H_{28}N_2$: C 86.50, H 6.78, N 6.72. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 12H), 6.69 (m, 2H), 7.31–7.56 (m, 14 H). ^{13}C NMR ($CDCl_3$): δ 18.29, 21.90. 123.16, 127.15, 127.98, 128.21, 128.93, 130.36, 131.54, 133,71, 148.21, 162.56.

(*N*,*N*′*E*,*N*,*N*′*E*)-*N*,*N*′-(ethane-1,2-diylidene)bis(2, 3-dichloroaniline) (10)

Glyoxal (0.01 mol, 0.58 g) and 2,3-dichloroanilne (0.02 mol, 3.24 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 2.77 (80%). Found: C 48.69, H 2.04, N 8.43, M^+ 344.92. Calcd for $C_{14}H_8N_2Cl_4$: C 48.59, H 2.33, N 8.10. ^{1}H NMR ($CDCl_3$): δ 8.22 (s, 2H), 7.32–7.47 (m, 4H), 6.89 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 118.21, 120.89, 125.22, 135.46, 134.77, 148.51.

(*N*,*N*′*E*,*N*,*N*′*E*)-*N*,*N*′-(butane-2,3-diylidene)bis(2, 3-dichloroaniline) (11)

Butane-2,3-dione (0.01 mol, 0.86 g) and 2,3-dichloroanilne (0.02 mol, 3.24 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 2.92 (78%). Found: C 51.02, H 3.36, N 7.61, M^+ 370.69. Calcd for $C_{16}H_{12}N_2Cl_4$: C 51.37, H 3.23, N 7.49. ^{1}H NMR ($CDCl_3$): δ 2.14 (s, 6H), 6.71 (d, 2H), 7.45–7.47 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 16.18, 117.43, 119.77, 120.72, 125.67, 128.38, 132.16, 146.91, 174.42.

(*N*,*N*′*E*,*N*,*N*′*E*)-*N*,*N*′-(1,2-diphenylethane-1, 2-diylidene)bis(2,3-dichloroaniline) (12)

Benzil (0.01 mol, 2.1 g) and 2,3-dichloroanilne (0.02 mol, 3.24 g) gave analogously to the procedure described for **1** a pale yellow solid. Yield 3.52 (71%). Found: C 62.29, H 3.21, N 5.86, M^+ 496.13. Calcd for $C_{26}H_{16}N_2Cl_4$: C 62.68, H 3.24, N 5.62. ^{1}H NMR ($CDCl_3$): δ 6.71 (m, 2H), 7.36–7.57 (m, 14H, aromatic). ^{13}C NMR ($CDCl_3$): δ 119.45, 121.16, 125.74, 126.13, 126.28, 129.45, 130.51, 130.98, 132.47, 142.94, 165.53.

$PdCl_2$(1), (13)

A suspension of $PdCl_2$ (0.17g, 1 mmol) in CH_3CN (10 ml) was refluxed until a clear orange solution of $Pd(CH_3CN)_2Cl_2$ was formed. Compound **1** (0.26g, 1 mmol) was then added, whereupon the color of the solution change from orange to yellow. After the mixture had been refluxed for 12 h the solvent was removed under vacuum and the resulting solid was washed with diethyl ether. Yield 0.32 (73%). Decomposition temperature: 320 °C. Found: C 48.59, H 4.41, N 6.03, M^+ 440.71. Calcd for $C_{18}H_{20}Cl_2N_2Pd$: C 48.95, H 4.56, N 6.34. ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 6H), 2.53 (s, 6H), 6.73–8.13 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 19.51, 24.43, 121.44, 123.58, 136.43, 147.14, 151.28,3 154.28.

$PdCl_2$(2), (14)

This complex was prepared similarly to **13** with $PdCl_2$ (0.177g, 1 mmol) and **2** (0.26g, 1 mmol) as starting materials. Yield 2.71 (62%). Decomposition temperature: 301 °C. Found: C 48.77, H 4.53, N 6.21, M^+ 439.98. Calcd for $C_{18}H_{20}Cl_2N_2Pd$: C 48.95, H 4.56, N 6.34. ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 6H), 2.41 (s, 6H), 6.89–8.12 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 23.42, 24.51, 128.71, 132.59, 136.19, 140.74, 147.53, 152.14, 159.27.

$PdCl_2$(3), (15)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17g, 1 mmol) and (**3**) (0.26 g, 1 mmol) as starting material. Yield 3.19 (73%). Decomposition temperature: 296 °C. Found: C 48.82, H 4.69, N 6.01, M^+ 440.72. Calcd for $C_{18}H_{20}Cl_2N_2Pd$: C 48.95, H 4.56, N 6.34. ^{1}H NMR ($CDCl_3$): δ 2.47 (s, 12H), 6.81–7.51 (m, 6H), 8.02 (2H). ^{13}C NMR ($CDCl_3$): δ 22.53, 26.42, 132.63, 139.12, 143.51, 149.67, 152.28, 155.54, 158.66.

$PdCl_2$(4), (16)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **4** (0.29 g, 1 mmol) as starting materials. Yield 2.13 (46%). Decomposition temperature: 319 °C. Found: C 51.39, H 5.48, N 5.71, M^+ 467.03. Calcd for $C_{20}H_{24}Cl_2N_2Pd$: C 51.14, H 5.15, N 5.96. ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 6H), 2.46 (s, 6H), 2.51 (s, 6H), 6.89–7.84 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 19.66, 22.41, 24.29, 126.42, 132.86, 139.21, 142.28, 142.66, 152.71, 177.23.

$PdCl_2$(5), (17)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **5** (0.29 g, 1 mmol) as starting materials. Yield 2.86 (61%). Decomposition temperature: 322 °C. Found: C 51.18, H 5.22, N 5.83, M^+ 468.42. Calcd for $C_{20}H_{24}Cl_2N_2Pd$: C 51.14, H 5.15, N 5.96. ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 6H), 2.26 (s, 6H), 2.69 (s, 6H), 6.72–7.64 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 19.61, 23.49, 24.83, 129.14, 132.53, 135.91, 136.28, 136.92, 161.42, 172.19.

$PdCl_2$(6), (18)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **6** (0.29 g, 1 mmol) as starting materials. Yield 2.46 (52%). Decomposition temperature: 305 °C. Found: C 51.36, H 5.33, N 6.21, M^+ 467.72. Calcd for $C_{20}H_{24}Cl_2N_2Pd$: C 51.14, H 5.15, N 5.96. ^{1}H NMR ($CDCl_3$): δ 2.14 (s, 6H), 2.31 (s, 6H), 6.82–7.51 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 19.24, 21.59, 25.74, 131.42, 132.12, 131.65, 133.48 138.16, 152.44, 169.14.

$PdCl_2$(7), (19)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **7** (0.42 g, 1 mmol) as starting materials. Yield 3.78 (64%). Decomposition temperature: 327 °C. Found: C 60.31, H 4.83, N 4.64, M^+ 592.07. Calcd for $C_{30}H_{28}Cl_2N_2Pd$: C 60.67, H 4.75, N 4.72. ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 6H), 2.49 (s, 6H), 6.71 (d,2H), 7.36–7.45 (m, 4H), 7.62–7.68 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 15.28, 23.42, 126.11, 126.62, 127.14, 127.41, 127.91, 128.55, 132.21, 136.72, 141.28, 151.29, 169.14.

$PdCl_2$(8), (20)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **8** (0.42 g, 1 mmol) as starting materials. Yield 3.44 (58%). Decomposition temperature: 321 °C. Found: C 60.43, H 4.66, N 4.70, M^+ 591.41. Calcd for $C_{30}H_{28}Cl_2N_2Pd$: C 60.67, H 4.75, N 4.72. ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 6H), 2.73 (s, 6H), 7.06 (m, 2H), 7.22 (m, 4H), 7.63–7.87 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 22.71, 24.81, 129.84, 132.91, 133.25, 133.64, 134.48, 134.96, 134.41, 137.28, 140.42, 158.63, 168.25.

$PdCl_2$(9), (21)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **9** (0.42 g, 1 mmol) as starting materials. Yield 3.94 (67%). Decomposition temperature: 330 °C. Found: C 60.61, H 4.72, N 4.84, M^+ 592.83. Calcd for $C_{30}H_{28}Cl_2N_2Pd$: C 60.67, H 4.75 N 4.72. ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 12H), 6.81 (m, 2H), 7.53–7.81 (m, 14 H). ^{13}C NMR ($CDCl_3$): δ 21.53, 25.14. 128.41, 133.24, 133.83, 134.47, 134.99, 135.16, 135.72, 139,71, 152.19, 169.42.

$PdCl_2$(10), (22)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **10** (0.42 g, 1 mmol) as starting materials. Yield 3.94 (67%). Decomposition temperature: 267 °C (519.79). Found: C 31.97, H 1.63, N 5.48, M^+ 523.77. Calcd for $C_{14}H_8Cl_6N_2Pd$ C 32.13, H 1.54, N 5.35. ^{1}H NMR ($CDCl_3$): δ 8.41 (s, 2H), 7.59–7.62(m, 4H), 7.03 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 121.34, 123.42, 127.53, 136.55, 136.98, 150.72.

$PdCl_2$(11), (23)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **11** (0.42 g, 1 mmol) as starting materials. Yield 3.94 (67%). Decomposition temperature: 287 °C. Found: C 34.72, H 2.33, N 5.27, M^+ 553.77. Calcd for $C_{16}H_{12}Cl_6N_2Pd$: C 34.85, H 2.19, N 5.08. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 6H), 7.08 (d, 2H), 7.77–7.71 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 21.44, 121.73, 123.12, 123.63, 126.42, 130.72, 135.44, 149.42, 175.53.

$PdCl_2$(12), (24)

This complex was prepared similarly to **13** with $PdCl_2$ (0.17 g, 1 mmol) and **12** (0.42 g, 1 mmol) as starting materials. Yield 3.94 (67%). Decomposition temperature: 330 °C. Found: C 46.49, H 2.53, N 4.21, M^+ 673.41. Calcd for $C_{26}H_{16}Cl_6N_2Pd$: C 46.23, H 2.39, N 4.15. ^{1}H NMR ($CDCl_3$): δ 7.08 (m, 2H), 7.51–7.81 (m, 14H, aromatic). ^{13}C NMR ($CDCl_3$): δ 122.74, 123.45, 127.82, 128.11, 128.44, 131.52, 131.87, 132.19, 132.98, 149.12, 167.22.

General Suzuki procedure

Under an atmosphere of argon a solution catalyst (0.03 mmol) and ligand (0.03 mmol in dry dioxane (3 mL) were stirred at 80 °C for 45 min. Arylhalide (1 mmol), phenylboronic acid (1.5 mmol) and Cs_2CO_3 (2 mmol) were added and the mixture was stirred at 80 °C for an additional 3 h. After addition of 1 M NaOH solution (15 ml), the mixture was stirred for 20 min at room temperature. The layers were separated, and the water layer was extracted with Et_2O (10 × 5 ml). The combined organic layers were washed with water (2 × 10 mL) and a saturated NaCl solution (1 × 10 ml), dried over Na_2SO_4 and filtered. After evaporation of the solvent, the crude product was purified by flash chromatography.

General Heck reaction

Under an atmosphere of argon, a solution of catalyst (0.035 mmol) and ligand (0.035 mmol) in dry 1-methyl-2-pyrrolidine (3 ml) was stirred at 150 °C for 45 min. Arylbromide (1 mmol), methyl methacrylate (1.2 mmol) and NEt_3 (1.4 mmol) were added, and the mixture was stirred at 150 °C. A saturated NH_4Cl solution (10 ml) was added, and the mixture was extracted with CH_2Cl_2 (4 × 10 ml). The combined organic layers were washed with 2 M HCl (5 × 10 ml), water (1 × 10 ml) and saturated NaCl solution (2 × 10 ml), dried over Na_2SO_4 and filtered. The solvent was evaporated and the crude product was purified by flash chromatography.

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