A New Mixed P,S-Bidentate Ligand Featuring a λ^4-Phosphinine Anion and a Phosphanyl Sulfide Group − Synthesis, X-ray Crystal Structures and Catalytic Properties of Its Chloro(cymene)ruthenium and Allylpalladium Complexes

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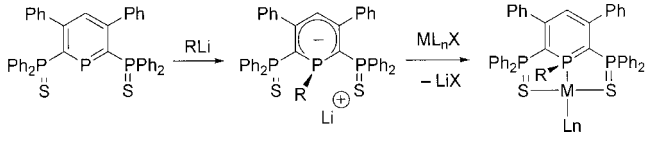
1,3,2-Diazaphosphinine (**1**) reacts successively with diphenylacetylene and diphenyl(1-propynyl)phosphane sulfide to afford the P,S-bidentate phosphinine **3**. Reaction of *n*BuLi with **3** followed by complexation with $[RuCl_2(C_{10}H_{14})]_2$ gave two diastereoisomers **5a**,**b**. Variable-temperature NMR spectroscopy and ONIOM DFT calculations were carried out to rationalize their formation. Complexes **5a**,**b** were used as catalysts in hydrogen-transfer hydrogenation (TON up to 200). Reaction of MeLi with **3** followed by complexation with $[PdCl_2(\eta^3\text{-}C_3H_5)]_2$ yielded two diastereomers **7a**,**b**, which were used as catalysts in the Suzuki–Miyaura cross-coupling reaction of aryl bromides with pinacolborane to yield the corresponding arylboronic esters (TON up to 799000).

Introduction

Since the pioneering work of Grim and co-workers in the mid-1970s,[1] there has been a continuing interest in the chemistry of mixed tertiary phosphane/monochalcogenide (λ^3,σ^3)P−X (X = O, S) ligands.[2−7] These systems, which combine soft σ-donor (P) and good π-donor (O, S) binding sites, display very unique steric and electronic properties that differ markedly from those of classical bidentate phosphorus ligands. Most importantly, in some cases, these compounds have been employed to build very active catalysts. For example, in 1995 it was shown that a rhodium(I) complex of the monosulfide of dppm (dppm = $Ph_2PCH_2PPh_2$) could efficiently catalyze the carbonylation of methanol.[8] Later on, palladium(II) complexes of the same ligands were shown to be active catalysts for the ethylene/CO copolymerization.[9] On the other hand, P,O-mixed ligands, such as monoxides of dppm and dppe ($Ph_2PCH_2CH_2PPh_2$) and dppp ($Ph_2PCH_2CH_2CH_2PPh_2$), give better results than classical bidentate phosphanes in the cobalt-catalyzed hydroformylation of epoxides due to their hemilability.[10]

In 2002 we reported the synthesis of a new type of S,P,S-pincer ligand that incorporates a pseudo-ylidic λ^4-phosphorus atom as the central binding site (Scheme 1).[11,12] These tridentate ligands, which are readily available from the reaction of nucleophiles with phosphinines, were found to exhibit very specific electronic properties. Thus, their rhodium(I) complexes show a high reactivity towards small molecules such as O_2, CO_2, CS_2 and SO_2.[13] Furthermore, their palladium(II) complexes proved to be active catalysts in the Miyaura cross-coupling reaction that allows the synthesis of arylboronic esters from pinacolborane and haloarenes.[14]



Scheme 1

Exploiting the same strategy, Yoshifuji et al. reported this year on the synthesis of mixed P,S-systems of the type (RP=C−P=S) featuring a kinetically stabilized phosphaalkene (λ^3,σ^2-phosphorus atom) and a phosphane sulfide group.[15,16] A cationic palladium(II) complex of these new low-coordinate, phosphorus-based ligands was employed as a catalyst in the direct conversion of allyl alcohol to allylaniline.[17]

Initially, we postulated that the presence of two ancillary phosphane sulfide groups was a prerequisite for the stabilization of these new types of σ complexes. Indeed, it is well-known that 1-alkylphosphininyllithium salts usually react

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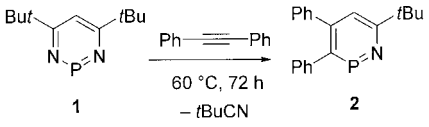
through their π-system with metal fragments to yield the corresponding η^5-coordinated complexes.[18−23] In this article, we show that anionic bidentate P,S-ligands featuring a pseudo-ylidic λ^4-phosphorus atom can be easily assembled from a diphenyl(2-phosphininyl)phosphane sulfide.

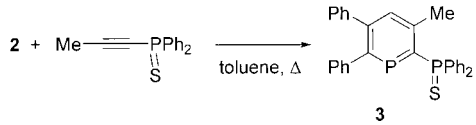
Results and Discussion

The synthetic strategy used for the synthesis of these new systems relies on the reactivity of 4,6-di-*tert*-butyl-1,3,2-diazaphosphinine (**1**) towards functionalised alkynes.[24,25] This precursor proved to be a very efficient source of tetrafunctionalised phosphinines through successive [4 + 2] cycloaddition/cycloreversion processes with functionalised alkynes. We first focused our work on the synthesis of diphenyl(3-R-5,6-diphenylphosphinin-2-yl)phosphane sulfide derivatives. Azaphosphinine **2**, which was only used as a transient species, was readily formed by warming equimolar amounts of **1** and diphenylacetylene at 60 °C in toluene for 3 d (Scheme 2).



Scheme 2

Compound **2** proved to be sufficiently reactive to undergo a second [4 + 2] cycloaddition/cycloreversion process with 1 equiv. of alkynyl-substituted diphenylphosphane sulfides in toluene at reflux. We chose Me−C≡C−P(S)Ph_2 for this reaction in order to increase the solubility of the ligand. We found that the reaction with diphenyl(1-propynyl)phosphane sulfide only yielded phosphinine **3**, which was isolated as an air-stable, white solid and was fully characterized by NMR techniques and elemental analysis. The presence of the diphenylphosphane sulfide group at the α-position of the phosphorus atom was evidenced in the ^{31}P NMR spectrum by a large $^2J_{P,P}$ coupling constant of 108.2 Hz (in $CDCl_3$ at 25 °C) (Scheme 3). The formulation proposed on the basis of NMR spectroscopic data was confirmed by an X-ray crystal structure analysis. A view of a molecule of **3** is presented in Figure 1; crystal data are summarized in the Exp. Sect. This structure deserves no particular comments as the metric parameters fall in the usual range for λ^3-phosphinines.



Scheme 3

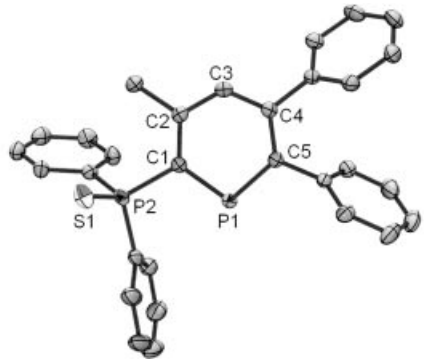
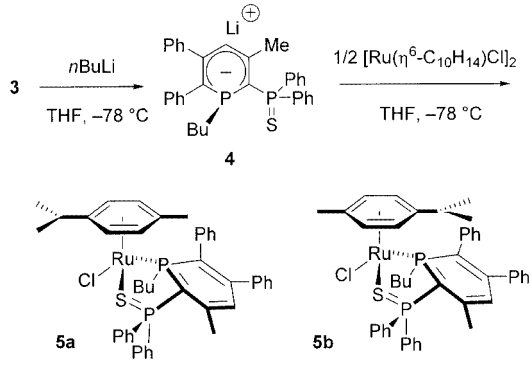


Figure 1. ORTEP view of a molecule of ligand **3**; ellipsoids are scaled to enclose 50% of the electron density; the numbering is arbitrary and different from that used in the assignment of the NMR spectra; selected distances [Å] and bond angles [°]: P1−C1 1.739(2), C1−C2 1.406(2), C2−C3 1.395(2), C3−C4 1.392(2), C4−C5 1.404(2), C5−P1 1.736(2), C1−P2 1.824(2), P2−S1 1.954(1); P1−C1−C2 124.4(1), C1−C2−C3 120.8(2), C2−C3−C4 126.6(2), C3−C4−C5 121.7(2), C4−C5−P1 123.9(1), C5−P1−C1 102.60(7), P1−C1−P2 115.1(1); (mean plane C1−C2−C4−C5)−P1 0.45, (mean plane C1−C2−C4−C5)−C3 0.8

As previously explained, the synthesis of the corresponding 1-alkylphosphininyllithium salts can be conventionally achieved by treating equimolar amounts of phosphinines with nucleophiles. Thus, **3** was treated with *n*-butyllithium in THF at −78 °C to afford the lithium salt **4**, which was identified by ^{31}P NMR spectroscopy. The lithium salt **4** appears as an AB system [δ = −37.6 (P−Bu) and 42.4 ppm (PPh_2) in THF at 25 °C; $^2J_{P,P}$ = 151.9 Hz]. The chemical shift of the ring phosphorus atom (δ = −37.6 ppm) is similar to those of other 1-alkylphosphininyllithium salts.[14,23]

Reaction of **4** with the dimer [Ru(η^6-$C_{10}H_{14}$)Cl_2]$_2$ was carried out in THF at low temperature. After warming to room temperature, the ^{31}P NMR spectrum of the crude mixture indicated that two complexes **5a** and **5b** had formed in a 3:1 ratio (Scheme 4).



Scheme 4

Both complexes appear as an AB spin-system with close chemical shifts (δ = 40.7 and 44.3 ppm for **5a** and δ = 43.4 and 45.9 ppm for **5b**) and $^2J_{P,P}$ coupling constants (115.5 Hz for **5a** and 97.2 Hz for **5b**). The only major difference between **5a** and **5b** in the ^1H NMR spectra arises from

the chemical shifts of the aromatic protons of the cymene ligand: in **5a** two hydrogen signals are shifted to high field (doublets at δ = 3.17 and 3.69 ppm with $^3J_{H,H}$ = 5.5 and 6.1 Hz, respectively) compared with those of **5b** (doublets at δ = 4.13 and 4.17 ppm with $^3J_{H,H}$ = 6.0 and 5.6 Hz, respectively) and other reported complexes.[26] Fortunately, complex **5a** proved to be insoluble in diethyl ether, thus allowing the separation of the two diastereomers. Single crystals of complex **5a** were obtained at room temperature from C_6D_6 as solvent (crystals deposited during the recording of the NMR spectra). An ORTEP view of a molecule of **5a** is presented in Figure 2; crystal data are presented in the Exp. Sect. As can be seen, the complex adopts a classical pianostool structure with the *n*-butyl substituent at the phosphorus atom pointing backwards probably to avoid steric congestion with the cymene ligand. The most interesting finding is related to the external P−C and P=S bond lengths. The shortening of the C1−P2 bond from 1.824(2) in **3** to 1.745(2) Å in **5a** and the elongation of the P2=S1 bond from 1.954(1) in **3** to 2.0283(7) Å in **5a** suggests a slight delocalization over the P1−C1−P2−S1−Ru1 skeleton. This induces a relocalization of the internal P−C and C−C bonds within the phosphinine ring: for instance, C2−C3 and C4−C5 shorten [1.372(3) and 1.376(3) Å, respectively] with respect to the free ligand [1.395(2) and 1.404(2) Å] whereas C1−C2, C3−C4 and C5−P1 lengthen [1.422(3), 1.435(2) and 1.805(2) Å in **5a** compared with 1.404(2), 1.394(2) and 1.736(2) Å in **3**]. The S−Ru bond [2.4239(5) Å] falls in the usual range of P=S−Ru bond lengths.[27,28] As previously noted in the structures of Ni, Pd, Pt and Rh complexes,[12,13] the phosphorus atom and the C3 carbon atom lie out of the plane defined by the C1, C2, C4 and C5 atoms by 12.6° and 1.8°, respectively, to yield a boat-like conformation. The phosphorus atom is now pyramidal (sum of angles at P1 = 313.8°) and compares well with classical tertiary phosphanes.

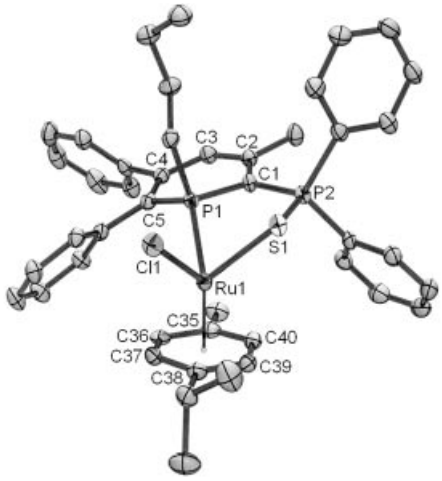
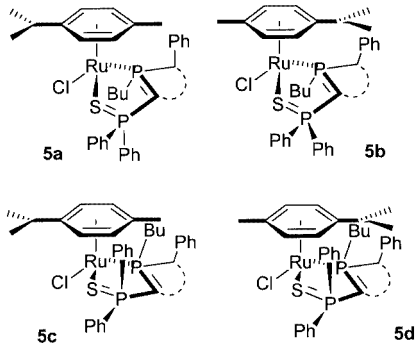


Figure 2. ORTEP view of a molecule of complex **5a**; ellipsoids are scaled to enclose 50% of the electron density; the numbering is arbitrary and different from that used in the assignment of the NMR spectra; selected distances [Å] and bond angles [°]: P1−C1 1.790(2), C1−C2 1.422(3), C2−C3 1.372(3), C3−C4 1.435(2), C4−C5 1.376(3), C5−P1 1.805(2), P1−Bu 1.852(2), C1−P2 1.745(2), P2−S1 2.0283(7), Ru1−P1 2.3351(5), Ru1−S1 2.4239(5), Ru1−Cl1 2.4186(5), Ru1−C35 2.237(2), Ru1−C36 2.239(2), Ru1−C37 2.196(2), Ru1−C38 2.276(2), Ru1−C39 2.257(2), Ru1−C40 2.189(2), Ru1−Ct 1.725, C35−C36 1.442(3), C36−C37 1.401(3), C37−C38 1.420(3), C38−C39 1.408(3), C39−C40 1.430(3), C40−C35 1.402(3); P1−C1−C2 121.1(1), C1−C2−C3 122.5(2), C2−C3−C4 125.3(2), C3−C4−C5 125.1(2), C4−C5−P1 119.2(1), C5−P1−C1 102.82(8), P1−C1−P2 111.9(1); (mean plane C1−C2−C4−C5)−P1 12.55, (mean plane C1−C2−C4−C5)−C3 1.75

Additional experiments were carried out in order to see which factors control the ratio between **5a** and **5b**. However, whatever the experimental conditions used (concentration and reaction temperature) the 3:1 ratio initially obtained could not be significantly modified. Variable-temperature NMR experiments were also carried out on the mixture of **5a** and **5b** but, even under reflux in THF, no interconversion could be observed. The stereochemistry of **5a** could not be established on the sole basis of its NMR spectroscopic data. In theory, four diastereomers can be formed (**5a**,**b**,**c**,**d**; Scheme 5) depending on the orientation of the substituent at the phosphorus atom (backwards in **5a** and **5b**, inwards in **5c** and **5d**) and on the orientation of the methyl and isopropyl groups of the cymene ligand. Although simple molecular modelling strongly suggests that diastereomers **5c** and **5d** could not be formed because of the important steric congestion between the cymene ligand and both the substituent at the phosphorus atom and one of the phenyl groups of the diphenylphosphane sulfide group, the four diastereomers were computed using the ONIOM method at the B3LYP/UFF level (see Exp. Sect. for details on basis sets and partition of the molecule into QM and MM shells). In these calculations the *n*-butyl group at the phosphorus atom was replaced by a methyl group to minimize the degrees of freedom. Optimizations of the theoretical complexes **5c** and **5d** failed and no minima could be located, the ligand being displaced away from the Ru−Cl fragment during the optimization. The introduction of an *n*-butyl group at the phosphorus atom would not yield a different result due to the bulkiness generated by the alkyl chain. However, two minima could be located for structures **Ia** (model of **5a**) and **Ib** (model of **5b**). Two views of these theoretical structures are presented in Fig-



Scheme 5

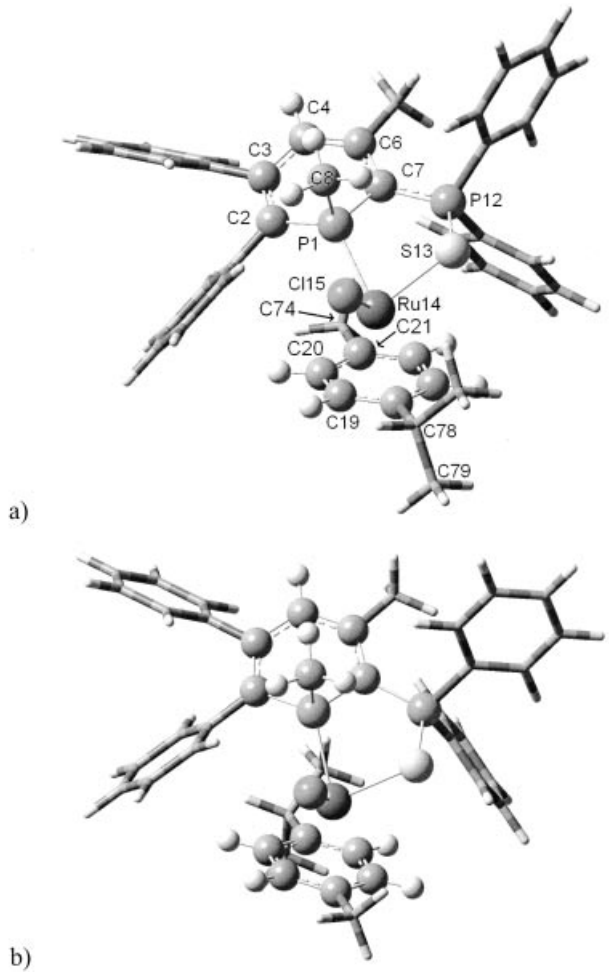


Figure 3. Optimized structures of model complexes **Ia** (a) and **Ib** (b) obtained at the ONIOM(B3LYP/UFF) level of theory; atoms included in the QM part are shown in ball-and-stick format and atoms included in the MM part are represented by tubes; the numbering is the same for **Ia** and **Ib**

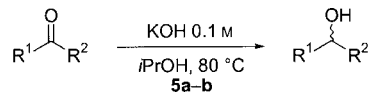
ure 3; fully labelled molecules of **Ia**,**b** are presented in the Supporting Information. The most significant bond lengths and bond angles of **Ia,b** are reported in Table 1. As can be seen by examining these data, there is an acceptable fit between theoretical and experimental parameters. In **Ia** the P,S-ligand and the Ru−Cl, Ru−S and Ru−P bond lengths are very close to those of the X-ray structure of **5a**: for instance, in **Ia** the P1−C2, C7−P12, P12−S13, Ru14−S13 and Ru14−P1 bond lengths are 1.812, 1.757, 2.061, 2.449 and 2.385 Å, respectively, versus 1.805, 1.745, 2.028, 2.424 and 2.335 Å in **5a**. The only discrepancies arise in the cymene ring. Despite excellent agreement between the C−C bond lengths (for example C19−C20, C74−C21, C78−C79 are 1.407, 1.511 and 1.534 Å, respectively, in **Ia** versus 1.401, 1.511 and 1.534 Å in **5a**), the cymene ring is too far away from the ruthenium atom (the C16−Ru14 distance is 2.328 Å in **Ia** compared to 2.189 Å in **5a**). Modification of the basis set for Ru (all-electron basis sets rather than ECP) was not performed due to the already long computational time. The same trends are observed between **Ia** and **Ib** and deserve no other comment.

Table 1. Selected bond lengths [Å] for calculated structures **Ia**,**b**

	Ia	**Ib**
P1−C2	1.812	1.810
C2−C3	1.388	1.387
C3−C4	1.440	1.439
C4−C6	1.386	1.386
C6−C7	1.429	1.431
C7−P1	1.806	1.814
P1−R8	1.851	1.851
C26−C2	1.492	1.491
C37−C3	1.491	1.491
C48−C6	1.512	1.513
C7−P12	1.757	1.759
P12−S13	2.061	2.059
P1−Ru14	2.385	2.391
S13−Ru14	2.449	2.432
Cl15−Ru14	2.443	3.329
C16−Ru14	2.328	2.407
C17−Ru14	2.391	2.357
C18−Ru14	2.385	2.349
C19−Ru14	2.228	2.291
C20−Ru14	2.327	2.361
C21−Ru14	2.321	2.442
C74-cycle	1.499	1.499
C78-cycle	1.517	1.519
C79−C78	1.531	1.532
C80−C78	1.536	1.530

Single-point calculations at the B3LYP level of theory carried out on both optimized ONIOM structures revealed that the model complex **Ia** is more stable than the isomer **Ib** ($\Delta\Delta H = -4.8$ kcal/mol), thus confirming the experimental results. Most importantly, no transition state could be located between **Ia** and **Ib**, the rotation of the cymene ligand around its centroid−ruthenium axis being completely blocked by the two peripheral phenyl groups. This result allows us to rationalize why no interconversion between **5a** and **5b** is observed, even under heating.

The catalytic activity of complexes **5a,b** in the transfer hydrogenation of ketones was tested (Scheme 6).[29−34] Reactions were conducted in 2-propanol as a proton source and solvent and KOH as base using 0.5 mol % of catalysts in most cases. The results are summarized in Table 2. As can be seen, although conversion is acceptable, long reaction times are needed to achieve complete conversions. It must be noted that no efforts have been made, so far, to improve these figures (solvents, role of the base, amount of catalyst).



Scheme 6

The synthesis of a $[Pd(\eta^3\text{-}C_3H_5)]^+$ complex of the lithium salt **4** was also investigated. As previously reported for the synthesis of **5a**,**b**, reaction of phosphinine **3** with methyllithium in THF at −78 °C afforded the lithium salt **6**, which was identified by ^{31}P NMR spectroscopy. Like **4**, the lith-

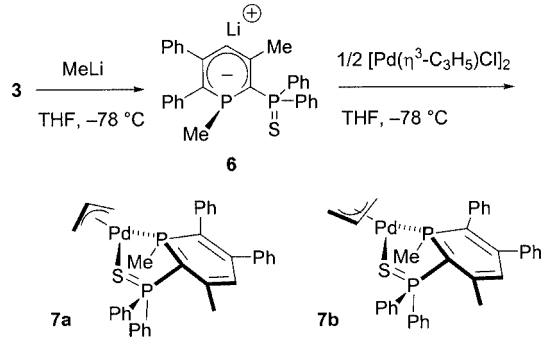
Table 2. Transfer hydrogenation of ketones using complex **5a**,**b** as catalyst; conditions: substrate (2 mmol), catalyst **5a**,**b** (0.5 mol %, unless stated otherwise), 10 mL of 0.1 M KOH in *i*PrOH, 80 °C, 2.5 d.

Entry	Substrate	Yield (%)[a]	Time[b]	TON
1	4-heptanone	91.6	2.5	183.2
2	1,3-diphenylacetone	100	2.5	200
3	cyclohexanone	100	2.5	200
4	2,6-dimethylcyclohexanone	100	2.5	200
5	acetophenone	82.1[c]	0.5	82.1
6	acetophenone	97.6	2.5	195.2
9	4-Br-acetophenone	96.6	2.5	193.2
10	4-F-acetophenone	100	2.5	200
11	4-methyl-acetophenone	94.1	2.5	182.8
12	benzophenone	98.5	2.5	197
13	4,4′-dimethoxy-benzophenone	72.1[d]	2.5	90.1
14	transchalcone	100	2.5	200

[a] Yields were determined by ^{1}H NMR spectroscopy, mass spectrometry or GC. [b] In days. [c] 1 mol % of catalyst. [d] 0.8 mol % of catalyst.

ium salt **6** appears as an AB system with comparable chemical shifts [δ = −40.7 (P−Me) and 42.5 ppm (PPh_2) in THF at 25 °C; $^2J_{P,P}$ = 156.7 Hz]. Reaction of **6** with the dimer [Pd(η^3-C_3H_5)Cl]$_2$ was carried out in THF at low temperature. After warming to room temperature, the ^{31}P NMR spectrum of the crude mixture indicated that complexes **7a** and **7b** had formed in a 3:1 ratio (Scheme 7). Complexes **7a** (major isomer) and **7b** (minor isomer) appear as an AB spin-system with very similar chemical shifts (δ = 24.6 and 52.4 ppm for **7a** and δ = 23.4 and 52.0 ppm for **7b**) and $^2J_{P,P}$ coupling constants (135.8 Hz for **7a** and 132.7 Hz for **7b**). Separation of complexes **7a** and **7b** could not be achieved despite many attempts. These complexes were, however, fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. In the ^{1}H NMR spectrum of **7**, two sets of five non-equivalent η^3-allyl proton resonances are observed. One of the signals of the minor isomer **7b** overlaps with those of the major isomer **7a**.

Isomer interconversion was investigated by variable-temperature NMR experiments but no conversion was observed. We suppose that the rotation of the allyl moiety is disfavoured by a repulsive interaction between the CH_2 allyl



Scheme 7

group and the phenyl group in the C6 position of the phosphinine ring. A similar phenomenon has already been reported for other complexes.[35,36]

Crystals of **7a** suitable for X-ray analysis were obtained by slow diffusion of hexanes into a solution of complexes **7a**,**b** in $CDCl_3$. An ORTEP view of **7a** is presented in Figure 4 and the refinement parameters are given in the Exp. Sect. This structure confirms the η^3-coordination of the allyl moiety and also that the geometry around the palladium atom is trigonal-planar. The P1−Pd [2.2778(6) Å] and the S1−Pd [2.3371(6) Å] bond lengths are similar to classical phosphane−palladium and P=S−Pd bond lengths,[36] although the P1−Pd distance is greater than in previously reported tridentate palladium complexes.[12] The Pd−C32, Pd−C33, Pd−C34 [2.138(3), 2.137(3), 2.199(3) Å] and C32−C33 and C33−C34 [1.359(4) and 1.383(5) Å] bond lengths and the C32−C33−C34 angle [123.8(3)°] are in the typical range of η^3-allylpalladium complexes.[37−40] The geometry of the phosphinine moiety is similar to that in complex **5a** and deserves no further comment. In the major isomer an H,C-HSQC NMR experiment showed that the signals of the two hydrogen atoms of the CH_2 allyl fragments at δ = 2.16 and 2.52 ppm are connected, as are those at δ = 3.00 and 4.21 ppm. An H,H-NOESY experiment also revealed that, in this same isomer, the P−Me group (C6 in the ORTEP view) is in the spatial neighbourhood of only two hydrogen atoms of the CH_2 allyl fragments (at δ = 2.16 and 2.52 ppm) and is far from the CH and the other CH_2 fragments (at δ = 4.89, 3.00 and 4.21 ppm, respectively). The major isomer is therefore complex **7a**.

The catalytic activity of complexes **7a**,**b** was tested in the Suzuki−Miyaura cross-coupling reaction, which allows the synthesis of arylboronic esters from haloarenes and phenylboronic acid (Scheme 8).[41−49] The reactions were conduc-

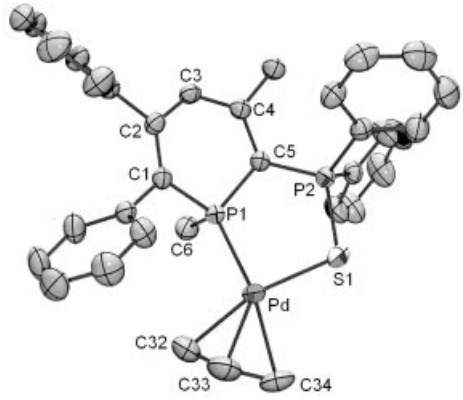
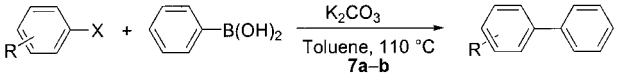


Figure 4. ORTEP view of one molecule of complex **7a**; ellipsoids are scaled to enclose 50% of the electron density; the numbering is arbitrary and different from that used in the assignment of the NMR spectra; selected distances [Å] and bond angles [°]: P1−C1 1.802(2); C1−C2 1.360(3), C2−C3 1.444(3), C3−C4 1.378(3), C4−C5 1.422(3), C5−P1 1.756(2), P1−C6 1.828(2), C5−P2 1.733(2), P2−S1 2.0288(8), Pd1−P1 2.2778(6), Pd−S1 2.3371(6), Pd−C32 2.138(3), Pd−C33 2.137(3), Pd−C34 2.199(3), C32−C33 1.359(4), C33−C34 1.383(5); P1−C1−C2 117.2(2), C1−C2−C3 123.4(2), C2−C3−C4 124.5(2), C3−C4−C5 121.0(2), C4−C5−P1 117.5(2), C5−P1−C1 101.7(1), P1−C5−P2 117.8(1), C32−C33−C34 123.8(3); (mean plane C1−C2−C4−C5)−P1 21.7; (mean plane C1−C2−C4−C5)−C3 7.3

ted in toluene in the presence of K_2CO_3 using 0.0001 mol % of catalyst in most cases. The results are summarized in Table 3. As can be seen, the conversions obtained in the transformation of aryl bromides are acceptable: turnover numbers (TONs) fall in the range of 242000 for electron-rich arenes (4-bromoanisole) to 799000 for electron-deficient species (4-bromoacetophenone). It must be noted that no efforts were made to improve these results (solvents, role of the base). However, under the same experimental conditions (toluene at reflux), no reaction was observed with the less-reactive aryl chlorides, even when using 2.0 mol % of catalyst.



Scheme 8

Table 3. Suzuki−Miyaura reaction of aryl halides using complex **7** as catalyst; conditions: aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol) catalyst **7** (0.0001 mol % unless stated otherwise), 10 mL of toluene, 110 °C, 24 h

Entry	Substrate	Yield (%)[a]	Benzene (%)[a]	TON
1	bromobenzene	80.9[b]	5.6	80 900
2	bromobenzene	50.0	5.4	500 000
3	4-bromoanisole	43.2	8.6	432 000
4	4-bromotoluene	24.4	9.8	244 000
5	4-bromoacetophenone	79.9	9.4	799 000

[a] Yields were determined by GC. [b] 0.01 mol % of catalyst.

Conclusion

We have developed an access to a new class of ligands that features a pseudo-ylidic phosphorus atom and a P=S ancillary arm. Interestingly, this allows to show that coordination through the phosphorus atom in 1-alkylphosphininyllithium salts does not require the presence of two pendant ancillary P=S ligands. Although the catalytic activity of the (cymene)Ru derivatives in the transfer hydrogenation of ketones was found to be modest, interesting conversion yields were obtained in the Pd-catalysed synthesis of arylboronic esters from bromoarenes and phenylboronic acid. Further studies are now focusing on the synthesis of other transition-metal complexes and investigation of their catalytic properties.

Experimental Section

General Remarks: All reactions were routinely performed under argon or nitrogen with Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone, dry diethyl ether from $CaCl_2$ and then NaH, and dry CH_2Cl_2 from P_2O_5. $CDCl_3$ was dried with P_2O_5 and stored over Linde molecular sieves (4 Å). C_6D_6 was used as purchased and stored in the glovebox. $[PdCl(C_3H_5)]_2$ was purchased from Fluka. NMR spectra were recorded with a Bruker Avance 300 spectrometer operating at 300.0 MHz for ^1H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to $SiMe_4$ for ^1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are quoted relative to an 85% H_3PO_4 external reference. Coupling constants are given in Hz. Mass spectra were obtained at 70 eV with an HP 5989B spectrometer coupled to an HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. Diazaphosphinine **1**,[24] diphenyl(1-propynyl)phosphane sulfide[50] and $[RuCl_2(\eta^6\text{-}C_{10}H_{14})]_2$ [51] were prepared according to reported procedures.

Phosphinine 3: Diphenylacetylene (3.79 g, 21 mmol) was added to a solution of diazaphosphinine **1** in toluene (8×10^{-5} mol/mL, 20 mmol) and the mixture was stirred at 60 °C for 72 h. Consumption of **1** (δ = 269.0 ppm) and formation of the 5,6-diphenyl-1,2-azaphosphinine **2** (δ = 267.4 ppm) was checked by ^{31}P NMR spectroscopy. Diphenyl(1-propynyl)phosphane sulfide (3.44 g, 22 mmol) (δ = 18.8 ppm) was then added and the solution was stirred at 120 °C for 96 h. After evaporation of the solvent, the solid was washed with hexanes (3 × 20 mL) and MeOH (20 mL) and the resulting solid was dissolved in hot MeOH and stored at 0 °C. The white solid that separated was washed several times with cold MeOH (3 × 30 mL). After drying, **3** was recovered as a white solid. Yield: 6.0 g (62%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of hexanes into a solution of **3** in CH_2Cl_2. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.67 (s, CH_3), 7.00−7.98 (m, 21 H, CH of Ph and H4) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 25.4 (d, $^3J_{C,P_B}$ = 8.2, CH_3), 127.2−133.5 (m, CH of Ph), 132.9 (dd, J_{C,P_B} = 84.6, J_{C,P_A} = 5.3, C), 138.6 (vt, $^3J_{C,P_A}$ = $^3J_{C,P_B}$ = 12.8, C4H), 141.3 (s, C), 141.7 (s, C), 148.0 (dd, J_{C,P_B} = 9.1, J_{C,P_A} = 3.8, C), 149.0 (dd, J_{C,P_B} = 12.8, J_{C,P_A} = 4.5, C), 159.4 (dd, J_{C,P_B} = 76.3, J_{C,P_A} = 67.2, C), 166.2 (dd, J_{C,P_B} = 58.9, J_{C,P_A} = 14.3, C) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 42.6 (d, $^2J_{P_A,P_B}$ = 108.1, P_BPh_2), 226.7 (d, $^2J_{P_A,P_B}$ = 108.1, P_A) ppm. MS (CH_2Cl_2): *m/z* = 479 [M^+], 447 [M − S]$^+$, 416 [M − PS]. $C_{30}H_{24}P_2S$ (478.49): calcd. C 75.30, H 5.06; found C 74.97, H 4.72.

Lithium Salt 4: A solution of BuLi (0.235 mL, 1.6 M, 0.38 mmol) was added through a syringe into a solution of **3** (180 mg, 0.38 mmol) in THF (6 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. After evaporation of the solvent, the solid was washed several times with hexanes (3 × 2 mL). After drying, **4** was recovered as a red solid. Yield: 100%.^{31}P NMR (121.5 MHz, THF, 25 °C): δ = −37.6 (d, $^2J_{P_A,P_B}$ = 151.9, P_A−Bu), 42.4 (d, $^2J_{P_A,P_B}$ = 151.9, P_BPh_2).

Ruthenium Complexes 5a,b: A solution of BuLi (0.235 mL, 1.6 M, 0.38 mmol) was syringed into a solution of **3** (180 mg, 0.38 mmol) in THF (6 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. Complete formation of the lithium salt **4** was checked by ^{31}P NMR spectroscopy. In a glovebox, $[RuCl_2(cymene)]_2$ (115 mg, 0.19 mmol) was added to the solution and the solution was stirred for 1 h. After removing the solvent,

the resulting solid was dissolved in toluene and filtered through Celite. After drying, **5** was recovered as a red solid containing a mixture of two diastereoisomers (25:75). Yield: 242 mg (80%). The major diastereoisomer, which is insoluble in diethyl ether, could be obtained by washing the red solid several times with diethyl ether (3 × 10 mL). The resulting filtrate was kept at 0 °C overnight during which time the minor diastereoisomer separated as a red solution.

Major Diastereoisomer 5a: Yield: 150 mg (49%). Crystals suitable for X-ray crystallography were deposited from a solution of **5a** in C_6D_6. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.97 (d, $^3J_{H,H}$ = 7.0, 3 H, *CH*$_3$−CH of cymene), 0.97 (t, $^3J_{H,H}$ = 7.2, 3 H, CH_3 of *n*Bu), 1.17 (d, $^3J_{H,H}$ = 6.7, 3 H, *CH*$_3$−CH of cymene), 1.50−1.58 (m, 2 H, CH_2 of *n*Bu), 1.72 (s, 3 H, CH_3 of phosphinine), 1.95 (s, 3 H, Ar−*CH*$_3$ of cymene), 2.14−2.28 (m, 1 H, CH_2 of *n*Bu), 2.32−2.50 (m, 1 H, CH_2 of *n*Bu), 2.52−2.69 (m, 1 H, CH_2 of *n*Bu), 2.99−3.09 (m, 2 H, Ar−*CH* of cymene and CH_2 of *n*Bu), 3.17 (d, $^3J_{H,H}$ = 5.5, Ar−H of cymene), 3.69 (d, $^3J_{H,H}$ = 6.1, Ar−H of cymene), 4.67 (d, $^3J_{H,H}$ = 6.1, Ar−H of cymene), 5.06 (d, $^3J_{H,H}$ = 5.5, Ar−H of cymene), 5.43 (d, $^4J_{H,P}$ = 6.3, H4), 6.88−7.12 (m, 12 H, H of Ph), 7.55−7.58 (m, 2 H, H of Ph), 7.69−7.80 (m, 4 H, H of Ph), 7.88−7.95 (m, 2 H, H of Ph) ppm. ^{13}C NMR (75.5.5 MHz, C_6D_6, 25 °C): δ = 13.2 (s, CH_3 of *n*Bu), 15.4 (s, Ar−CH_3 of cymene), 18.2 (s, CH_3 of isopropyl), 22.9 (vt, $\Sigma J_{C,P}$ = 5.1, CH_3 of isopropyl), 23.6 (d, $^3J_{C,P_A}$ = 11.6, CH_2 of *n*Bu), 24.5 (s, CH_3 of phosphinine), 25.9 (d, $^2J_{C,P_A}$ = 7.5, CH_2 of *n*Bu), 29.1 (s, CH of isopropyl), 42.5 (d, $^1J_{C,P_A}$ = 19.8, P_A−CH_2), 60.0 (dd, $^1J_{C,P_A}$ = 104.9, $^1J_{C,P_B}$ = 55.9, C2), 67.5 (s, C of cymene), 75.1 (s, CH of cymene), 87.1 (s, CH of cymene), 89.1 (s, CH of cymene), 90.4 (d, $^2J_{C,P_A}$ = 9.1, CH of cymene), 94.4 (s, C of cymene), 99.3 (dd, $^1J_{C,P_A}$ = 43.8, $^3J_{C,P_B}$ = 7.6, C6), 112.6 (dd, $J_{C,P}$ = 12.8, $J_{C,P}$ = 6.8, C4H), 114.8 (d, $J_{C,P}$ = 9.1, C), 123.3−132.8 (m, CH of Ph), 134.1 (m, C), 134.7 (m, C), 141.8 (dd, $J_{C,P}$ = 15.9, $J_{C,P}$ = 2.3, C), 144.2 (d, $J_{C,P}$ = 5.3, C3), 145.1 (d, $J_{C,P}$ = 7.6, C5), 150.2 (d, $J_{C,P}$ = 1.5, C) ppm. ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): δ = 40.7 (d, $^2J_{P_A,P_B}$ = 115.5, P), 44.3 (d, $^2J_{P_A,P_B}$ = 115.5, P) ppm.

Minor Diastereoisomer 5b: Yield: 33 mg (11%). ^{1}H NMR (121.5 MHz, C_6D_6, 25 °C; selected data): δ = 0.88−2.44 (m, 25 H, Bu, *i*Pr, 3 × Me), 4.13 (d, $^3J_{H,H}$ = 6.0, Ar−H of cymene), 4.17 (d, $^3J_{H,H}$ = 5.6, Ar−H of cymene), 4.91 (d, $^3J_{H,H}$ = 6.0, Ar−H of cymene), 4.96 (d, $^3J_{H,H}$ = 5.7, Ar−H of cymene), 5.31 (d, $^4J_{H,P}$ = 5.5, H_4), 6.70−8.25 (m, 20 H, H of Ph) ppm. ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): δ = 43.4 (d, $^2J_{P_A,P_B}$ = 97.2, P), 45.9 (d, $^2J_{P_A,P_B}$ = 97.2, P). $C_{44}H_{47}ClP_2RuS$ (806.34): calcd. C 65.54, H 5.87; found C 65.22, H 5.48.

Hydrogenation of Ketones: A mixture of complexes **5a**,**b** (8 mg, 0.01 mmol, 0.5 mol %) was added to a solution of ketone (2 mmol, 1 equiv.) in KOH/2-propanol (0.1 M, 10 mL). The mixture was stirred at 80 °C for 2.5 d. The progress of the reaction was monitored by GC, mass spectrometry or ^{1}H NMR spectroscopy. The mixture was then neutralized with a saturated solution of 3 M HCl (3 mL) and $NaHCO_3$ (15 mL), and it was then extracted with dichloromethane (3 × 15 mL). The organic layers were collected and dried with $MgSO_4$ and the solvents evaporated to yield the corresponding alcohol. The alcohols were characterised by comparing their ^{1}H and ^{13}C NMR spectra with reported NMR spectroscopic data and by mass spectrometry.

Characterization of Secondary Alcohols: 4-Heptanol,[52] 1,3-diphenyl-2-propanol,[53] *syn*-2,5-dimethylcyclohexanol,[54] 1-phenylethanol,[55] diphenylmethanol,[56] 1-(*p*-bromophenyl)ethanol,[57] bis(*p*-methoxyphenyl)methanol.[58]

Lithium Salt 6: A solution of MeLi (0.235 mL, 1.6 M, 0.38 mmol) was added through a syringe into a solution of **3** (180 mg, 0.38 mmol) in THF (6 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. After evaporation of the solvent, the solid was washed several times with hexanes (3 × 2 mL). After drying, **6** was recovered as a red solid. Yield: 100%.^{31}P NMR (121.5 MHz, THF, 25 °C): δ = −46.7 (d, $^2J_{P_A,P_B}$ = 156.7, P_A−Me), 42.5 (d, $^2J_{P_A,P_B}$ = 156.7, $P_B$$Ph_2$) ppm.

Palladium Complexes 7a,**b:** A solution of MeLi (0.156 mL, 1.6 M, 0.25 mmol) was added through a syringe into a solution of **3** (120 mg, 0.25 mmol) in THF (5 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. Complete formation of the lithium salt **6** was checked by ^{31}P NMR spectroscopy. In a glovebox, $[PdCl(C_3H_5)]_2$ (44 mg, 0.12 mmol) was added to the solution and the mixture stirred for 1 h. After removing the solvent, the resulting solid was dissolved in CH_2Cl_2 and filtered through Celite. After drying, **7** was recovered as a brown solid containing a mixture of two diastereoisomers (25:75). No further purification was carried out to separate the two diastereoisomers. Crystals of **7a** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **7a**,**b** Yield: 123 mg (77%).

Major Diastereoisomer 7a: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.19 (d, $^2J_{H,P_A}$ = 8.1, 3 H, P_AMe), 1.65 (s, 3 H, Me), 2.16 (d, $^2J_{H,H}$ = 13.2, 1 H, CH_2 allyl), 2.52 (d, $^3J_{H,H}$ = 6.4, 1 H, CH_2 allyl), 3.00 (dd, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 10.4, 1 H, CH_2 allyl), 4.21 (vt, $^2J_{H,H}$ = $^3J_{H,H}$ = 6.5, 1 H, CH_2 allyl), 4.89 (m, CH allyl), 5.57 (d, $^4J_{H,P_A}$ = 5.9, H4), 7.04−8.09 (m, 20 H, H of Ph) ppm. ^{13}C NMR (75.5.5 MHz, $CDCl_3$, 25 °C): δ = 17.1 (dd, $^1J_{C,P}$ = 20.6, $^3J_{C,P}$ = 2.7, P_AMe), 25.9 (dd, $^3J_{C,P}$ = 4.2, $^3J_{C,P}$ = 3.1, Me), 55.0 (dd, $J_{C,P}$ = 111.7, $J_{C,P}$ = 54.2, C2/6), 59.6 (d, $^2J_{C,P}$ = 5.7, CH_2 allyl), 69.1 (dd, $^2J_{C,P}$ = 32.4, $^4J_{C,P}$ = 4.5, CH_2 allyl), 109.8 (dd, $J_{C,P}$ = 47.9, $J_{C,P}$ = 5.1, C2/6), 113.4 (dd, $J_{C,P}$ = 12.6, $J_{C,P}$ = 10.1, C4), 117.0 (d, $^2J_{C,P}$ = 6.4, CH allyl), 125.1−133.1 (m, CH and C of Ph), 136.9 (dd, $J_{C,P}$ = 78.1, $J_{C,P}$ = 7.2, C3/5), 143.5 (dd, $J_{C,P}$ = 8.8, $J_{C,P}$ = 2.9, C3/5), 144.4 (d, $J_{C,P}$ = 15.6, C of Ph), 145.4 (d, $J_{C,P}$ = 1.9, C of Ph) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 24.6 (d, $^2J_{P,P}$ = 135.8, P_A), 52.4 (d, $^2J_{P,P}$ = 135.8, $P_B$$Ph_2$).

Minor Diastereoisomer 7b: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.16 (br. s, 3 H, PMe), 1.65 (s, 3 H, Me), 1.72 (d, $^2J_{H,H}$ = 13.3, 1 H, CH_2 allyl), 2.90 (d, $^2J_{H,H}$ = 13.4, 1 H, CH_2 allyl), 3.18 (d, $^2J_{H,H}$ = 7.0, 1 H, CH_2 allyl), 5.01 (m, 1 H, CH allyl), 7.04−8.09 (m, 20 H, H of Ph) ppm; signals of 1 H of CH_2 allyl and H4 were not observed. ^{13}C NMR (75.5.5 MHz, $CDCl_3$, 25 °C): δ = 18.2 (dd, $^1J_{C,P}$ = 20.0, $^3J_{C,P}$ = 2.7, P_AMe), 25.9 (m, Me), 55.0 (m, C2/6), 59.1 (d, $^2J_{C,P}$ = 5.1, CH_2 allyl), 70.0 (m, CH_2 allyl), 108.7 (m, C2/6), 113.6 (dd, $J_{C,P}$ = 12.8, $J_{C,P}$ = 9.5, C4), 116.8 (d, $^2J_{C,P}$ = 6.3, CH allyl), 124.4−133.5 (m, CH and C_q of Ph), 136.2 (d, $J_{C,P}$ = 83.9, $C_{3/5}$), 143.2 (dd, $J_{C,P}$ = 11.7, $J_{C,P}$ = 3.0, C3/5), 144.2 (d, $J_{C,P}$ = 8.8, C of Ph), 145.7 (d, $J_{C,P}$ = 2.1, C of Ph) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 23.4 (d, $^2J_{P,P}$ = 132.7, P−Me), 52.0 (d, $^2J_{P,P}$ = 132.7, PPh_2) ppm. $C_{34}H_{32}P_2PdS$ (641.00): calcd. C 63.70, H 5.03; found C 63.46, H 4.81.

Suzuki−Miyaura Reaction of Aryl Halides: Catalyst **7** as a toluene solution (1.00 mL), made up to the correct concentration by multiple volumetric dilutions of a stock solution, was added to a mixture of the aryl halide (1.0 mmol), $PhB(OH)_2$ (0.183 g, 1.5 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) in toluene (10 mL). The resultant mixture was then heated at 110 °C for 24 h, cooled and quenched with HCl(aq) (2 M, 40 mL). The organic layer was removed and the aqueous layer was extracted with toluene (3 × 50 mL). The combined organic layers were washed with water, dried ($MgSO_4$), fil-

Table 4. Crystal data and structural refinement details for **3**, **5a** and **7a**

	3	**5a**	**7a**
Empirical formula	$C_{30}H_{24}P_2S$	$C_{44}H_{47}ClP_2RuS$	$C_{34}H_{32}P_2PdS$
M_r	478.49	806.34	641.00
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	6.611(5)	11.3830(10)	11.2180(10)
b [Å]	42.648(5)	22.7280(10)	12.0220(10)
c [Å]	17.464(5)	14.6770(10)	12.7300(10)
α [°]	90	90	67.8200(10)
β [°]	92.430(5)	91.5450(10)	77.4300(10)
γ [°]	90	90	69.3200(10)
V [Å^3]	4919(4)	3795.7(5)	1480.3(2)
Z	8	4	2
ρ [g cm^{-3}]	1.292	1.411	1.438
μ [cm^{-1}]	0.278	0.654	0.827
Crystal size [mm]	0.20 × 0.20 × 0.20	0.18 × 0.14 × 0.10	0.22 × 0.18 × 0.05
F(000)	2000	1672	656
Index ranges	$-8 \le h \le 8$	$-16 \le h \le 16$	$-15 \le h \le 15$
	$-55 \le k \le 57$	$-29 \le k \le 31$	$-16 \le k \le 15$
	$-23 \le l \le 23$	$-20 \le l \le 20$	$-17 \le l \le 17$
$2\Theta_{max}$ [°]	28.70	30.03	30.03
Parameters refined	597	447	360
Data/parameters	16	18	17
Reflections collected	22198	18845	18500
Independent reflections	12430	11031	8591
Reflections used	9562	8413	6275
$wR2$	0.1143	0.1046	0.0790
$R1$	0.0414	0.0377	0.0344
Goodness of fit	1.054	1.007	1.018
Largest diff peak/hole [e·Å^{-3}]	0.352(0.060)/−0.404(0.060)	0.983(0.084)/−0.932(0.084)	0.853(0.072)/−0.750(0.072)

tered and the solvent removed under reduced pressure. The residue was dissolved in toluene (6 mL), hexadecane (0.068 M in CH_2Cl_2, 1.00 mL, internal standard) was added and the conversion into product determined by GC.

Characterizations of Suzuki−Miyaura Coupling Products: The NMR spectra of the biphenyl compounds were compared with those of commercial products (Aldrich); 4-methylbiphenyl,[59] 4-methoxybiphenyl,[59] 4-acetylbiphenyl.[60]

X-ray Crystallographic Study: Crystals of **3** and **7a** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **3** and **7a**. Crystals of **5a** suitable for X-ray diffraction deposited overnight from a solution in C_6D_6. Data were collected at 150.0(1) K with a Nonius Kappa CCD diffractometer equipped with an Mo-K_α (λ = 0.71070 Å) X-ray source and a graphite monochromator, using φ and ω scans. The crystal structures were solved by using SIR 97[61] and SHELXL-97.[62] For ORTEP drawings ORTEP III for Windows was used.[63] Further details can be found in Table 4. CCDC-242764 to -242766 (for **3**, **5a** and **7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Theoretical Mmethods: All calculations were performed with the Gaussian 03 set of programs using the ONIOM method.[64] The two complexes were optimized at the ONIOM(B3LYP/UFF) level,[65] where the QM part was treated within the framework of density functional theory at the B3LYP level (B3 for Becke's three-parameter exchange functional[66] and LYP for the Lee−Yang−Parr non-local correlation functional[67]) and the UFF force field[68] was used for the molecular mechanic calculations. In all calculations (QM and QM/MM), the lanl2dz basis set was used for the ruthenium atom.[69] The 6-31+G(d) basis set was used for all atoms directly bound to the ruthenium centre (P, S, Cl atoms as well as the C atoms of the aromatic part of the cymene ligand). The C and H atoms of the phosphinine ring were calculated using the 6-31G(d) basis set. Full optimizations were realized at the ONIOM level, followed by analytical computation of the Hessian matrix to confirm the nature of the located minima on the potential energy surface. A single-point calculation was performed on the ONIOM optimized structures at the B3LYP level of theory using the 6-31G(d) basis sets for C, H, P, S, and Cl atoms and the lanl2dz basis set for Ru.

Supporting Information: See footnote on the first page of this article. Fully labelled structures of **Ia** and **Ib** and the geometrical parameters of the theoretical structures.

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