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Suzuki reaction catalysed by a $PC_{sp3}P$ pincer Pd(II) complex: Evidence for a mechanism involving molecular species

Daniel Olsson, Ola F. Wendt *

Organic Chemistry, Department of Chemistry, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

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ABSTRACT

{*Cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]cyclohexyl}palladium(II)trifluoroacetate (**1**) acts as a precatalyst for the Suzuki reaction of aryl halides with phenylboronic acid in the absence or presence of mercury to give the product in modest to reasonably good yields. The reaction was monitored by ^{31}P- and ^{1}H NMR spectroscopy in a stepwise fashion, concluding that complex **1** reacts with activated boronic acids in the first reaction step to yield the corresponding phenyl complex **2**. Complex **2** thereafter generates the Suzuki cross-coupling product upon addition of aryl halide. This shows that (PCP)Pd complexes, in addition to the previously demonstrated Pd(0)/Pd(II) mechanism, can mediate cross-coupling reactions using molecular species in a non-zero oxidation state.

1. Introduction

The Suzuki–Miyaura reaction [1], the coupling of arylboronic acids and aryl halides, is a versatile and important tool in organic chemistry [2]. Numerous palladium sources have been used as catalysts including palladium PCP-pincer complexes [3]. Most such complexes are based on an aromatic framework, but we and others have also reported the use of $PC_{sp3}P$ complexes in catalysis [4–7]. Thus, we have earlier reported both the catalytic and kinetic behaviour of {*cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]cyclohexane}palladium(II)trifluoroacetate, **1**, in the Heck and Stille reaction [6] and here we report the application in the Suzuki reaction. Numerous reports regarding catalytic carbon–carbon coupling with PCP palladium complexes and other palladacycles conclude that it is actually colloidal palladium (or soluble palladium(0)) that is responsible for the catalysis [6,8,9]. The palladacycles are initially reduced and the catalysis is performed via a classical Pd(0)/Pd(II) cycle. In a few instances a Pd(II)/Pd(IV) mechanism could not be ruled out. Thus, both Crabtree and Frech have reported that catalysis with bis-carbene and aminophosphine pincer complexes, respectively, is unaffected by mercury [10]. In a later report Frech and coworkers still conclude that in the aminophosphine case the actual catalyst is most probably palladium nanoparticles [11].

In addition to the catalytic results, we here report a mechanistic investigation showing that mercury does not inhibit catalysis and based on this and stoichiometric model reactions we propose an alternative parallel reaction mechanism based on soluble palladium(II) species only.

2. Experimental section

2.1. General considerations

Solvents and commercially available reagents were used as received from Aldrich. Strauss-flasks and J. Young tubes were rinsed with aqua regia and oven dried prior to use. Complex **1** (*cis*-[2,6-bis(di-*tert*-butylphosphinomethyl)cyclohexyl]trifluoroacetatepalladium(II)) [12] was prepared according to literature procedures and a stock solution (0.010 M) was prepared in toluene. All the samples for NMR spectroscopy were prepared in a Braun glove box. ^{1}H-, ^{13}C- and ^{31}P NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer working at 499.77 MHz (^{1}H). The NMR spectroscopic measurements were performed in toluene-d_8, C_6D_6 or THF-d_8. Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H-, ^{13}C NMR) or H_3PO_4 (^{31}P NMR δ 0) as reference. Coupling constants for virtual triplets in ^{1}H and ^{13}C NMR spectra are reported according to Cohen and Sheppard [13]. Gas chromatography analyses were performed with a Varian 3300 gas chromatograph with FID and fitted with a 30 m CP-Sil 5 CB (CP8770) capillary column.

2.2. Catalytic investigation

All catalytic reactions were performed in sealed Strauss-flasks (to prevent solvent evaporation) under air and they were studied using gas chromatography. In a typical experiment (Table 1, entry

* Corresponding author. Tel.: +46 46 2228153.
E-mail address: ola.wendt@organic.lu.se (O.F. Wendt).

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Table 1
Crystal data for **1** and **2**.

	1	2
Formula	$C_{26}H_{49}F_3O_2P_2Pd$	$C_{30}H_{54}P_2Pd$
Fw	618.99	583.07
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.6569(4)	8.4146(3)
b (Å)	21.4131(12)	35.4171(12)
c (Å)	16.4958(8)	11.0370(4)
β (°)	101.590(5)	112.009(4)
V (Å^3)	2995.5(3)	3049.55(19)
Z	4	4
D_{calcd} (g cm^{-3})	1.373	1.270
μ (mm^{-1})	0.765	0.729
θ Range (°)	2.28–33.18	2.30–33.16
Number of reflections collected	21 950	31 065
Number of unique reflections	9902	10 574
Number of reflections $I > 2\sigma(I)$	2302	4334
R (F) ($I > 2\sigma(I)$)[a]	0.0554	0.0582
wR_2 (F^2) (all data)[b]	0.0937	0.1609
S[c]	0.646	0.922
R_{int}	0.1535	0.0913

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.
[b] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.
[c] $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

5), a Strauss flask was charged with **1** (50 μL {5.0×10^{-7} mol} of a 1.0×10^{-2} M stock solution in toluene), phenyl bromide (0.11 mL, 1.0×10^{-3} mol), phenylboronic acid (0.18 g, 1.5×10^{-3} mol), K_3PO_4 (0.42 g, 2.0×10^{-3} mol), 2-methylnaphthalene (as internal standard) and toluene (10 ml) in open air. The flask was sealed and placed in a preheated oil bath at 160 °C for 24 h. During the preliminary investigation the Strauss flask was removed from the oil bath, cooled and opened for sample withdrawal. To accomplish GC-analysis, 5–10 drops of the reaction mixture were taken out and added to an extraction mixture containing 0.3 ml Et_2O and 0.3 ml 1 M HCl (aq). The organic phase was separated and sealed in a GC-vial. The products were not separated and isolated, but identified through comparison with commercial samples of the products. The yields were calculated on the basis of product integrals and the use of an internal standard. In some experiments, mercury (4.0 g, 0.020 mol) was added to the reaction mixture before heating and it was allowed to be present in the reaction vessel for the full reaction time.

2.3. Preparation of cis-[2,6-bis(di-tert-butylphosphinomethyl)cyclohexyl-]phenylpalladium(II) (2)

Complex **1** (12 mg, 20 μmol) and an excess of Ph–Li (containing bromide) were placed in a J. Young NMR-tube in a glove box. Dry THF (1.0 ml) was distilled in to the tube at −78 °C. The reaction solution was slowly allowed to reach room temperature and a ^{31}P NMR spectrum of the red solution showed that **1** was completely converted into two new compounds. Integration showed the mixture to contain 80% of the title compound. Quenching the excess Ph–Li, by exposing the reaction solution to air resulted in decolourisation. Replacement of THF with pentane and repeated decantation and washing of the solid material gave a tint yellow pentane suspension that was filtered through a short pad of celite to remove all traces of lithium salts. Reduction of the pentane volume and crystallisation at −18 °C resulted in a crystalline material containing both **2** and the corresponding bromide, **3**. However, upon slow evaporation in air at 25 °C the mother liquor produced colourless fibres of **2** suitable for X-ray crystallography. ^{1}H NMR (C_6D_6): δ 2.2–0.80 (m region, CH & CH_2), 1.12 (vt, J_{PH} = 12.8 Hz, 18H, C(CH_3)$_3$), 1.19 (vt, J_{PH} = 12.7 Hz, 18H, C(CH_3)$_3$), 7.05 (t, J_{HH} = 7.1 Hz, 1H, H_p of C_6H_5), 7.23 (m, 2H, H_m of C_6H_5), 8.00 (t, J_{HH} = 6.4 Hz, 2H, H_o of C_6H_5), ^{31}P{^{1}H} NMR (C_6D_6): δ 70.6 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 27.71 (t, J_{PC} = 1 Hz,$CH_2CH_2CHCHPd$), 29.67 (vt, J_{PC} = 7 Hz, C(CH_3)$_3$), 30.38 (vt, J_{PC} = 7 Hz, C(CH_3)$_3$), 34.93 (vt, J_{PC} = 14 Hz, $CH_2CHCHPd$), 35.05 (vt, J_{PC} = 24 Hz, CH_2P), 35.68 (vt, J_{PC} = 13 Hz, C(CH_3)$_3$), 36.18 (vt, J_{PC} = 17 Hz, C(CH_3)$_3$), 48.97 (vt, J_{PC} = 16 Hz, $CHCHPd$), 64.52 (t, J_{PC} = 1 Hz, $CHPd$), 121.62 (t, J_{PC} = 1 Hz, C_p of C_6H_5), 125.52 (t, J_{PC} = 1 Hz, C_m of C_6H_5), 125.72 (vt, J_{PC} = 1 Hz, C_m of C_6H_5), 143.45 (t, J_{PC} = 2 Hz, C_o of C_6H_5), 144.45 (t, J_{PC} = 2 Hz, C_o of C_6H_5), 168.93 (t, J_{PC} = 15 Hz, C_i of C_6H_5).

2.4. Crystallography

The crystallographic experiments were performed as previously reported [14]. There was a large disorder in the trifluoroacetate of **1** and running the data collection at low temperature partly resolved this; however, the fluorines still show large temperature factors. Crystal data and details about data collection are given in Table 1. A DIAMOND drawing of **1** showing the atomic numbering is given in Fig. S5.

3. Results and discussion

Using **1** as precatalyst we investigated the coupling of arylboronic acids with aryl halides in a sealed vessel with air. Selected results are listed in Table 2 and all results are given in the Supplementary material (Tables S1–S3). In the preliminary investigation with a catalytic load of 0.1% it was concluded that no product formation could be confirmed below 100 °C; instead a temperature increase to 160 °C was needed to accomplish acceptable results. The homo-coupling product was identified in less than 4% yield and also the protodeboration products were identified in small quantities. Evaluating the bases it was evident that potassium phosphate was most efficient using phenyl bromide whereas the corresponding chloride and iodide worked best with potassium carbonate, but still gave poor yields. To our surprise the activated, electron-poor substrate 4-bromoacetophenone had lower reactivity than the analogous electron rich anisole. Substituted boronic acids showed poor reactivity. Variation of the catalyst concentration also established that high catalyst loading gave higher yields. The yields are overall modest and were not fully optimised; instead we focused on the reaction mechanism.

Table 2
Suzuki reaction catalysed by **1**. [a]

Entry	PhX	Base	TON[b]	Yield[c] (%)
1	PhCl	K_2CO_3	583	29
2	PhCl	K_3PO_4	144	7
3	PhBr	K_2CO_3	812	41
4	PhBr	NaOH	1104	55
5	PhBr	K_3PO_4	1469	73
6	PhI	K_2CO_3	528	26
7	4-MeO–C_6H_4–Cl	K_3PO_4	–	trace
8	4-MeO–C_6H_4–Cl	K_2CO_3	285	14
9	4-MeO–C_6H_4–Br	K_3PO_4	1082	54
10	4-Me–C_6H_4–Br	K_3PO_4	741	37
11	4-Ac–C_6H_4–Br	K_3PO_4	696	35
12[d]	Ph–Br	K_3PO_4	205	10
13[e]	4-Ac–C_6H_4–Br	K_2CO_3	626	63
14[e,f]	4-Ac–C_6H_4–Br	K_2CO_3	600	60
15[f,g]	4-Ac–C_6H_4–Br	K_2CO_3	0	0
16[g]	4-Ac–C_6H_4–Br	K_2CO_3	0	0

[a] *Reaction conditions*: 160 °C, 24 h, [**1**] = 5×10^{-4} mmol, aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol) and toluene (10 ml).
[b] [Prod]/[Pd] (mol/mol).
[c] Yield determined by GC based on product formation using 2-methylnaphthalene as internal standard.
[d] Using 4-MeO–C_6H_4–$B(OH)_2$ as nucleophile.
[e] [**1**] = 1×10^{-4} mmol.
[f] 20 mmol Hg(l) added.
[g] No Pd added.

High temperature barriers are usually indicative of a brake-down threshold where the palladium complex is reduced and the catalysis is performed by a palladium(0) species. To test for the presence of soluble or colloidal palladium(0) we performed a poisoning test with 20 000 equivalents of mercury (Fig. 1). The mercury poisoning test is a simple way to probe for Pd(0) since mercury effectively amalgamates any Pd(0) species [15]. If the reaction was supported by colloidal or other palladium(0) species the yield would be drastically diminished by mercury addition. Our reaction profile reveals excellent product formation but an initial decrease of reaction rate. The overall yield after 24 h is about the same as without mercury. There was no induction period except in the presence of large amount of mercury, which we attribute to mass transfer problems (see also Figs. S1–S4). In the absence of palladium complex (with or without mercury) no cross-coupling takes place.

The mercury test strongly indicates that as opposed to other (PCP) systems investigated by this method the current carbon–carbon coupling formation is catalysed by a homogeneous, metal complex in a higher formal oxidation state [16]. It should be noted that not only colloidal Pd(0) but also molecular Pd(0) complexes have been reported to be destroyed by elemental mercury [17].

To further investigate the mechanism we decided to study the reaction of **1** with the different reactants individually using ^{31}P- or ^{1}H NMR spectroscopy as outlined in Scheme 1. The existence of phosphorus in key positions in the ligand of complex **1** and the conspicuous virtual triplets of the methyl groups gave spectroscopic handles that we decided to employ in the same way as others [18]. Thus, **1** was reacted with potassium carbonate (50 eq), phenyl bromide (33 eq) or phenylboronic acid (33 eq) separately in toluene-d_8 at 170 °C for 24 h. The phenyl bromide test resulted in a 4% yield of the corresponding bromo complex **3**; a similar halide exchange has previously been reported by Frech and coworkers [11]. The potassium carbonate test resulted in a 3% yield of an unidentified product, which is probably the carbonate complex. The phenylboronic acid gave no reaction at all. During these experiments it was evident that phenyl bromide and phenylboronic acid were stable under the reaction conditions. Additionally, no palladium black formation was observed. However, a combination of potassium carbonate (100 eq) and phenylboronic acid (67 eq) gave a reaction.

Within 30 seconds at 170 °C compound **1** was quantitatively converted to a new compound, shifted 1.1 ppm downfield in the ^{31}P NMR spectrum. The product was never identified due to its dynamic behaviour, but we believe it to be a coordinated boronate. More importantly, a second complex started to appear after 2 min and after 24 h there was a 25% conversion which seemed to be an equilibrium value. This complex could be identified as

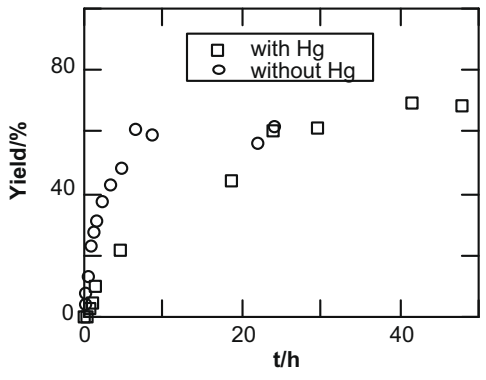
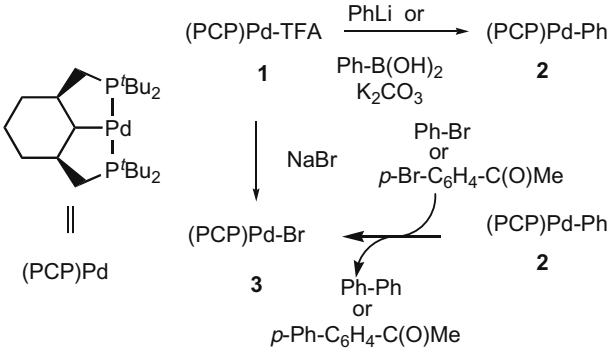


Fig. 1. Reaction yield with and without added mercury. Reaction conditions: 160 °C, **1** (0.1%), 4-bromoacetophenone (1.0 mmol), $PhB(OH)_2$ (1.5 mmol), K_2CO_3 (2.0 mmol) and toluene (10 ml).



Scheme 1.

the phenyl analogue **2**, which was independently prepared by reaction of precatalyst **1** and phenyl lithium and was characterised by NMR spectroscopy and X-ray crystallography (cf. Fig. 2) [19]. The peak from complex **2** was not the only new peak in ^{31}P NMR spectroscopy: two small signals, 1.8 and 0.76 ppm upfield from **2** also appeared. The ^{31}P-signal that is closest to **2** is represented as a triplet in ^{1}H NMR spectroscopy and this triplet is the same as observed when precatalyst **1** was reacted separately with potassium carbonate. Therefore we believe this to be the carbonate complex but it was observed first after 15 h, speaking against its involvement in the catalytic cycle. Apparently, there are equilibria and side reactions involved when aryl halides are not present in the system to tap off **2**. The protodeboronation product, benzene was also detected but not the homo-coupled biphenyl.

Addition of phenyl bromide (67 eq) and heating at 170 °C for 2.5 h results in the formation of **2** (44%) and the corresponding bromo complex **3** (56%). Complex **3** was characterised by comparison with an authentic sample [20]. Prolonged heating resulted in conversion of **2** (12%) into **3** (88%) simultaneously as biphenyl formation was recorded. Analysis of the full Suzuki set up revealed that **3** was very rapidly formed and quickly became the dominant palladium species in the catalytic mixture, whereas **2** was only detected in low concentration (Max. 4%), and not fully observable until all precatalyst **1** is consumed. Already during this conversion process (**1** into **3**) the formation of biphenyl is recorded. To verify the cross-coupling behaviour we reacted **2** with 4-bromoacetophenone, which gave 4-phenylacetophenone and complex **3** at 125 °C.

Based on these results and the mercury test we propose the catalytic cycle in Scheme 2 involving reversible transmetallation

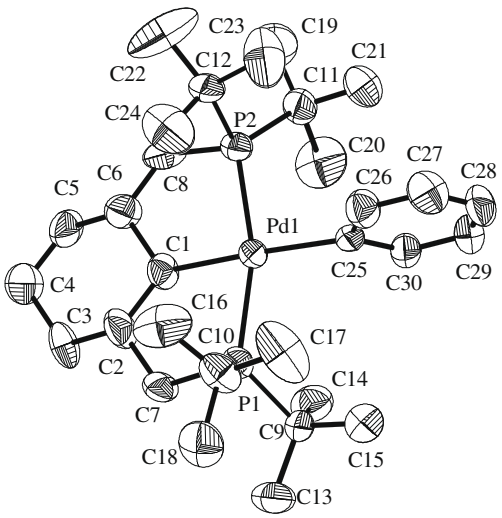
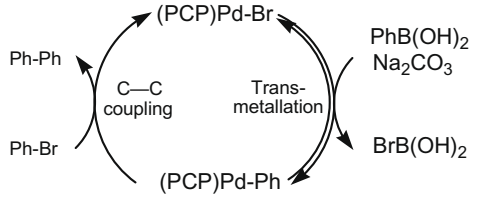


Fig. 2. DIAMOND [25] drawing of **2**. Hydrogen atoms are omitted for clarity.



Scheme 2.

followed by fast metathesis with the aryl halide. The transmetallation probably takes place via a pre-coordination of the boronic acid as proposed before [21], and the NMR experiments show that under catalytic conditions (i.e. in the presence of aryl halide) it becomes effectively irreversible and rate determining. A similar transmetallation in a palladium(II) cycle has been proposed by Szabo and coworkers for cross-coupling of organoboronic acids with vinyl epoxides and aziridines [22]. The reaction between a (PCP)Pd–Ph complex and an aryl halide has been reported by Milstein and coworkers [3]. It can take place either via metathesis (4-centre transition state) or an oxidative addition/reductive elimination path. We favour a 4-centre transition state where there is no formal oxidation to Pd(IV). Such transition states have been proposed for similar (PCP)Pd systems involving hydrocarbon exchange and hydrogenolysis of hydroxide [23]. In the latter case the proposal was supported also by theoretical calculations. As in the hydrogenolysis the current 4-centre transition state will be assisted by the lone pair on the halide. OA/RE pathways for halide exchange of a (PCP)PdX with ArX has been proposed based on calculations but barriers were substantially higher than for the 4-centre pathway found for the hydrogenolysis [11]. Based on the mercury test and the changed shape of the reaction curve we cannot rule out a parallel catalysis based on a traditional Pd(0)/Pd(II) cycle as observed for other (PCP) complexes [8,9] but it is clear that also a catalytic cycle involving molecular Pd(II) species is operating. It can be noted that the catalytic performance of the present system is inferior to those based on nano-particles/colloidal Pd(0), also suggesting the operation of a different mechanism. The proposed cycle also differs from those proposed earlier by not necessarily invoking Pd(IV), also the presence of such species cannot be ruled out [24]. It can be noted that the investigation of the mechanism of the Heck reaction catalysed by **1** was performed using NEt_3 as a base and concluded the operation of a Pd(0)/Pd(II) cycle [6b]. Aliphatic amines are notorious in reducing palladium(II) and in the present case the use of organic bases gives no reaction whatsoever (cf. Table S1).

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Appendix A. Supplementary material

CCDC 693016 and 693017 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.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.025.

References

[1] N. Miyaura, T. Yanagi, A. Suzuki, Synth. Commun. 11 (1981) 513.
[2] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[3] R.B. Bedford, S.M. Draper, P. Noelle Scully, S.L. Welch, New J. Chem. 24 (2000) 745;
The complex was of phosphinite type and the investigation was inspired by the observations that Milstein reported on the use of palladium PCP pincer complex as catalysts in the Heck reaction: M. Ohff, A. Ohff, M.E. van der Boom, D. Milstein, J. Am. Chem. Soc. 119 (1997) 11687;
For a review see: J.T. Singleton, Tetrahedron 59 (2003) 1837;
J. Dupont, C.S. Consorti, J. Spencer, in: D. Morales-Morales, C.M. Jensen (Eds.), The Chemistry of Pincer Compounds, Elsevier, Amsterdam, 2007.
[4] C.J. Moulton, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1976) 1020.
[5] (a) A.L. Seligson, W.C. Trogler, Organometallics 12 (1993) 744;
(b) S. Sjövall, O.F. Wendt, C. Andersson, J. Chem. Soc., Dalton Trans. (2002) 1396.
[6] (a) D. Olsson, P. Nilsson, M. El Masnaouy, O.F. Wendt, Dalton Trans. (2005) 1924;
(b) P. Nilsson, O.F. Wendt, J. Organomet. Chem. 690 (2005) 4197.
[7] For aliphatic C–H activated pincers, see also: A. Castanguay, A.L. Beauchamp, D. Zargarian, Organometallics 27 (2008) 5723;
V. Pandarus, D. Zargarian, Organometallics 26 (2007) 4321;
V. Pandarus, D. Zargarian, Chem. Commun. (2007) 978;
V.F. Kuznetsov, A.J. Lough, D.G. Gusev, Inorg. Chim. Acta 359 (2006) 2806;
A. Castonguay, C. Sui-Seng, D. Zargarian, A.L. Beauchamp, Organometallics 25 (2006) 602;
M.E. van der Boom, S.-Y. Liou, L.J.W. Shimon, Y. Ben-David, D. Milstein, Inorg. Chim. Acta 357 (2004) 4015;
D. Olsson, A. Athimoolam, O.F. Wendt, Dalton Trans. (2007) 5427.
[8] (a) I.P. Beletskaya, A.N. Kashin, N.B. Karlstedt, A.V. Mitin, A.V. Cheprakov, G.M. Kazankov, J. Organomet. Chem. 622 (2001) 89;
(b) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009;
(c) R.B. Bedford, Chem. Commun. (2003) 1787;
(d) C.S. Consorti, M.L. Zanini, S. Leal, G. Ebeling, J. Dupont, Org. Lett. 5 (2003) 983;
(e) C. Rocaboy, J.A. Gladysz, New J. Chem. 27 (2003) 39;
(f) J.G. de Vries, Dalton Trans. (2006) 421;
(g) W.J. Sommer, K. Yu, J.S. Sears, Y. Ji, X. Zheng, R.J. Davis, C.D. Sherrill, C.W. Jones, M. Weck, Organometallics 24 (2005) 4351;
(h) M.R. Eberhard, Org. Lett. 6 (2004) 2125.
[9] Reviews: M. Weck, C.W. Jones, Inorg. Chem. 46 (2007) 1865;
N.T.S. Phan, M. Van Der Sluys, C.W. Jones, Adv. Synth. Catal. 348 (2006) 609;
J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem. 198 (2003) 317.
[10] (a) E. Peris, J.A. Loch, J. Mata, R.H. Crabtree, Chem. Commun. (2001) 201;
(b) E. Peris, R.H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239;
(c) J.L. Bolliger, O. Blacque, C.M. Frech, Angew. Chem. Int. Ed. 46 (2007) 6514.
[11] J.L. Bolliger, O. Blacque, C.M. Frech, Chem. Eur. J. 14 (2008) 7969.
[12] S. Sjövall, M.H. Johansson, C. Andersson, Eur. J. Inorg. Chem. (2001) 2907.
[13] A.D. Cohen, N. Sheppard, Proc. Roy. Soc. A A252 (1959) 488–505.
[14] R. Johansson, L. Öhrström, O.F. Wendt, Cryst. Growth Des. 7 (2007) 1974.
[15] (a) C. Paal, W. Hartmann, Ber. Dtsch. Chem. Ges. 51 (1918) 711;
(b) D.R. Anton, R.H. Crabtree, Organometallics 2 (1983) 855;
(c) G.M. Whitesides, M. Hackett, R.L. Brainard, J.P.P.M. Lavalleye, A.F. Sowinski, A.N. Izumi, S.S. Moore, D.W. Brown, E.M. Staudt, Organometallics 4 (1985) 1819.
[16] As mentioned in the introduction Crabtree reports catalysis unaffected by mercury and Weck has also reported homo-coupling in the presence of mercury: Ref. [10a,b]: W.J. Sommer, M. Weck, Adv. Synth. Catal. 348 (2006) 2101.
[17] R. van Asselt, C.J. Elsevier, J. Mol. Catal. 65 (1991) L13.
[18] W.J. Sommer, K. Yu, J.S. Sears, Y. Ji, X. Zheng, R.J. Davis, C.D. Sherrill, C.W. Jones, M. Weck, Organometallics 24 (2005) 4351–4361;
H.-B. Kraatz, M.E. Van der Boom, Y. Ben-David, D. Milstein, Israel J. Chem. 41 (2001) 163.
[19] A similar transmetallation has been reported for *ortho*-metalated catalysts but was not believed to be involved in the catalytic cycle: D.A. Albisson, R.B. Bedford, P. Noelle Scully, S.E. Lawrence, Chem. Commun. (1998) 2095.
[20] D. Olsson, J.M.J. van Rensburg, O.F. Wendt, Acta Cryst. E63 (2007) m1969.
[21] A.A.C. Braga, N.H. Morgon, G. Ujaque, F.J. Maseras, J. Am. Chem. Soc. 127 (2005) 9298;
For a review see:O.F. Wendt, Curr. Org. Chem. 11 (2007) 1417.
[22] J. Kjellgren, J. Aydin, O.A. Wallner, I.V. Saltanova, K.J. Szabo, Chem. Eur. J. 11 (2005) 5260.
[23] (a) R. Johansson, O.F. Wendt, Organometallics 26 (2007) 2426;
(b) G.R. Fulmer, R.P. Muller, R.A. Kemp, K.I. Goldberg, J. Am. Chem. Soc. 131 (2009) 1346.
[24] (a) D. Morales-Morales, R. Redon, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619;
(b) B.L. Shaw, Chem. Commun. (1998) 1361;
(c) B.L. Shaw, New J. Chem. 22 (1998) 77.
[25] K. Brandenburg, K., DIAMOND2, Crystal Impact, Bonn, Germany, 2000.