ChemComm
www.rsc.org/chemcomm

A σ^4, λ^5-phosphinine palladium complex: a new type of phosphorus ligand and catalyst. Application to the Pd-catalyzed formation of arylboronic esters†

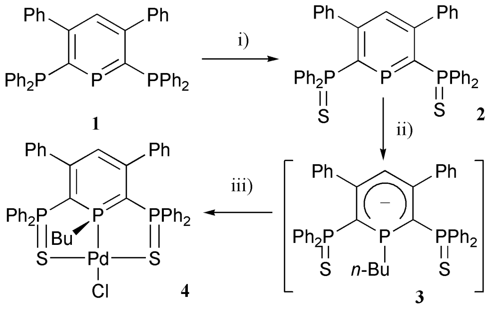
Marjolaine Doux, Nicolas Mézailles, Mohand Melaimi, Louis Ricard and Pascal Le Floch*
Laboratoire 'Hétéroéléments et Coordination' UMR CNRS 7653, Ecole Polytechnique, 91128 Palaiseau Cedex, France. E-mail: lefloch@poly.polytechnique.fr

Received (in Cambridge, UK) 11th April 2002, Accepted 7th June 2002
First published as an Advance Article on the web 20th June 2002

A palladium(II) complex of a S–P–S pincer ligand featuring a metallated ylidic P-atom efficiently catalyzes the coupling between pinacolborane and various iodoaryls to yield the corresponding arylboronic esters (TON between 5100 and 76500).

Tertiary phosphines play a central role as ligands in homogeneous catalysis where they are essentially used as two-electron donor ligand *via* coordination of the phosphorus atom lone pair.[1] Though the use of metal phosphide-based complexes is well-documented in heterogeneous catalysis,[2] complexes involving a sigma bonding between the metal and a σ^3 or σ^4-coordinated phosphorus atom are still rare.[3] This void results from the high reactivity of the P–metal bond in most metal–phosphide complexes (σ^3 compounds) and from the preference for C–metal bonding in ylidic type structures.[4] We recently found that a possible way to circumvent this limitation is to incorporate the phosphorus atom in a ylidic delocalized type-structure such as λ^5-phosphinines. Indeed, recent calculations have showed that these heterocycles possess a mixed ylidic–aromatic character depending on the substitution scheme of the P-atom.[5] Metal complexes of λ^5-phosphinines are very rare and only one example, partially characterized, was reported by Dimroth and coworkers in the case of a cyclopentadienyl iron complex.[6]

As part of a program aimed at studying mixed phosphinine-based S–P–S pincer ligands, we recently found that the reaction of butyllithium with the easily available sulfide **2** (made by sulfurization of **1**)[7] resulted in the formation of the corresponding 1-*n*-butylcyclophosphahexadienylanion **3**. Subsequent reaction of **3** with one equivalent of [Pd(COD)Cl$_2$] cleanly affords the palladium complex **4** which was structurally characterized (Scheme 1).[8] An ORTEP view of one molecule of **4** is presented in Fig. 1.‡ Complex **4**, which was recovered as an orange powder, is highly robust and can be stored without special precautions. Thus, no apparent decomposition was observed after heating **4** with water for hours. The structure of **4** deserves some comments. As expected for a d^8 center the overall geometry around palladium is square planar. Both intracyclic P–C bond lengths appear to be rather short, attesting the ylidic character of the ligand. The most significant feature concerns the external P–C bond distances at 1.758(8) and 1.760(7) which are relatively short for single P–C bonds. Conversely, the P=S bonds at 2.031(4) and 2.037(3) are found to be slightly lengthened suggesting a substantial electronic delocalisation in each C–P–S moity.



Scheme 1 *Reagents and conditions*: i, ⅛ S$_8$, toluene reflux, 12 h; ii, BuLi (1 equiv.), thf, −78 to 25 °C, 10 min; iii, [Pd(COD)Cl$_2$] (1 equiv.), thf, −78 to 25 °C, 15 min.

The catalytic activity of **4** was first tested in the classical Heck reaction in the coupling of methyl–acrylate with iodobenzene. Heating a mixture of the compounds at 100 °C in *N*-methylpyrolidone for 5 days with 0.01% of catalyst yielded the methyl *trans*-cinnamate in quantitative yield. A conversion yield of 31% was obtained after 4 days with 1×10^{-4} mol% of catalyst under the same experimental conditions. In view of this promising result and taking into account the importance of arylboronic esters in organic synthesis, we then turned our attention on the Myaura cross-coupling process which still requires quite substantial loading of catalyst even when iodoaryls are used as substrates.[9] Last year, we reported on a very efficient catalyst which allows this coupling reaction, in the case of iodoaryls, with a TON up to 3000.[10] The catalytic activity of **4** was investigated in the coupling of pinacolborane with some iodoaryls (Scheme 2).[11] As can be seen in Table 1, though the reaction proceeds quite slowly, only a low-loading of catalyst is needed. In the case of iodobenzene, which yielded the

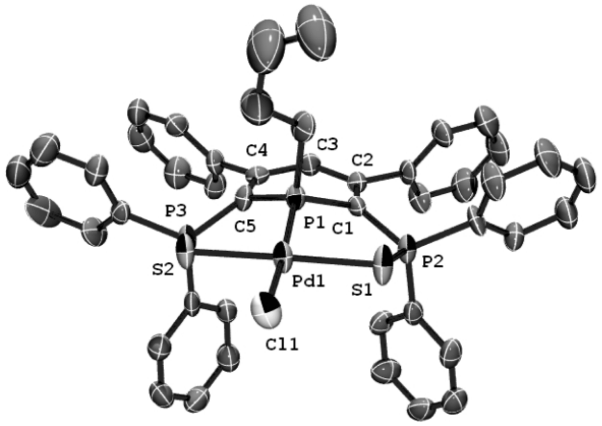
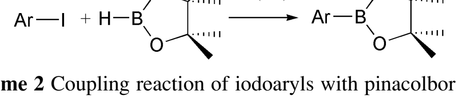


Fig. 1 Molecular structure of complex **4** (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)–Pd(1) 2.180(2), Pd(1)–Cl(1) 2.377(3), Pd(1)–S(1) 2.321(2), Pd(1)–S(2) 2.317(2), P(3)–S(2) 2.031(4), P(2)–S(1) 2.037(3), P(1)–C(1) 1.762(7), P(1)–C(5) 1.761(7), C(1)–P(2) 1.760(7), C(5)–P(3) 1.758(8); P(1)–Pd(1)–S(1) 87.32(8), P(1)–Pd(1)–S(2) 88.09(8), Cl1–Pd(1)–S(1) 93.84(8).



Scheme 2 Coupling reaction of iodoaryls with pinacolborane.

---

† Electronic supplementary information (RSI) available: experimental procedures for a detailed preparation of complex **4** and cross-coupling experiments. See http://www.rsc.org/suppdata/cc/b2/b203550b/

DOI: 10.1039/b203550b

Table 1 Myaura cross-coupling reaction of iodoaryls with pinacolborane using complex **4** as catalyst

Entry	Substrate	*t*	GC[a] (%)	Yield[b] (%)	TON
1	Iodobenzene	15 h	100	95	10000
2	4-Iodotoluene	48 h	100	96	10000
3	2-Iodotoluene	5 d	50	45	5000
4	2-Iodothiophene	5 d	73	68	7300
5	2-Iodonaphthalene	5 d	90	87	9000
6	4-Bromoiodobenzene	5 d	66	62	6600
7	4-Iodoanisole	5 d	51	45	5100

[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.

best result, a TON of 76500 was obtained after 10 days using 1 $\times$ 10^{-3} mol% of catalyst.

In conclusion, we have developed a straightforward access to a new type of phosphorus based catalyst involving a sigma bonding between the phosphorus and the metal. The high activity of such systems very likely results from the rigidity provided by the pincer type backbone but also from the conjugated ring structure which stabilizes the ylide form. Note that the particular electronic structure of these ligands, which combines a strong donor binding site (P atom) with two pendant acceptor ligands (S atoms), may also play an important role.

Studies aimed at elucidating the nature of the active species, as well as expanding this procedure to arylbromides and chlorides by modifying the nature of the substituents at phosphorus or by using a more reactive borane precursor, are currently in progress.[12,13] The use of these new ligands in coordination chemistry and in other catalytic processes will also constitute a priority.

Notes and references

‡ *Crystal data* for [C$_4$Ph$_2$P(PPh$_2$S)$_2$]PdCl·CH$_2$Cl$_2$ (**4**): C$_{45}$H$_{40}$ClP$_3$PdS$_2$·CH$_2$Cl$_2$, M = 964.62. orthorhombic, space group $Pna2_1$, a = 19.482(5), b = 24.081(5), c = 9.337(5) Å, U = 4380(3) Å^3, T = 150.0(10), Z = 4, D_c = 1.463 g cm^{-3}, μ = 0.844 cm^{-1}, KappaCCD diffractometer, λ(Mo-Kα) = 0.71069 Å, 5292 independent reflections, $wR(F^2)$ = 0.1106, $R1$ = 0.0475 for 4122 reflections used with $F_o > 2\sigma(I)$ and 497 parameters. Flack parameter = 0.01(4). CCDC reference number 185527. See http://www.rsc.org/suppdata/cc/b203550b/ for crystallographic data in CIF or other electronic format.

1 *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996.

2 R. Iwamoto and J. Grimblot, *J. Adv. Catal.*, 1999, **44**, 417.

3 See for example:K. Kunz, G. Erker, S. Döring, R. Fröhlich and G. Kehr, *J. Am. Chem. Soc.*, 2001, **123**, 6181.

4 (*a*) W. C. Kaska, *Coord. Chem. Rev.*, 1983, **48**, 58; (*b*) H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 907.

5 Z.-X. Wang and P. v. Ragué Schleyer, *Helv. Chim. Acta*, 2001, **84**, 1578.

6 T. Dave, S. Berger, E. Bilger, E. Kaletsch, J. Pebler, J. Knecht and K. Dimroth, *Organometallics*, 1985, **4**, 1565.

7 (*a*) N. Avarvari, P. Le Floch and F. Mathey, *J. Am. Chem. Soc.*, 1996, **118**, 11978; (*b*) N. Avarvari, L. Ricard, P. Le Floch and F. Mathey, *Organometallics*, 1997, **16**, 4089.

8 *Synthesis* of **2** and **4**: phosphinine **1** (4.0 g, 6.5 mmol) was heated in toluene with elemental sulfur (0.415 g, 13 mmol) under reflux for 12 h. After cooling to room temperature, sulfide **2** was collected by filtration and washed with toluene: Yield: 4.23 g (96%); ^{31}P NMR (121.5 MHz, CD$_2$Cl$_2$, 298 K), δ 43.4 (AB$_2$, m, $^2J_{PP}$ 115.0 Hz, P$_B$), 253.1 (AB$_2$, P$_A$). A solution of *n*-butyllithium (1.6 M in hexane) (3.4 mL, 4.4 mmol) was added at -80 °C to a solution of sulfide **2** (3 g, 4.4 mmol) in THF (100 mL). After 10 min stirring, the solution was warmed to room temperature and stirred for an additional 10 min. The complete formation of intermediate **3** was checked by ^{31}P NMR (121.5 MHz, THF, 298 K), δ 45.8 (d, J_{PP} 156.0 Hz) and –66.2 (t). After cooling to -78 °C, [Pd(COD)Cl$_2$] (1.25 g) was added and the solution was warmed to room temperature. After evaporation of the solvent and washings with hexane (3 $\times$ 10 mL), complex **4** was recovered as a very stable orange solid; Yield: 3.29 g (85%); ^{31}P NMR (121.5 MHz, CD$_2$Cl$_2$, 298K), δ49.17 (AB$_2$, m, $^2J_{PP}$ 87.0 Hz, P$_B$), 55.38 (AB$_2$, m, $^2J_{PP}$ 87.0 Hz, P$_A$). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K, TMS), δ 1.06 (t, $^3J_{HH}$ 7.4 Hz, 3H, CH$_3$), 1.60 (qt, $^3J_{HH}$ 7.4 Hz, CH$_2$), 2.00 (m, 2H, CH$_2$), 2.26 (m, 2H, CH$_2$), 5.50 (A$_2$X, t, $^4J_{HP}$ 4.7 Hz, 1H, H$_4$), 6.60–7.80 (m, 30H, CH of C$_6$H$_5$). ^{13}C NMR (75.5 MHz, CD$_2$Cl$_2$, 298 K), δ 13.9 (s, CH$_3$), 24.2 (s, CH$_2$), 24.6 (d, $^2J_{CP}$ 2.6 Hz, CH$_2$), 38.0 (m, CH$_2$), 72.5 (ABB'X, m, C$_2$), 118.7 (AB$_2$X, m, C$_4$H), 127.7–133.3 (m, CH and C$_q$ of C$_6$H$_5$), 139.9 (m, C$_3$), 159.4 (s, C$_q$ of C$_6$H$_5$).

9 (*a*) See for example: A. Fürstner and G. Seidel, *Org. Lett.*, 2002, **4**, 541; (*b*) T. Ishiyama, K. Ishida and N. Miyaura, *Tetrahedron*, 2001, **57**, 9813; (*c*) O. Baudoin, D. Guénard and F. Guéritte, *J. Org. Chem.*, 2000, **65**, 9268; (*d*) M. Murata, T. Oyama, S. Watanabe and Y. Masuda, *J. Org. Chem.*, 2000, **65**, 164.

10 M. Melaimi, F. Mathey and P. Le Floch, *J. Organomet. Chem.*, 2001, **640**, 197.

11 *Procedure for coupling reactions*: a solution of catalyst **4** (1.0 mg mL^{-1}) in CH$_2$Cl$_2$ was prepared. 100 µl (1 $\times$ 10^{-4} mmol) of this solution were placed in a Schlenk tube and the solvent was evaporated. The iodoaryl (1.0 mmol), pinacolborane (1 M in THF, 1.5 mmol), triethylamine (3.0 mmol) in dioxane (4 mL) were then successively added. The resulting solution was then heated at 80 °C and the progress of the reaction was monitored by GC. All arylboronic esters were purified by chromatographic separation on silicagel (pretreated with Et$_3$N).

12 A. Albrecht and G. Van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750.

13 Pd P–C–P pincer-based catalysts have been successfully used in the Suzuki cross-coupling reaction (formation of C–C bonds) but not in the Myaura cross-coupling process (formation of C–B bonds). For a reference, see: R. B. Bedford, S. M. Draper, P. Noelle Scully and S. L. Welch, *New. J. Chem.*, 2000, **24**, 745.