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Communication

Evidence on palladacycle-retaining pathway for Suzuki coupling. Inapplicability of Hg-drop test for palladacycle catalysed reactions

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ABSTRACT

Investigation of the model atroposelective Suzuki reaction catalysed by chiral *CN*-palladacycles have shown that two types of catalytic cycle may operate simultaneously, with strong dependence of their contributions upon the palladacycle structure and conditions used. Dominant contribution of palladacycle retaining pathway was provided by the non-metallocene planar chiral iminate *CN*-palladacycle (R_{pl})-**4a** using as catalyst, in reaction performed in toluene under aerobic conditions with KF as a base, affording (S_a)-2-methoxy-1,1′-binaphthalene with enantioselectivity up to 53% *ee*. The catalyst was recovered almost quantitatively as an iodide-bridged dimer, whose structure was confirmed by an X-ray diffraction study of its phosphine derivative. It was also shown that the common Hg drop test was unsuitable for mechanistic testing of palladacycle-catalysed reactions because of the transmetallation product formation, whose structure was confirmed by an X-ray diffraction study.

1. Introduction

Herrmann's discovery of the unique catalytic activity of palladacycles for cross-coupling reactions [1] launched a new era in homogeneous catalysis. Impressive advances in its achiral versions [2] have stimulated the development of enantioselective catalysis by chiral cyclopalladated compounds (CPCs) [3]. Excellent results have been obtained for transformations based on palladacycles acting as mild Lewis acids, especially in Overman rearrangement [3,4] and hydrophosphination reactions [5]. In contrast, attempts to catalyse asymmetric cross-coupling reactions have so far been unsuccessful [6]. Such failures are usually explained by palladacycle destruction in the frames of the traditional Pd^0/Pd^{II} redox cycle.

However, recent computational [7] and experimental [8] research has provided a great deal of evidence in favour of alternative mechanistic schemes that may retain an intact state of palladacycle(s) in the catalysis. The negative Hg drop test, absence of an induction period in the catalysis without visible Pd black formation, and the high yield of recovered (after the reaction) cyclopalladated catalyst are in contradiction with a classical Pd^0/Pd^{II} scenario. The most valuable experimental evidence in support of the Pd^{II}/Pd^{IV} catalytic cycle for the Heck cross-coupling has been provided by Vicente's recent research [9]. Although the possibility of two reaction pathways operating in parallel is often recognized [8c,10], any attempts to estimate the relative contributions of two catalytic cycles were not attempted until now.

This preliminary communication describes our efforts to estimate some factors determining the contribution of palladacycle-retaining pathway of Suzuki reaction (via Pd^{IV} or anionic $[(E^{\cap}C)Pd^0]^-$ intermediates [10b]), required for the development of its asymmetric version. The important advantage of Suzuki cross-coupling is that it can normally occur under milder conditions [11] than those required for the Heck reaction (140–180 °C [12]), with some reactions even proceeding at room temperature (rt) [13]. The use of low-temperature regime is important not only for improving the enantioselectivity but also as a route for decreasing the possible contribution of a parallel Pd^0/Pd^{II} pathway. Therefore, the enantioselective catalysis of Suzuki cross-coupling by chiral CPCs seemed to be more promising. To the best of our knowledge, only two prior studies have involved the catalysis of the Suzuki reaction by chiral *NCN*- [14] or *PCN*-pincer complexes [15] with moderate enantioselectivity (20–49% *ee*).

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2. Results and discussion

Previously, we have shown that the use of the known *CN*-palladacycle *rac*-**1** as the (pre)catalyst provides extremely mild conditions for Suzuki cross-coupling: the model non-chiral reaction of *p*-tolyl bromide with phenylboronic acid can be conducted not only at rt but even at −18 °C [16]. Taking into account these results and numerous other evidence of high catalytic activity of *CN*-palladacycles in non-chiral Suzuki reactions [17], CPCs of this kind were used to find conditions for palladacycle-retaining pathway for the Suzuki reaction.

We have selected planar chiral *CN*-palladacycles with ferrocenyl (**1** [18], **2** [19]) or [2.2]paracyclophanyl backbone (**3** [20], **4a** [21]) as potential (pre)catalysts; the *C**-chiral *CN*-dimer **5** [22] was employed for comparison purposes (Fig. 1).

The catalytic activity and enantioselectivity of selected CPCs was estimated for the model atroposelective reaction of 1-naphthylboronic acid **6** with 1-iodo-2-methoxy-1-naphthalene **7** to afford 2-methoxy-1,1′-binaphthalene **8** (Table 1).

The efficiency of *CN*-dimer **1** in *binaphthyl* **8** formation (entries 1, 2) was decreased compared to that previously found for *biphenyl* formation under conditions more typical for Pd(II)/Pd(0)-catalysis [16]. After base and solvent screening, the better results were obtained using its α-Me-substituted analogue **2** (entries 3–10). This catalyst can operate at rt and at decreased loading (1.0 and 0.1 mol% of Pd, entries 5, 6), providing a high yield of binaphthyl product **8**, with optimal conditions affording 87–89% (entries 8, 9). General drawbacks of aminate *CN*-catalysts **1**–**3** include Pd black precipitation and the complete absence of asymmetric induction in reactions conducted in methanol (entries 3, 8, and 9).

Enantioselectivity of the aminate *CN*-catalysts appears to be relatively low, even in toluene varying in the range of <2% *ee* for (S_{pl})-**1** to ~8% *ee* for ($S_C R_{pl}$)-**2**, and ~10% *ee* for (R_C)-**5** (entries 2, 10, and 17, respectively). The best optical yields were obtained in experiments using imine catalyst (R_{pl})-**4a**, with enantioselectivity increasing from 15% *ee* in MeOH up to ~29% *ee* in toluene at rt, and then to 53% *ee* on reducing the temperature to 5 °C (entries 12, 14, and 16, respectively).

Imine catalyst (R_{pl})-**4a** has several advantages: it can operate at rt and at reduced temperatures, providing good yields of binaphthyl **8** even at only 1 mol% Pd loading (94%, entry 15), and without visible evidence of Pd black formation. This catalyst can be almost quantitatively recovered after the reaction (92–96% for entries 13, 14, and 16) as an iodide-bridged dimer (R_{pl})-**4b**, whose structure was confirmed by spectral and X-ray diffraction studies of its phosphine derivative (R_{pl})-**4c** (Fig. 2).

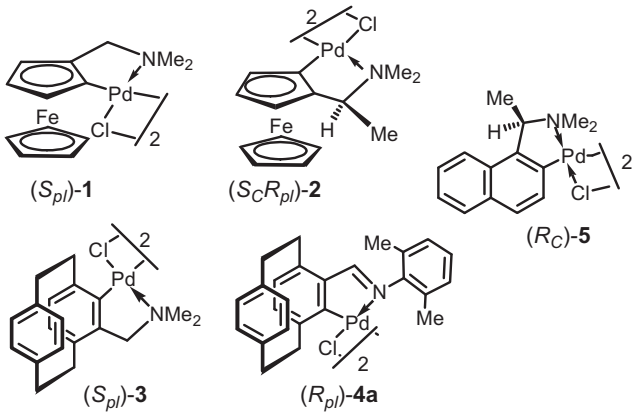
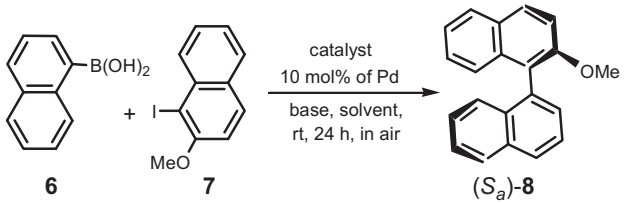


Fig. 1. CPCs selected for catalytic testing.

Table 1
Catalyst and reaction condition screening.[a]



Entry	Catalyst	Base	Solvent	Yield[b] (%)	*ee* (%)[c] (config)[d]
1	*rac*-**1**	K_2CO_3	MeOH	40	–
2	(S_{pl})-**1**	KF	Toluene	29	1.7(S_a)
3	($S_C R_{pl}$)-**2**	K_2CO_3	MeOH	41	0
4	*rac*-**2**	Cs_2CO_3	MeOH	45	–
5[e]	*rac*-**2**	KF	MeOH	51	–
6[f]	*rac*-**2**	KF	MeOH	60	–
7	($S_C R_{pl}$)-**2**	K_3PO_4	Toluene	79	0
8	($S_C R_{pl}$)-**2**	CsF	MeOH	89	0
9	($S_C R_{pl}$)-**2**	KF	MeOH	87	0
10	($S_C R_{pl}$)-**2**	KF	Toluene	70	7.9(R_a)
11	*rac*-**3**	KF	Toluene	52	–
12	(R_{pl})-**4a**	KF	MeOH	93	15.0(S_a)
13	(R_{pl})-**4a**	K_3PO_4	DCE	68	23.5(S_a)
14	(R_{pl})-**4a**	KF	Toluene	77	29.3(S_a)
15[e,g]	(R_{pl})-**4a**	KF	Toluene	**94**	37.3(S_a)
16[h]	(R_{pl})-**4a**	KF	Toluene	38	**53.0(S_a)**
17	(R_C)-**5**	KF	Toluene	28	10.2(S_a)

[a] Conditions: 0.212 mmol of aryl boronic acid **6**, 0.106 mmol of aryl iodide **7**, 5.0 eq. of base (0.5302 mmol), 5 mol% of dimeric catalyst (0.0053 mmol), and 2 mL of solvent were reacted in air at the rt for 24 h, unless otherwise noted.
[b] Isolated yields.
[c] Determined by HPLC on a Chiralcel OJ Column.
[d] The absolute configuration of product (+)$_D$-**8** was determined to be (S_a) by comparison with the reported HPLC-data.
[e] Catalyst loading was decreased to 1.0 mol% of Pd.
[f] Catalyst loading was decreased to 0.1 mol% of Pd and reaction time increased to 96 h.
[g] Reaction time was increased to 7 days.
[h] Reaction was conducted at 5 °C for 35 days.

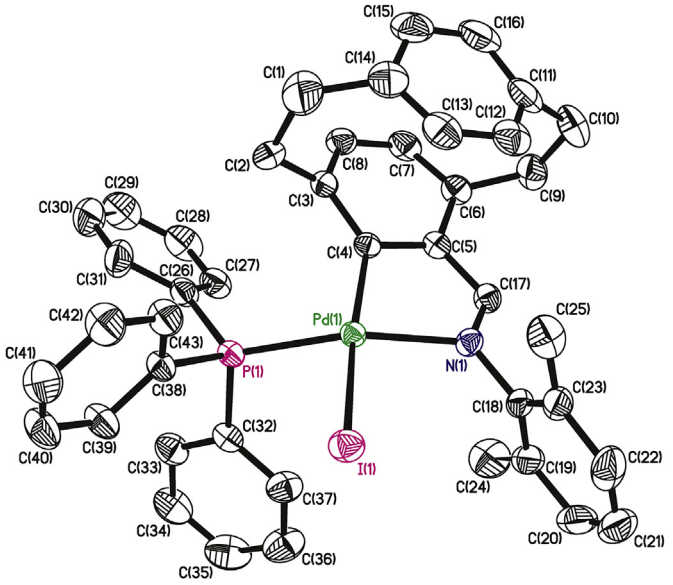


Fig. 2. Molecular structure of (R_{pl})-**4c**; selected bond lengths (Å): Pd(1)–C(4) 2.024(3); Pd(1)–I(1) 2.7085(4); Pd(1)–N(1) 2.110(3); Pd(1)–P(1) 2.2715(10). Selected bond angles (°): C(4)–Pd(1)–N(1) 80.44(13); C(4)–Pd(1)–P(1) 97.51(10); I(1)–Pd(1)–N(1) 96.30(8); P(1)–Pd(1)–I(1) 90.26(3).

Our experimental findings are in agreement with the presence of two different catalytic cycles operating simultaneously, with their contributions strongly dependent on both catalyst structure and reaction conditions. One pathway, based on the common Pd^0/Pd^{II} redox cycle, is dominant in all *CN*-palladacycle catalysed reactions carried out in methanol. As well as the progressive Pd black precipitation, the absence of enantioselectivity may be considered as additional stereochemical evidence of heterogeneous Pd^0 catalysis. Aminate palladacycle destruction due to the Pd^{II} to Pd^0 reduction, even in toluene, was indicated by the formation of the near-racemic product **8** in the reaction catalysed by the planar chiral complex (S_{pl})-**1** (<2% *ee*, entry 2), which is in accordance with the catalyst transformation into a non-chiral compound after Pd–C bond cleavage.

There is a great deal of experimental evidence in favour of the dominant contribution of a palladacycle-retaining pathway for the imine dimer (R_{pl})-**4a** catalysed Suzuki coupling in toluene. Firstly, the rather high enantioselectivity (up to 53% *ee*) indicates that the palladacyclic structure of the catalyst is preserved during the reaction. Secondly, the two-fold higher enantiomeric enrichment of product (S_a)-**8** isolated from the reaction in toluene compared to that of product (S_a)-**8** isolated from the reaction in methanol (29 and 15% *ee*, entries 14 and 12, respectively) may be caused by a decreased contribution of the destructive Pd^{II}/Pd^0 redox cycle in the aprotic solvent. Thirdly, all reactions conducted in toluene occurred in air without any visible evidence of Pd black formation. And finally, the cyclopalladated catalyst was almost quantitatively recovered after the reaction.

To support our mechanistic assumptions, we measured the kinetics of dimer (R_{pl})-**4a**-catalysed reactions in toluene and methanol at rt (entries 14 and 12) using a ^{1}H NMR control (Fig. 3).

The reaction in toluene did not reveal any induction period (Fig. 3a), which is required for palladacycle reduction during the pre-activation stage [23], and it is indicative of the dominant contribution of the palladacycle-retaining pathway under these conditions. The decreased conversion is caused by the conditions of NMR-monitoring excluding efficient stirring. By contrast, a sigmoidal-shaped kinetic curve was obtained for the reaction conducted in methanol (Fig. 3b). However, during the induction period of *ca.* 2–3 h the reaction rate was low but not zero, followed by a drastic increase in conversion to ~100% after 6 h. This anomaly allows us to assume that initially the coupling reaction is mainly catalysed by the palladacycle, providing some asymmetric induction, followed by more rapid non-chiral catalysis by the formed Pd^0 particles.

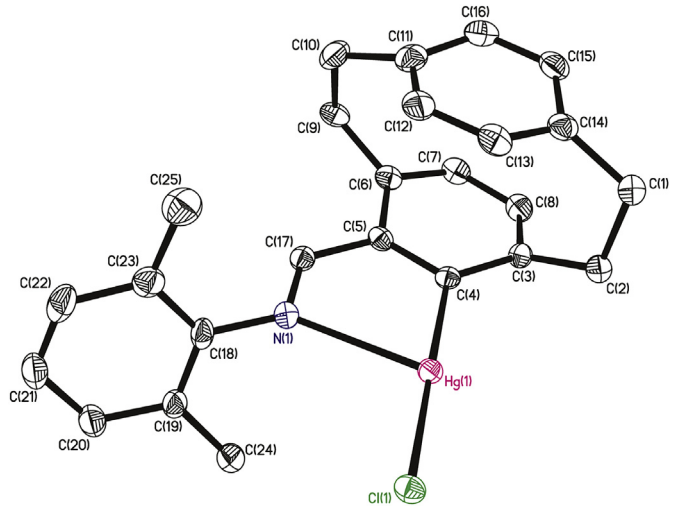


Fig. 4. Molecular structure of *rac*-**9**; selected bond lengths (Å): Hg(1)–C(4) 2.075(4); Hg(1)–Cl(1) 2.3435(10); Hg(1)–N(1) 2.586(3). Selected bond angles (°): C(4)–Hg(1)–N(1) 76.65(13); C(4)–Hg(1)–Cl(1) 179.10(11); Cl(1)–Hg(1)–N(1) 104.07(8).

In support of this conjecture we can mention more than two-fold decreasing of the final product (S_a)-**8** enantiopurity (16.8% *ee* at 83% conversion) compared to that of the binaphthyl (S_a)-**8** isolated at the initial stage (36.0% *ee* at 4% conversion) due to its subsequent "dilution" with racemic binaphthyl *rac*-**8** formed via Pd^0/Pd^{II} pathway. In contrast, only minor changes in the product (S_a)-**8** enantiopurity were observed in course of the reaction performed in toluene (31.9 and 29.4% *ee* at 15 and 50% conversion, respectively).

Furthermore, these two reactions were subjected to the Hg drop test. Unexpectedly, the suppression of catalysis by Hg^0 (which is usually considered as evidence for heterogeneous catalysis [23b] or catalysis via a Pd^0 intermediates [23a,c]) was observed in the reactions conducted both in methanol and toluene (<1% conversion). As this was not consistent with our other acquired data, control experiments were carried out. In reactions of dimer *rac*-**4a** with *ca.* 300 eq. of Hg^0 in both solvents, CPC conversion into a new complex was observed. This was identified as the redox-transmetallation product [{κ^2(*N*,*C*)-L}HgCl] (*rac*-**9**) by spectral and X-ray diffraction studies (Fig. 4).

Consequently, the efficient inhibition of catalysis by Hg^0 may be caused not only by the amalgamation of heterogeneous or soluble

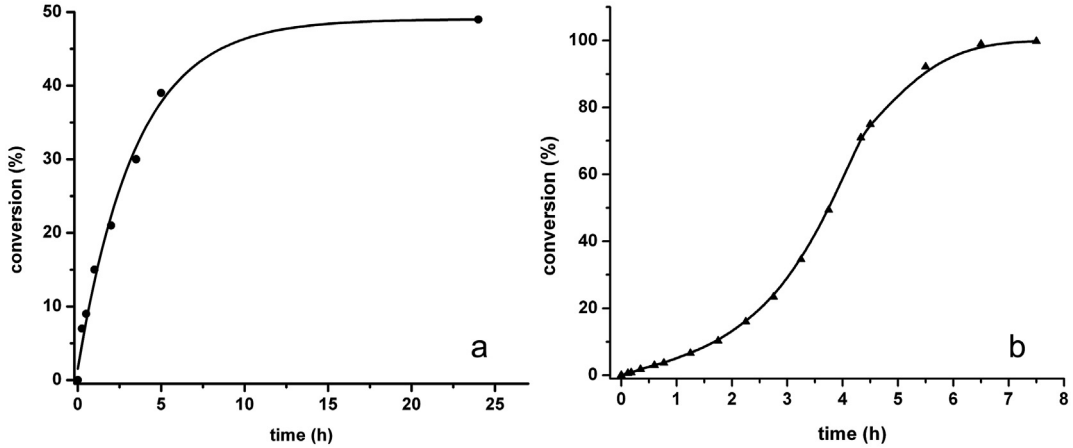
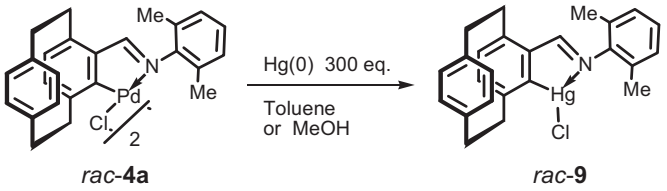


Fig. 3. Conversion *vs.* time: (R_{pl})-**4a** catalysed reactions in d_8-toluene (a) and in d_4-methanol (b).



rac-**4a** *rac*-**9**

Scheme 1. Redox-transmetallation of the catalyst *rac*-**4a**.

Pd^0 species [23a,c,24], but also by the decomposition of the homogeneous Pd^{II} containing catalyst, due to its interaction with Hg^0 (Scheme 1).

In order to avoid erroneous mechanistic conclusions from the Hg poisoning test, it would be necessary to perform control experiments to exclude the possibility of cyclopalladated catalyst reaction with metallic Hg. Unfortunately, examples of such control studies for cross-coupling catalyst behaviour towards Hg^0 are very rare [25]; in their absence the deductions about the Pd^0/Pd^{II} catalytic cycle cannot be considered as absolutely correct.

3. Conclusion

In summary, this preliminary study has shown that the non-pincer type *CN*-palladacycle (R_{pl})-**4a** may work as a true catalyst in the Suzuki reaction under aprotic conditions, providing enantioselectivity up to 53% *ee* at low temperatures. We have also shown that the use of the Hg poisoning test for mechanistic studies of palladacycle-catalysed reactions requires preliminary control experiments because the suppression of the catalysis may be caused by a CPC/Hg^0 interaction, which was unambiguously confirmed by X-ray studies of the transmetallation product.

4. Experimental

4.1. General information

The ^1H and ^{31}P NMR spectra were recorded on the Agilent 400-MR spectrometer operating at the frequencies 400.0 and 161.9 MHz for ^1H and ^{31}P nuclei, respectively. The measurements were carried out at ambient temperature in $CDCl_3$ solutions. The chemical shifts are reported in δ-scale in parts per million relative to TMS as an internal standard for ^1H NMR and relative to H_3PO_4 as an external reference for the ^{31}P NMR spectra. The signal assignments were performed using COSY and NOESY techniques. Unless otherwise stated, the reactions were carried out without precautions against light or atmospheric oxygen or moisture. Reaction progress and purity of compounds formed were monitored by TLC on Silufol UV-254 with visualization under the UV light or in iodine vapour. "Short dry column" [26] or flash-chromatography on Fluka 60 silica gel was used for preparative isolation and purification of compounds obtained. Enantiomeric analysis of the (S_a)-2-methoxy-1,1′-binaphthyl (**8**) samples was performed by HPLC (Bischoff) on Chiralcel OJ (250 × 4.6 mm) with heptane/^{i}PrOH 9/1 as eluent; the absolute configuration of $(+)_D$-**8** was assigned by comparison with literature data [27].

Toluene was dried over $CaCl_2$, refluxed over Na and then distilled. Anhydrous MeOH was prepared by distillation from MeONa. Chloroform and dichloromethane were passed through a short Al_2O_3 column and distilled under argon. Hexane and light petroleum ether were distilled from Na. Acetonitrile was distilled under argon from P_2O_5. DME, 1-Naphthylboronic acid (**6**), 2-methoxynaphthalene, *N*-iodosuccinimide, (R_C)-1-(1′-*N*,*N*-dimethylaminoethyl)naphthalene, $CDCl_3$ (from Aldrich), KF (from Acrus) and mercury (from Merck, >99.998% purity) were used as received.

4.2. General procedure for the CPC-catalysed Suzuki coupling reaction

A mixture of 1-naphthylboronic acid **6** (0.211 mmol), 1-iodo-2-methoxynaphtalene **7** (0.106 mmol), selected base (0.53 mmol) and dimeric cyclopalladated catalyst (0.0053 mmol) in the selected solvent (2 mL) was stirred at indicated temperature in air and evaporated. The residue was dissolved in dichloromethane (5 mL), washed with water (3 × 5 mL), the combined organic solutions were dried over magnesium sulphate, and solvent was removed under reduced pressure. The crude material was purified using dry column chromatography on silica ($h = 3.5$ cm, $d = 2$ cm; petroleum ether/dichloromethane 8:1, 5:1, 3:1 and 1:1) to give target 2-methoxy-1,1′-binaphtalene **8** as a colourless amorphous powder. If TLC data indicates palladacycle retaining after catalysis, an additional dry column chromatography ($h = 4$ cm, $d = 2$ cm; petroleum ether, toluene, toluene/acetone 15:1) was used to recover the catalyst as the iodide-bridged dimer ($R_{pl}R_{pl}$)-**4b**: mp (decomp.) 160–161 °C; R_f 0.56 (toluene); $[\alpha]_D^{22}$ −80 (*c* 0.25, CH_2Cl_2). For confirmation of the iodide-bridged dimer ($R_{pl}R_{pl}$)-**4b** structure it was transformed into its mononuclear PPh_3 derivative [(C^N)PdI(PPh_3)] (R_{pl})-**4c** by standard method [21]. Single crystals of phosphine adduct (R_{pl})-**4c** were obtained by slow diffusion of light petroleum ether into its solution in CH_2Cl_2. Its ^1H and ^{31}P NMR spectra are identical with those of the complex *rac*-**4c** prepared by independent route (see ESI).

4.3. Kinetic studies of Suzuki coupling reaction

A mixture of 1-naphtaleneboronic acid **6** (0.0181 g, 0.1055 mmol), 1-iodo-2-methoxynaphtalene **7** (0.015 g, 0.0527 mmol) and KF (0.0153 g, 0.2634 mmol) in d_8-toluene or d_4-methanol (0.5 mL) was loaded into the NMR-tube, and ^1H NMR spectrum was measured before catalyst bringing in. Then dimer (R_{pl})-**4a** (0.00251 g, 0.00265 mmol) was added into the same tube, and after 1 min spectra measurements were started. The conversion was calculated using integral values of 2-MeO group signals of product **8** and starting iodide **7**.

4.4. Independent synthesis of the transmetallation product rac-9

A mixture of dimer *rac*-**4a** (0.0102 g, 0.0106 mmol) and metallic mercury excess (0.708 g, 0.00252 mmol, 330 eq.) in toluene (5 mL) was intensively stirred at r.t. for 48 h, that is accompanied by colour changing from yellow to light-yellow. After removing the metallic mercury by filtration, the light-yellow solution was evaporated in a vacuum to dryness. The crude product was purified using short dry column chromatography on silica ($h = 4$ cm, $d = 2.5$ cm; petroleum ether, toluene, toluene/acetone 10:1) to afford transmetallation product *rac*-**9** (0.0073 g, 60%) as an yellow amorphous powder. Monocrystals of the complex *rac*-**9** were obtained by slow evaporation of its solution in a solvent mixture toluene/petroleum ether/chloroform. Data for *rac*-**9**: mp (decomp.) 239–241 °C; $R_f = 0.27$ (toluene); ^1H NMR ($CDCl_3$): aromatic protons of the [2.2] paracyclophane moiety: δ 6.43 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{13}), 6.56 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{12}), 6.57 (d, 1H, $^3J_{HH}$ 7.7, H^7), 6.59 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{16}), 6.63 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{15}), 6.83 (dd, 1H, $^3J_{HH}$ 7.7, $^4J_{HgH}$ 78.0, H^8); methylene protons of the [2.2]paracyclophane moiety: δ 2.89 (ddd, 1H, $^2J_{HH}$ 13.3, $^3J_{HH}$ 6.6, $^3J_{HH}$ 10.3, H^{10s}), 3.06 (ddd, 1H, $^2J_{HH}$ 14.0, $^3J_{HH}$ 6.6, $^3J_{HH}$ 10.4, H^{9a}), 3.17 (ddd, 1H, $^2J_{HH}$ 13.5, $^3J_{HH}$ 4.0, $^3J_{HH}$ 10.9, H^{2s}), 3.24 (ddd, 1H, $^2J_{HH}$ 13.5, $^3J_{HH}$ 4.0, $^3J_{HH}$ 10.8, H^{1a}), 3.27 (ddd, 1H, $^2J_{HH}$ 13.5, $^3J_{HH}$ 3.7, $^3J_{HH}$ 10.9, H^{1s}), 3.29 (ddd, 1H, $^2J_{HH}$ 13.3, $^3J_{HH}$ 2.1, $^3J_{HH}$ 10.4, H^{10a}), 3.39 (ddd, 1H, $^2J_{HH}$ 13.5, $^3J_{HH}$ 3.7, $^3J_{HH}$ 10.8, H^{2a}), 3.59 (ddd, 1H, $^2J_{HH}$ 14.0, $^3J_{HH}$ 2.1, $^3J_{HH}$ 10.3, H^{9s}); side chain protons: δ 2.30 (s, 6H, 2Me), 7.01–7.05 (m, 1H, A

part of AB_2 system, J_{AB} 7.5, *para*-H, C_6H_3), 7.13 (ps. d, 2H, B part of AB_2 system, J_{AB} 7.5, *meta*-H, C_6H_3), 8.63 (s, 1H, $^4J_{HgH}$ 10.4, C*H*=N).

Acknowledgements

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Appendix A. Supplementary material

CCDC 897289 and 888751 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary information

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.03.050.

References

[1] (a) W.A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem. Int. Ed. 34 (1995) 1844;
(b) M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Brossmer, Angew. Chem. Int. Ed. 34 (1995) 1848.
[2] (a) R.B. Bedford, Palladacyclic Pre-Catalysts for Suzuki Coupling, Buchwald–Hartwig Amination and Related Reactions, in: J. Dupont, M. Pfeffer (Eds.), Palladacycles. Synthesis, Characterization and Applications, Wiley-VCH, Weinheim, 2008, p. 209;
(b) C. Nájera, D.A. Alonso, Application of Cyclopalladated Compounds as Catalysts for Heck and Sonogashira Reactions, in: J. Dupont, M. Pfeffer (Eds.), Palladacycles. Synthesis, Characterization and Applications, Wiley-VCH, Weinheim, 2008, p. 155;
(c) J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527;
(d) R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283.
[3] V.V. Dunina, O.N. Gorunova, P.A. Zykov, K.A. Kochetkov, Russ. Chem. Rev. 80 (2011) 51.
[4] (a) J.S. Cannon, A.C. Olson, L.E. Overman, N.S. Solomon, J. Org. Chem. 77 (2012) 1961;
(b) M. Weiss, W. Frey, R. Peters, Organometallics 31 (2012) 6365;
(c) S.F. Kirsch, P. Klahn, H. Menz, Synthesis (2011) 3592;
(d) H. Nomura, C.J. Richards, Chem. Asian J. 5 (2010) 1726. (Review).
[5] (a) C. Xu, G.J.H. Kennard, F. Hennersdorf, Y. Li, S.A. Pullarkat, P.-H. Leung, Organometallics 31 (2012) 3022;
(b) Y. Huang, S.A. Pullarkat, S. Teong, R.J. Chew, Y. Li, P.-H. Leung, Organometallics 31 (2012) 4871;
(c) Y. Huang, S.A. Pullarkat, Y. Li, P.-H. Leung, Inorg. Chem. 51 (2012) 2533;
(d) Y. Huang, R.J. Chew, S.A. Pullarkat, Y. Li, P.-H. Leung, J. Org. Chem. 77 (2012) 6849;
(e) J.-J. Feng, X.-F. Chen, M. Shi, W.-L. Duan, J. Am. Chem. Soc. 132 (2010) 5562.
[6] (a) F.K. Friedlein, K. Kromm, F. Hampel, J.A. Gladysz, Chem. Eur. J. 12 (2006) 5267;
(b) K. Yuan, T.K. Zhang, X.L. Hou, J. Org. Chem. 70 (2005) 6085;
(c) M. Rosol, A. Moyano, J. Organomet. Chem. 690 (2005) 2291;
(d) D. Morales-Morales, R.E. Cramer, C.M. Jensen, J. Organomet. Chem. 654 (2002) 44;
(e) J. Bravo, C. Cativiela, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 650 (2002) 157;
(f) J. Dupont, A.S. Gruber, G.S. Fonsec, A.L. Monteiro, G. Ebeling, Organometallics 20 (2001) 171.
[7] (a) R. Gerber, O. Blacque, C.M. Frech, Dalton Trans. 40 (2011) 8996;
(b) O. Blacque, C.M. Frech, Chem. Eur. J. 16 (2010) 1521;
(c) J.L. Bolliger, O. Blacque, C.M. Frech, Chem. Eur. J. 14 (2008) 7969;
(d) A. Sundermann, O. Uzan, J.M.L. Martin, Chem. Eur. J. 7 (2001) 1703.
[8] (a) H. Zhang, A. Lei, Dalton Trans. 40 (2011) 8745. (Review);
(b) R. Gerber, O. Blacque, C.M. Frech, ChemCatChem 1 (2009) 393;
(c) D. Olsson, O.F. Wendt, J. Organomet. Chem. 694 (2009) 3112;
(d) J.L. Bolliger, O. Blacque, C.M. Frech, Angew. Chem. Int. Ed. 46 (2007) 6514;
(e) S. Sjövall, O.F. Wendt, C. Andersson, J. Chem. Soc. Dalton Trans. (2002) 1396;
(f) D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen, J. Chem. Soc. Chem. Commun. (2000) 1619.
[9] (a) F. Juliá-Hernández, A. Arcas, J. Vicente, Chem. Eur. J. 18 (2012) 7780;
(b) J. Vicente, A. Arcas, F. Juliá-Hernández, D. Bautista, Angew. Chem. Int. Ed. 50 (2011) 6896.
[10] (a) M.R. Eberhard, Org. Lett. 6 (2004) 2125;
(b) W.A. Herrmann, V.P.W. Böhm, C.-P. Reisinger, J. Organomet. Chem. 576 (1999) 23. (Review);
(c) W.A. Herrmann, C. Brossmer, C.-P. Reisinger, T.H. Riermeier, K. Ofele, M. Beller, Chem. Eur. J. 3 (1997) 1357.
[11] (a) A. Suzuki, Angew. Chem. Int. Ed. 50 (2011) 6722. (Nobel lecture);
(b) F. Bellina, A. Carpita, R. Rossi, Synthesis (2004) 2419. (Review);
(c) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[12] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
[13] (a) J. Yang, S. Liu, J.-F. Zheng, J. (St.) Zhou, Eur. J. Org. Chem. (2012) 6248;
(b) F.-S. Liu, Y.-T. Huang, Ch. Lu, D.-S. Shen, T. Cheng, Appl. Organomet. Chem. 26 (2012) 425;
(c) D. Zim, A.S. Gruber, G. Ebeling, J. Dupont, A.L. Monteiro, Org. Lett. 2 (2000) 2881;
(d) D.A. Albisson, R.B. Bedford, P.N. Scully, Tetrahedron Lett. 39 (1998) 9793.
[14] T. Takemoto, S. Iwasa, H. Hamada, K. Shibatomi, M. Kameyama, Y. Motoyamac, H. Nishiyama, Tetrahedron Lett. 48 (2007) 3397.
[15] B.-S. Zhang, W. Wang, D.-D. Shao, X.-Q. Hao, J.-F. Gong, M.-P. Song, Organometallics 29 (2010) 2579.
[16] O.N. Gorunova, P.A. Zykov, M.V. Livantsov, K.A. Kochetkov, Yu K. Grishin, V.V. Dunina, Russ. Chem. Bull. 59 (2010) 1840.
[17] (a) Y.-J. Kim, J.-H. Lee, T. Kim, J. Ham, Z.N. Zheng, S.W. Lee, Eur. J. Inorg. Chem. (2012) 6011;
(b) B. Mu, T. Li, J. Li, Y. Wu, J. Organomet. Chem. 693 (2008) 1243;
(c) J. Ma, X. Cui, B. Zhang, M. Song, Y. Wu, Tetrahedron 63 (2007) 5529;
(d) O. Navarro, R.A. Kelly, S.P. Nolan, J. Am. Chem. Soc. 125 (2003) 16194;
(e) R.B. Bedford, C.S.J. Cazin, S.J. Coles, Th. Gelbrich, M.B. Hursthouse, V.J.M. Scordia, J. Chem. Soc. Dalton Trans. (2003) 3350;
(f) H. Weissman, D. Milstein, J. Chem. Soc. Chem. Commun. (1999) 1901.
[18] (a) M.E. Günay, C.J. Richards, Organometallics 28 (2009) 5833;
(b) J.C. Gaunt, B.L. Shaw, J. Organomet. Chem. 102 (1975) 511.
[19] L.L. Troitskaya, L.A. Bulygina, V.I. Sokolov, Russ. Chem. Bull. 43 (1994) 1253.
[20] V.V. Dunina, E.I. Turubanova, O.N. Gorunova, M.V. Livantsov, K.A. Lyssenko, D.Y. Antonov, Y.K. Grishin, Polyhedron 31 (2012) 413.
[21] V.V. Dunina, E.I. Turubanova, M.V. Livantsov, K.A. Lyssenko, N.V. Vorontsova, D.Yu. Antonov, Y.K. Grishin, Tetrahedron Asym. 20 (2009) 1661.
[22] D.G. Allen, G.M. McLaughlin, G.B. Robertson, W.L. Steffen, G. Salem, S.B. Wild, Inorg. Chem. 21 (1982) 1007.
[23] (a) N.T.S. Phan, M. Van Der Sluys, C.W. Jones, Adv. Synth. Catal. 348 (2006) 609–679. (Review);
(b) J.A. Widegren, R.G. Finke, J. Mol. Catal. A 198 (2003) 317. (Review);
(c) K. Yu, W. Sommer, M. Weck, Ch. W. Jones, J. Catal. 226 (2004) 101.
[24] R. van Asselt, C.J. Elsevier, J. Mol. Catal. 65 (1991) L13.
[25] (a) M.C. Lipke, R.A. Woloszynek, L. Ma, J.D. Protasiewicz, Organometallics 28 (2009) 188;
(b) K. Yu, W. Sommer, J.M. Richardson, M. Weck, C.W. Jones, Adv. Synth. Catal. 347 (2005) 161.
[26] J.T. Sharp, I. Gosney, A.G. Rowley, Separation of Organic Mixtures by Chromatography, in: Practical Organic Chemistry – A Student Handbook of Techniques, Chapman and Hall, London, 1989, p. 160.
[27] (a) A. Bermejo, A. Ros, R. Fernández, J.M. Lassaletta, J. Am. Chem. Soc. 130 (2008) 15798;
(b) J.M. Wilson, D.J. Cram, J. Org. Chem. 49 (1984) 4930.