Dibenzo[*a*,*d*]cycloheptenyl dibenzophosphole palladium dichloride: Synthesis, X-ray-crystal structure and application in the Suzuki–Miyaura coupling†

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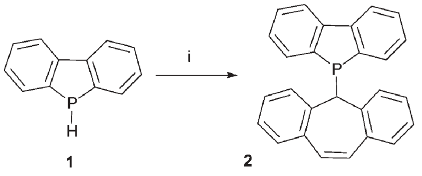
A highly rigid dibenzo[*a*,*d*]cycloheptenyl dibenzophosphole with a pre-organized concave shaped binding site acts as an efficient ligand in the palladium catalyzed Suzuki–Miyaura coupling process between halogenoaromatics and phenylboronic acid.

There is a continuing interest in the elaboration of polydentate ligands featuring electronically different binding sites. The fine tuning of electronic and steric effects is a difficult task and no definitive model allowing one to rationalize and predict the optimal combination ligand–metal has been achieved yet.[1] Combinations of two or more heteroatoms in the same ligand already proved to be particularly active and most of the studies are currently focussing on this topic.[2] On the other hand, olefins have been rarely used as ligands in homogeneous catalysis[3] and the combination of one phosphorus and one olefin as binding sites in the same skeleton remains also largely unexploited.[4] In this article we present the synthesis of a mixed phosphole–dibenzotropylidene ligand and its use in the palladium catalyzed formation of C–C bonds through the Suzuki–Miyaura coupling process.

The synthesis of ligand **2** was conventionally achieved through the reaction of the P–H phosphole **1** with chlorodibenzotropilydene.[5] Compound **2** which proved to be slightly oxygen sensitive was isolated in good yield after usual work-up and fully characterized by NMR spectroscopy and elemental analyses (Scheme 1).

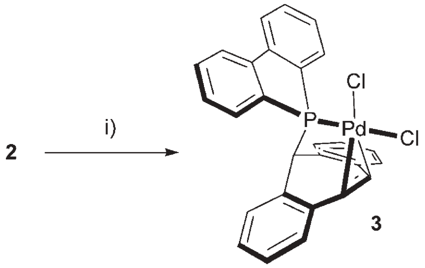
Additional evidence was given by an X-ray crystal structure analysis.‡ Phosphole **2** is soluble in common organic solvents and was reacted with [Pd(COD)Cl$_2$] to quantitatively afford the dichloride complex **3** which was fully identified by NMR spectroscopy, elemental analyses and X-ray crystallography (Scheme 2). A view of one molecule of **3** is presented in Fig. 1.



Scheme 1 Synthesis of phosphole **2**. i) Chlorodibenzotropilydene (1 eq), toluene, reflux 15 h.

As can be seen, the overall geometry around palladium is square planar and coordination of the olefin group occurs in an η^2-fashion as expected. Bond lengths and bond angles fall in the usual range.

Comlex **3** contains a ligand combining the σ-donor strength of a phosphine group with the good π-accepting capability of an olefin.



Scheme 2 Synthesis of complex **3**. i) [Pd(COD)Cl$_2$], CH$_2$Cl$_2$, RT 10 min.

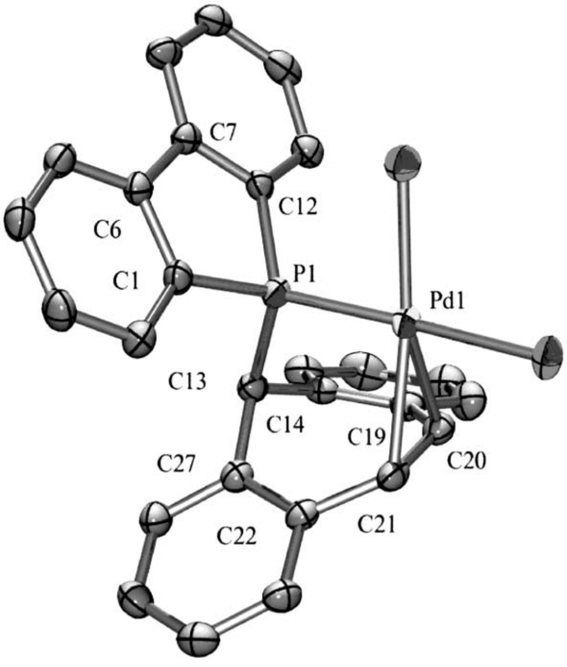


Fig. 1 Solid state structure of complex **3**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are at 50% probability.

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† Electronic supplementary information (ESI) available: General considerations; syntheses and characterizations of P–H phosphole **1** and complex **3**; general procedure for catalytic reactions; X-ray crystal structures of **2** and **3**. See http://www.rsc.org/suppdata/cc/b4/b417716a/
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Table 1 Cross-coupling reaction of halogenoaryls with phenylboronic acid using complex **3** as catalyst precursor and method A

Entry	Substrate	**3**/mol%	*t*/h	*T*/°C	GC[a] (%)	Yield[b] (%)	TON
1	Bromobenzene	0.0001	14	100	99.9	96	9.9×10^5
2	Bromobenzene	0.0005	2	100	94.5	93	1.9×10^5
3	Bromobenzene	0.00001	21	100	8.3	7	8.3×10^5
4	4-Bromotoluene	0.0001	14	100	81	76	8.1×10^5
5	4-Bromoanisole	0.0001	14	100	39	38	3.9×10^5
6	4-Bromoacetophenone	0.0001	14	100	63	61	6.3×10^5

[a] Based on GC analysis with external standards. [b] Isolated yields by column chromatography; products fully characterized by NMR and MS by comparison with literature data.

Moreover, this push–pull ligand is especially rigid and contains no rotating groups. We evaluated the activity of **3** in a catalyzed C–C cross-coupling process. These transformations are thought to be facilitated by ligands that combine a good σ-donor strength (to favour the oxidative addition) with a good π-accepting capacity (to favour reductive elimination).

3 was reacted with some halogenoarenes in the presence of phenylboronic acic under various conditions to form the corresponding biphenyl derivatives.[6] These data are summarized in Tables 1 and 2.

A very good activity was obtained with bromoarenes using a low loading of catalyst in toluene at 100 °C using K_2CO_3 as a base. Under these conditions, 10^{-4} mol% of complex **3** is sufficient to convert bromobenzene into biphenyl in 14 h (TON = 9.9×10^5, Table 1, entry 1). Conversions of 4-bromoacetophenone, and 4-bromotoluene proceeded with TON's of 6.3×10^5 and 8.1×10^5 respectively, under the same experimental conditions (Table 1, entries 4–6). Under exactly the same conditions, less than 15% of bromobenzene was converted into biphenyl with 10^{-4} mol% of $Pd(OAc)_2$ (GC yield). We can therefore assume that our catalyst does not decompose at this temperature. Coupling reactions with chlorobenzene were also attempted. Among different experimental conditions, the most satisfactory results were obtained using iPrOH as solvent and t-BuOK as base with 1–2 mol% of catalyst. Unfortunately, as can be seen in Table 1, only low conversions were observed (Table 2, entry 1–2) and the formation of benzene as side-product could not be avoided. Note that under these conditions, bromobenzene could also be converted into biphenyl but here again the formation of benzene could not be totally precluded. A yield of 90% was obtained by using 10^{-2} gmol% of catalyst **3** at 60 °C for 12 h (Table 2, entry 4).

However, these preliminary results are very encouraging and further investigations on this unusual type of ligand combination are worth the effort. In our laboratories, we are currently pursuing our studies on the synthesis of other phosphole based derivatives featuring the tropylidene backbone and their use as highly rigid ligand in different catalytic processes.

Table 2 Cross-coupling reaction of halogenoaryls with phenylboronic acid using complex **3** as catalyst and method B

Entry	Substrate	**3**/mol%	*t*/h	*T*/°C	GC[a] (%)	Yield[b] (%)	TON
1	Chlorobenzene	2	96	RT	32.4	31	16.2
2	Chlorobenzene	1	16	50	14.6	13	14.6
3	Bromobenzene	0.1	3	RT	77.6	76	776
4	Bromobenzene	0.01	12	60	91.3	90	9130

[a] Based on GC analysis with external standards. [b] Isolated yields by column chromatography; products fully characterized by NMR and MS by comparison with literature data.

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Notes and references

‡ *Crystal data for* **2**: ($C_{27}H_{19}P$), *M* = 374.39: monoclinic, space group $P2_1/c$, *a* = 10.4290(10), *b* = 10.1650(10), *c* = 18.9660(10) Å, β = 101.6900(10)°, *U* = 1968.9(3) $Å^3$, *Z* = 4, d_{calc} = 1.263 g cm^{-3}, *F*(000) = 784, μ = 0.149 cm^{-1}, (MoKα, λ = 0.71069 Å), *T* = 150.0(1) K, R_1 = 0.0526, wR_2 = 0.1697, GoF = 1.096, unique data = 5724 (R_{int} = 0.0184, KappaCCD diffractometer), 254 refined parameters. CCDC 256941. *Crystal data for* **3**: $C_{27}H_{19}Cl_2PPd,2(CH_2Cl_2)$, *M* = 721.54, orthorhombic, space group $P2_12_12_1$, *a* = 10.3990(10), *b* = 15.8850(10), *c* = 17.0640(10) Å, *U* = 2818.8(4) $Å^3$, *Z* = 4, d_{calc} = 1.700 g cm^{-3}, *F*(000) = 1440, μ = 1.304 cm^{-1} (MoKα, λ = 0.71069 Å), *T* = 150.0(1) K, R_1 = 0.0356, wR_2 = 0.0858, GoF = 1.017, unique data = 8152 (R_{int} = 0.0000, KappaCCD diffractometer), 353 refined parameters, Flack's parameter = −0.05(2). CCDC 256942. See http://www.rsc.org/suppdata/cc/b4/b417716a/ for crystallographic data in .cif or other electronic format. *Synthesis of ligand* **2**: to a solution of the P–H phosphole **1** (0.54 mmol, 100 mg) in toluene (1 mL), under an inert atmosphere of nitrogen, was slowly added a solution of dibenzo[*a*,*d*]cyclohepten-5-yl chloride (0.54 mmol, 123 mg) in toluene (1 mL). The mixture was then refluxed for 15 h during which time evolution of gaseous HCl was observed. The solvent was then evaporated and the product was filtered in hexanes and washed with dry deoxygenated acetonitrile. Ligand **2** was obtained as a white, air and moisture sensitive solid (150 mg, 74%). Crystallization was achieved from hot acetonitrile. ^{31}P NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ −19.7. ^1H NMR(300 MHz, CD_2Cl_2, 25 °C, TMS): δ 3.61 (d, J_{PH} = 8.1 Hz, 1H, H_{13}), 6.41 (dvd, AA′XX′, Σ *J* = 11.6 Hz, 2H, H_5–H_8), 6.61 (vd, AA′XX′, Σ *J* = 7.6 Hz, 2H, H_{15}–H_{26}), 7.03 (vt, AA′XX′, Σ *J* = 17.6 Hz, 2H, H_3–H_{10}), 7.11 (s, 2H, H_{20}–H_{21}), 7.18 (vt, AA′XX′, Σ *J* = 14.9 Hz, 2H, H_{17}–H_{24}), 7.31 (vt, AA′XX′, Σ *J* = 14.9 Hz, 2H, H_{16}–H_{25}), 7.38 (vt, AA′XX′, Σ J_{HH} = 14.7 Hz, 2H, H_4–H_9), 7.42 (vt, AA′XX′, Σ J_{HH} = 17.1 Hz, 2H, H_{18}–H_{23}), 7.89 (vd, AA′XX′, Σ *J* = 7.8 Hz, 2H, H_5–H_8); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C) : δ 58.6 (d, J_{PC} = 22.1 Hz, C_{13}), 121.3 (s, C_2–C_{11}), 126.7 (d, J_{PC} = 6.8 Hz, C_3–C_{10}), 127.4 (d, J_{PC} = 1.8 Hz, C_{16}–C_{25}), 128.6 (s, C_4–C_9), 128.8 (s, C_{17}–C_{24}), 130.0 (d, J_{PC} = 1.8 Hz, C_{18}–C_{23}), 130.6 (d, J_{PC} = 3.4 Hz, C_{15}–C_{26}), 131.0 (d, J_{PC} = 20.5 Hz, C_5–C_8), 132.7 (d, J_{PC} = 4.4 Hz, C_{20}–C_{21}), 135.6 (d, J_{PC} = 5.3 Hz, C_{14}–C_{27}), 137.9 (d, J_{PC} = 8.9 Hz, C_{19}–C_{22}), 143.2 (d, J_{PC} = 11.9 Hz, C_1–C_{12}), 144.1 (s, C_6–C_7). *General procedures for the coupling reactions*: *Method A*: preparation of the catalyst was achieved by dilution of **3** (3 mg, 0.0056 mmol) in dichloromethane (30 mL) at room temperature under an inert atmosphere. 22 μL (0.0001%) of the solution was taken with a syringe, poured into a Schlenck tube, and the solvent was evaporated. The Schlenk tube was then filled with phenylboronic acid (6 mmol, 731.6 mg), K_2CO_3 (8 mmol, 1.1 g) and the halogenoarene (4 mmol) in toluene (6 mL). The mixture was heated

at 100 °C for 14 h. The progress of the reaction was monitored by GC. When the reaction reached completion, a small amount of silica gel was added and the solvent was evaporated *in vacuo*. The product was then isolated by column chromatography on silica gel (petroleum ether 40–65 °C) and characterized by comparison with the literature.*Method B*: the catalyst **3** (5.5 mg, 1%), phenylboronic acid (1.4 eq, 170.7 mg), KO^{t}Bu (1.5 eq, 168.3 mg) and chlorobenzene (1 mmol) were mixed in iPrOH (1.5 mL). The mixture was stirred at ambient temperature and the progress of the reaction was monitored by GC. Purification was carried out as above.

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