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# Phosphino-(α-sulfinylalkyl)phosphonium ylide complexes (Rh, Pd) with a configurationally stable asymmetric ylidic carbon

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Dedicated to Professor Henri Kagan on the occasion of his 80th birthday

ABSTRACT

The synthesis and structure of Rh(I) and Pd(II) complexes of chiral P,C-chelating phosphino-(α-sulfinylalkyl)phosphonium ylide ligands with a trisubstituted asymmetric ylidic center $P^+$–C*R(S*(O)*p*-Tol)–M (R = alkyl group) have been investigated, and compared to those of the analogous disubstituted ylide complexes (R = H). Reaction of the ethyl onium ylide of *o*-bis(diphenylphosphino)benzene with (−)-menthyl-(*S*)-*p*-tolylsulfinate afforded the corresponding racemic *erythro* phosphino-(α-sulfinylethyl)phosphonium in 90% de (R = Me). The racemization process is interpreted by a Berry-like pseudorotation mechanism driven by the steric repulsion between the α-methyl substituent and the bulky menthyloxy S-substituent or sulfur lone pair in the intermediate ylide-sulfinyl adduct. The ylide of phosphino-(α-sulfinylethyl)phosphonium reacts with $[Rh(cod)_2][PF_6]$ and $PdCl_2(MeCN)_2$ to afford the corresponding P,C*-chelated *threo*-Rh(I) and *erythro*-Pd(II) mononuclear complexes in 70% yield and total diastereoselectivity. These respective complexes act as efficient catalytic precursors for the hydrogenation of (*Z*)-α-acetamidocinnamic acid and allylic substitution of 3-acetoxy-1,3-diphenyl-1-propene with sodium dimethyl malonate. The bonding features of the *erythro*-Pd(II) complex exhibiting a sulfinyl O···Pd interaction are studied theoretically at the DFT level using ELF and MESP analyses. The $\eta^2$-P,C haptomeric form of the ylide ligand is estimated to compete at 19% with the $\eta^1$-C haptomeric form dominating at 81%.



## 1. Introduction

For more than 50 years, phosphonium ylides have been widely used as reactants in the Wittig olefination reaction of carbonyl compounds (aldehydes, ketones, lactones, etc.).[1] These ylides can be classified according to the olefination stereoselectivity:[2] while stabilized and salt-free non-stabilized ylides ($R_3P{=}CHZ$) lead preferentially to *trans*-olefination products,[3] non-salt-free non-stabilized ylides ($R_3P{=}CHR' + LiX$) lead to *cis*-olefination products.[4] In the '*trans*' category, the configuration of the ylidic carbon atom is quasi-planar (for $Z = CO_2R'$, even in the presence of salt with O···Li interaction) or pyramidal with a very small pyramidalization barrier of ca. 1 kcal/mol (for Z = H or alkyl group).[5] In the '*cis*' category (generated by in situ deprotonation of a phosphonium precursor $R_3P^+–CH_2R'$, $X^-$ with a lithium base),[6] the carbon center is made tetrahedral through a C···Li interaction.[7] Although free ylidic carbon centers are thus non-stereogenic (in salt-free non-stabilized ylides the rotation about the $P^+–C^-$ bond is also very small),[7] non-salt-free non-stabilized ylides are intrinsically chiral, albeit configurationally labile through exchange of the alkali cation. The configurational stability can however be enhanced by increasing the covalent character of the carbon–metal interaction (Fig. 1). This is achieved with less electropositive metal centers, such as transition metal centers $M_t$ (in the Pauling scale of electronegativity: $\chi(Li) = 1.0 \ll 1.6 \leqslant \chi(M_t) \leqslant 2.2 < 2.5 = \chi(C)$).[8]

The strength of the C→$M_t$ complexation of the neutral ylides is indeed illustrated by a rich coordination chemistry, previously reviewed by Schmidbaur.[9] All ylide complexes exhibit a $\eta^1$-$sp^3$-C-coordination mode (the $\eta^2$-P,C-coordination mode is not known), which is basically similar to the $\eta^1$-$sp^2$-C-coordination mode of the famous neutral diaminocarbene ligands.[10] This remarkable stability has been however only recently exploited in catalysis, where the coordinated ylides act as spectator ligands.[11] Most of the examples focus on asymmetric catalytic processes (hydrogenation, hydroformylation,[12] allylation,[13] and hydrosilylation,[14]) involving chiral ylide ligands with the atropochiral 1,1′-binaphthyl backbone of (*R*)- or (*S*)-binap ('binapium' ylides and 'yliphos').[15,16] As the chirality element of chiral phosphines can be located at either the backbone (e.g., in diop),[17] or the coordinating P atom (e.g., in

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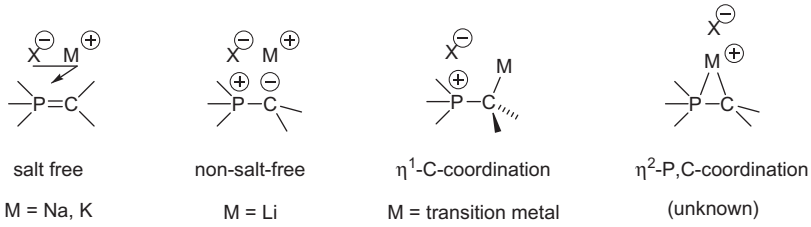


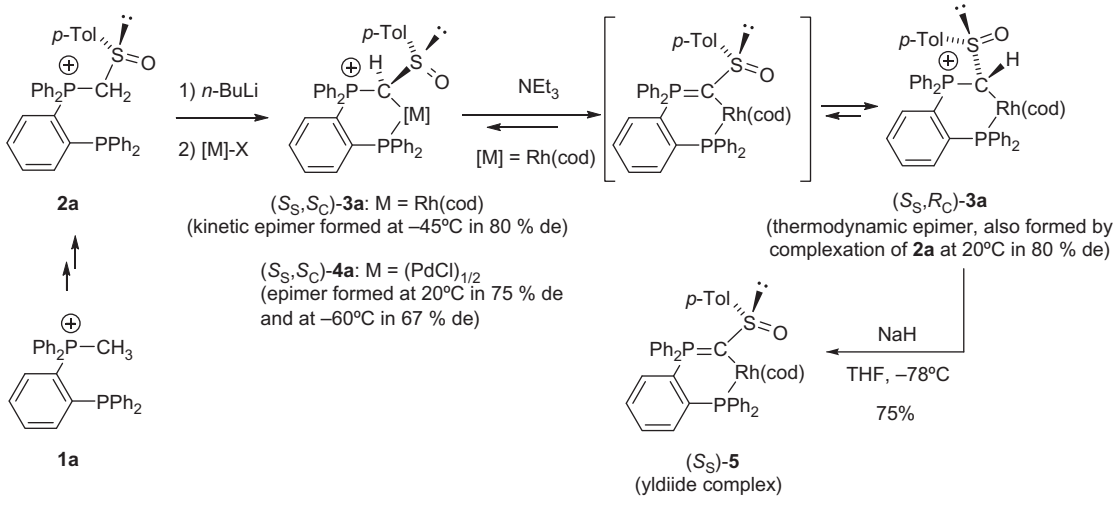

**Figure 1.** Schematic bonding typology of phosphonium ylides based on the relative electrostatic versus covalent components of interaction with neighboring metal salts. When the deprotonation of the phosphonium precursor is carried out with a sodium or potassium base, the resulting salt is insoluble and the ylide is said 'salt-free' (*left*). All X-ray crystal data of transition metal complexes of ylides indicate that the P···M distance is non-bonding (*right*).[9]

dipamp),[18] the chirality element of chiral ylide ligands can also be located not only at the backbone[12,15b,16,19] but also at the coordinating C atom. Complexes with asymmetric ylidic carbon atoms (derived from $R_3P^+$–CHR′R″ phosphoniums where R′ ≠ R″ and R,R′ ≠ $^+PR_3$) are numerous, but the first enantiomerically resolved examples have been reported in 2003 in the rhodium series,[20] and in 2004 in the palladium series.[21] These ligands are stabilized/semi-stabilized ylides of chiral (sulfinylmethyl)triarylphosphoniums,[22] based on the 1,2-bis(diphenylphosphino)benzene (*o*-dppb) core, and more precisely on Schmidbaur's phosphino-methylphosphonium **1a**.[23,15b] The chiral phosphonium precursor **2a** is stereogenic at the sulfinyl center, but not at the α-carbon atom. When treated with 1 equiv of *n*-BuLi followed with one equivalent of transition metal salt ($[Rh(cod)_2][PF_6]$ or $PdCl_2(MeCN)_2$), the resulting mononuclear complex **3a** or dinuclear complex **4a** is formed diastereoselectively at the asymmetric ylidic carbon atom.[20,21] This carbon center remains however acidic, and in the rhodium series, the kinetic diastereoisomer ($S_C$)-**3a** was shown to epimerize to the thermodynamic diastereoisomer ($R_C$)-**3a** under basic conditions.[20] The putative yldiide intermediate **5** was finally isolated after treatment of ($R_C$)-**3a** with NaH at low temperature (Scheme 1).[24]

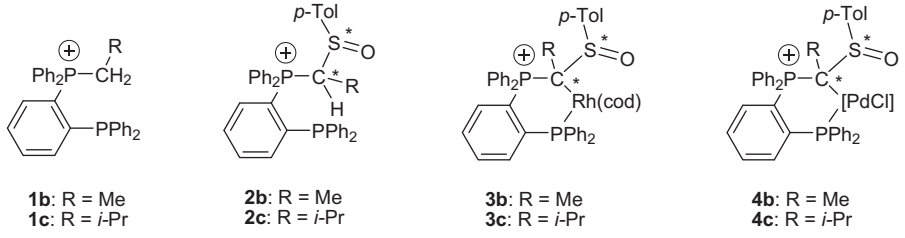
In order to prevent the stereochemical lability of the asymmetric ylidic carbon, the analogous complexes **3b–c** and **4b–c** of the ylides of phosphoniums **2b–c** were targeted (Scheme 2), where the acidic hydrogen atom of **3a** and **4a** is replaced by an alkyl group (R = Me, *i*-Pr). The results are detailed below.

## 2. Results and discussion

Two strategies for accessing ylide complexes with a resolved asymmetric trisubstituted ylidic carbon atom could be envisaged




**Scheme 1.** Coordination chemistry of chiral phosphino-(sulfinylmethyl)phosphonium ylide ligands from Rh(I) and Pd(II) precursors [M]–X = $[Rh(cod)_2][PF_6]$ or $PdCl_2(MeCN)_2$.[20,21] In the rhodium series, epimerization of the ylidic carbon center occurs through an yldiide complex **5** where this carbon atom is no longer stereogenic.[24]




**Scheme 2.** Targeted phosphonium precursors and rhodium and palladium complexes of phosphino-(α-sulfinylalkyl)phosphonium ylide ligands with a trisubstituted α-carbon center.

(Scheme 2): (i) through direct α-alkylation of the previously described complexes **3a**, **4a**, or their phosphonium precursor **2a** (with a disubstituted α-carbon atom: Scheme 1) and (ii) through α-sulfinylation of higher alkyl-phosphonium precursors **1b** or **1c** (Scheme 2).

### 2.1. Attempted α-alkylation of the (sulfinylmethyl) phosphoniums 2a and 3a

In a first approach to complex **3b** (R = Me), the yldiide rhodium complex **5** (generated by treatment of enantiomerically pure complex **3a**·$PF_6^-$ with NaH or KHMDS) was reacted with different methylating agents (MeOTf and $[Me_3O][BF_4]$). An unidentified product, exhibiting broad $^{31}P$ NMR signals at 27.4 and 20.6 ppm, could be purified by flash column chromatography, but underwent decomposition in acidic medium (slowly in $CDCl_3$ and quickly in the presence of $HBF_4$) to give another unidentified rhodium complex ($^{31}P$ NMR: $\delta$ (ppm) = 61.0 (d), $^1J_{RhP}$ = 150 Hz). Facing these difficulties which can be due to a poor regioselectivity of the alkylation reaction (four nucleophilic sites are a priori possible: C, S, O, and Rh), the phosphonium precursor **2b** was then targeted by methylation of the free ylide of phosphonium **2a**·$PF_6^-$, generated by treatment with *n*-BuLi or NaH. Different conditions using MeI and MeOTf as methylating agents were investigated, but in most cases only starting phosphonium **2a** and phosphonio-phosphine oxide **6** were observed.[23a] In one case only (NaH and MeOTf), the desired α-methylated phosphonium **2b** (later synthesized in good yield and fully characterized: see below) was obtained diastereoselectively in minute quantity and in a racemic form (Scheme 3).

### 2.2. α-Sulfinylation of alkylphosphoniums 1b–c

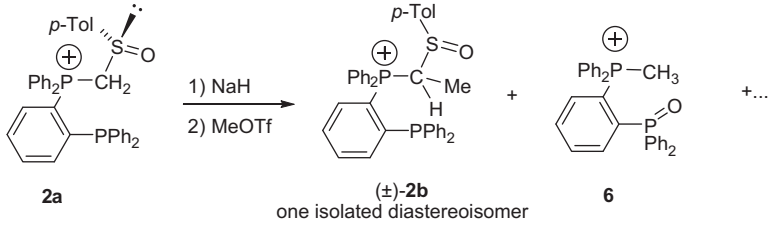
The second strategy relies on a possible α-sulfinylation of higher alkylphosphoniums **1b–c**, followed by complexation of the ylides of the resulting phosphoniums **2b–c** to rhodium or palladium centers. The alkylphosphoniums **1b–c** were first targeted by monoalkylation of *o*-dppb.

#### 2.2.1. Attempted α-sulfinylation of the *iso*-butylphosphonium 1c

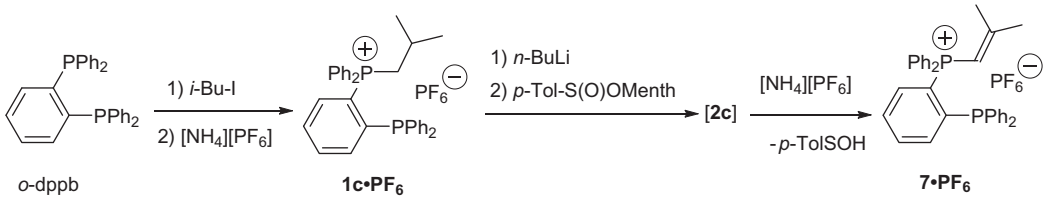
Reaction of *o*-dppb with *iso*-butyl iodide followed by anion exchange of the formed phosphonium iodide afforded *iso*-butylphosphonium **1c** ($^{31}P$ NMR: $\delta$ (ppm) = 22.51 (d) and −14.81 (d), $J_{PP+}$ = 22.3 Hz) in 90% yield. The ylide generated from **1c** by treatment with a base was then reacted with menthyl-(*S*)-*p*-tolylsulfinate, but regardless the conditions, the corresponding alkenyl phosphonium salt **7** was isolated in up to 46% yield ($^{31}P$ NMR: $\delta$ (ppm) = 11.07 (d) and −14.04 (d), $J_{PP+}$ = 32.4 Hz. Scheme 4). The steric strain of the putatively formed α-sulfinylalkylphosphonium intermediate **2c** thus likely promotes elimination of sulfenic acid to the trisubstituted phosphonioalkene **7**. A less bulky alkyl group than *iso*-butyl was therefore desired at the phosphonium center: the methylphosphonium **2b** was thus targeted.

#### 2.2.2. α-Sulfinylation of ethylphosphonium 1b

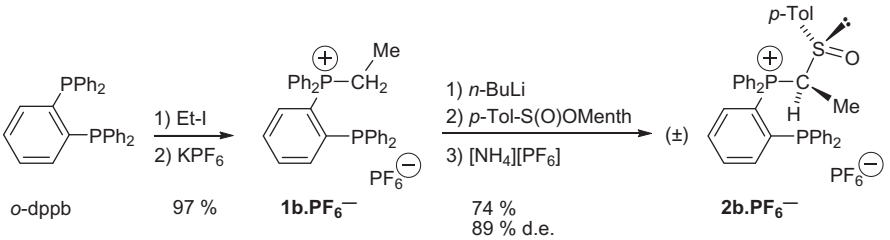
P-Ethylation of *o*-dppb was carried out by addition of ethyl iodide, and after metathesis with potassium hexafluorophosphate, the salt **1b**·$PF_6^-$ was isolated in 97% overall yield. Treatment of **1b** by a stoichiometric amount of *n*-Buli, followed by addition of




**Scheme 3.** Attempted preparation of the phosphino-(α-sulfinylethyl)phosphonium **2b** (obtained in trace amounts under the indicated conditions).




**Scheme 4.** Outcome of the attempted synthesis of (*S*)-α-sulfinylisopropylphosphonium **2c** (Scheme 2).




**Scheme 5.** Straightforward preparation of the (α-sulfinylethyl)phosphonium **2b** from *o*-ddpb.

menthyl-(*S*)-(*p*-tolyl)sulfinate afforded the sulfinylethylphosphonium **2b** in 74% yield (Scheme 5).

The $^{31}$P NMR spectrum of the crude product exhibited two systems at $\delta_P$ = 31.5, −10.3 ppm ($J_{PP}$ = 14.2 Hz) and $\delta_P$ = 30.0, −11.0 ppm ($J_{PP}$ = 20.2 Hz) in a 94.5/5.5 ratio, which were assigned to the two epimers of **2b**. The major epimer was purified by column chromatography and fully characterized by $^1$H and $^{13}$C NMR spectroscopy. In particular, the P$^+$–*CH*(*CH*$_3$)–*S*(O) protons resonate at 5.67 ppm (dq, $J_{HH}$ = 7.2 Hz, $J_{HP+}$ = 14.0 Hz) and 1.35 ppm (dd, $J_{HH}$ = 6.9 Hz, $J_{HP+}$ = 17.5 Hz). The stereochemistry of **2b** was finally assigned to the *R**,*R** (*erythro*) configuration by X-ray diffraction analysis of a single crystal (Fig. 2).[25]

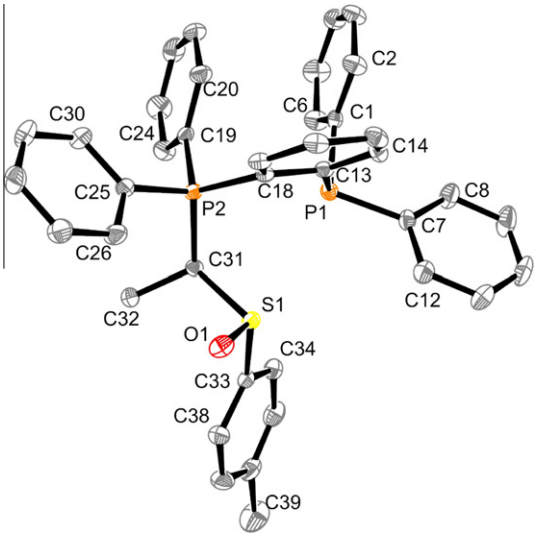



**Figure 2.** ORTEP view of the X-ray crystal structure of the ($S_S$,$S_C$)-enantiomer of the sulfinylethylphosphonium (*R**,*R**)-**2b** with thermal ellipsoids drawn at the 30% probability level (H atoms are omitted for clarity). Space group: $P^{-1}$ (triclinic), $R_1[I > 2\sigma(I)]$ = 0.0516. Selected bond distances (Å): C–Me = 1.539(4); C–P$^+$ = 1.845(3); C–S = 1.842(3); S–O = 1.489(2).[25]

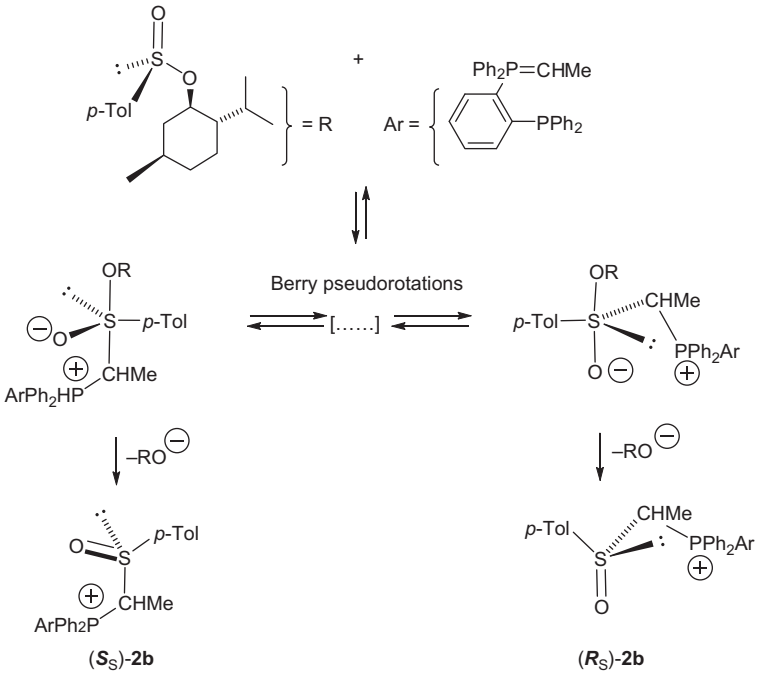
The triclinic space group ($P^{-1}$) is however achiral, and both the enantiomers ($R_S$,$R_C$)-**2b** and ($S_S$,$S_C$)-**2b** are present in the racemate crystal. Racemization was confirmed by the specific rotation of a polycrystalline sample ($[\alpha]_D^{25} = 0$). This unexpected racemization of the sulfinyl fragment can be tentatively explained by a Berry-like pseudorotation mechanism[26] of the intermediate pentacoordinated sulfurane adduct resulting from nucleophilic attack of menthyl-(*S*)-*p*-tolylsulfinate (Scheme 6).[27] In this mechanism, the steric strain specifically induced by the methyl substituent of **1b** (as compared to the unsubstituted phosphonium **1a** from which racemization does not occur[20,21]), would be the driving force of the epimerization at the sulfur center. In parallel, the control of the relative configuration of the ylidic carbon of (*R**,*R**)-**2b** in 89% de would correspond to the thermodynamic equilibrium between the racemic α-sulfinylethylphosphonium acid and the released lithium menthoxide base (Schemes 5 and 6).

## 3. Complexation of the ylide of ethylphosphonium 2b

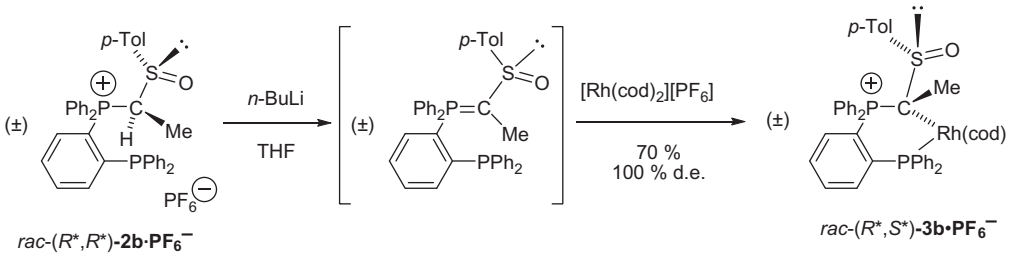
Attempts at complexation of the phosphonio-phosphine (*R**,*R**)-**2b** with [Rh(cod)$_2$]$^+$ failed to produce a stable complex, probably because of electrostatic repulsion between the cationic charges (the ethandiyl-bridged diphosphonium salt of *o*-dppb was obtained instead).[23b] By contrast, the neutral ylide of (*R**,*R**)-**2b** generated by addition of *n*-Buli in THF (detected by $^{31}$P NMR spectroscopy at $\delta$ (ppm) = −14.7 (d), +27.3 (d), $J_{PP}$ = 22 Hz, in the same range as the ylide of **2a**),[20] was expected to react with either cationic Rh(I) or neutral Pd(II) precursors to give the corresponding ylide complexes.

### 3.1. Rhodium(I) complex of the ylide of ethylphosphonium 2b

The transient ylide of *rac*-**2b** was first reacted with 0.5 equivalent of [RhCl(cod)]$_2$ in THF at room temperature to give the rhodium complex **3b** in 70% yield (Scheme 7). The $^{31}$P NMR spectrum of the reaction mixture indicated the presence of a single isomer at $\delta_P$ = 31.2 and 21.7 ppm ($J_{PP+}$ = 25.0 Hz, $J_{RhP+}$ = 8.1 Hz). The product was purified by flash column chromatography and fully




**Scheme 6.** Representative possible intermediates, interconverting via Berry pseudorotation processes, accounting for the racemization of the sulfur center during the formation of α-sulfinylethylphosphonium **2b** from menthyl-($S_S$)-*p*-tolylsulfinate and the ylide of ethylphosphonium **1b**.




**Scheme 7.** Complexation reaction of the ylide of *rac*-(α-sulfinylethyl)phosphonium **2b** at a 'soft' Rh(I) fragment.

characterized. The $^{1}$H NMR signal of the methyl group is slightly deshielded at 1.63 ppm (d, $J_{HP+}$ = 19.5 Hz), compared to the starting phosphonium **2b** at 1.35 ppm (see above). The stereochemistry of complex **3b** was unambiguously assigned to the (*R**,*S**) (*threo*) configuration by X-ray diffraction analysis of a single crystal (Fig. 3).[25] It shows that the rhodium center entered the same side from which the proton was abstracted by the base. The diastereoselectivity of the complexation process (100% de) is thus induced by the sulfinyl moiety: it is qualitatively identical to the 90:10 diastereoselectivity (80% de) of the formation, at 20 °C, of the analogous Rh(I) complex ($S_S$,$R_C$)-**3a** from optically pure α-disubstituted methylphosphonium **2a** (Scheme 1).[20]

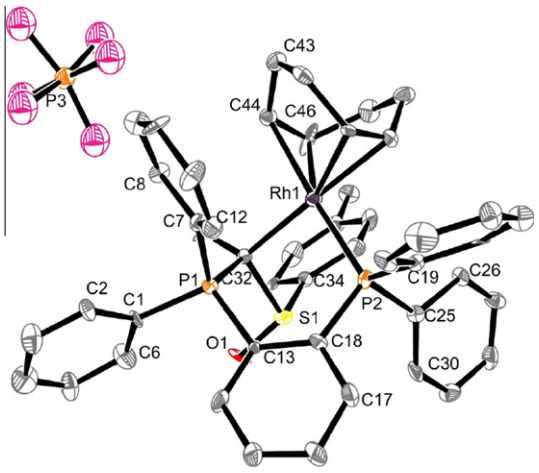



**Figure 3.** ORTEP view of the X-ray crystal structure of the ($S_S$,$R_C$)-enantiomer of the *threo* rhodium complex salt (*R**,*S**)-**3b**·$PF_6^-$, with thermal ellipsoids drawn at the 30% probability level (H atoms are omitted for clarity). Space group: $P_{21,21,21}$ (orthorhombic), $R_1[I > 2\sigma(I)] = 0.0849$. Selected bond distances (Å): C–Me = 1.552(14), MeC–P$^+$ = 1.818(12), MeC–S = 1.864(13), Rh–CMe = 2.231(11), S–O = 1.497(8).[25]

### 3.2. Palladium(II) complex of the ylide of ethylphosphonium 2b

The transient ylide of *rac*-**2b** was then treated with a stoichiometric amount of $PdCl_2(MeCN)_2$ in THF. As previously observed in the rhodium series, the corresponding complex **4b** was obtained as a single isomer ($^{31}$P NMR: $\delta_P$ = 26.3 and 19.3 ppm, $J_{PP+}$ = 30.6 Hz) in 70% yield (Scheme 8).

The stereochemistry of **4b** was assigned to the (*R**,*R**) configuration by X-ray diffraction analysis of a single crystal (Fig. 4),[25] showing that the palladium center entered the opposite side from which the proton was abstracted from (*R**,*R**)-**2b**.

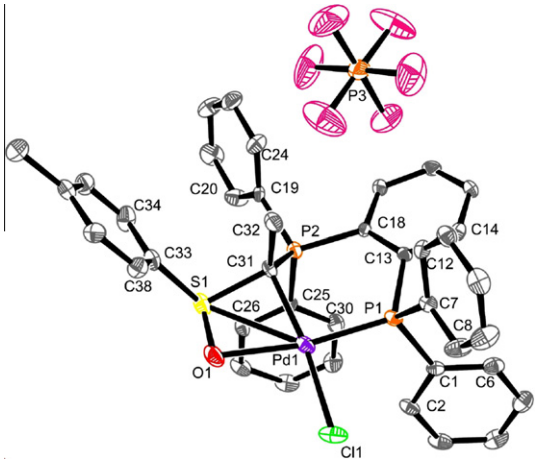
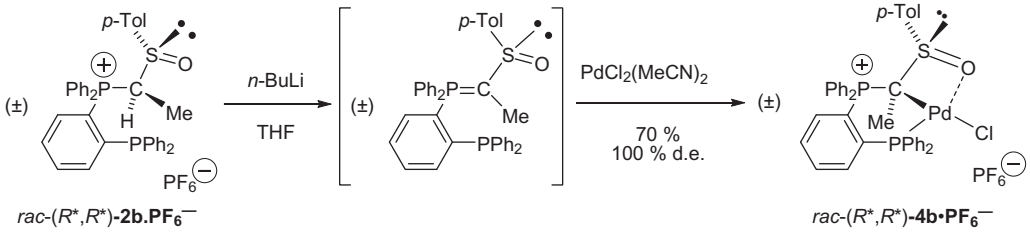



**Figure 4.** ORTEP view of the X-ray crystal structure of the ($S_S$,$S_C$)-enantiomer of the *erythro* palladium complex salt (*R**,*R**)-**4b**·$PF_6^-$, with thermal ellipsoids drawn at the 30% probability level (H atoms are omitted for clarity). Space group: $P_{21/n}$ (monoclinic), $R_1[I > 2\sigma(I)] = 0.0532$. Selected bond distances (Å): C–Me = 1.542(6), MeC–P$^+$ = 1.792(5), MeC–S = 1.818(5), Pd–CMe = 2.072(5), Pd–O = 2.162(3), Pd–S = 2.7243(16), S–O = 1.565(4).[25]

The total *erythro* diastereoselectivity of the complexation process leading to (*R**,*R**)-**4b** is thus qualitatively identical to the diastereoselectivity of the formation of the analogous Pd(II) complex ($S_S$,$S_C$)-**4a** from enantiomerically pure α-disubstituted methylphosphonium **2a** (Scheme 1).[21] The diastereoselectivity is also opposite to the *threo* diastereoselectivity observed in the formation of the rhodium complex (*R**,*S**)-**3b** (see above). This difference might be related to the stabilizing interaction occurring between the sulfinyl oxygen atom and the 'hard' Pd(II) center of **4b** (in contrast, the




**Scheme 8.** Complexation of the ylide of *rac*-α-sulfinylethylphosphonium **2b** at a 'hard' Pd(II) fragment.

Rh(I) center of **3b** can be classified as 'soft'). This interaction indeed provides the mononuclear **2b**-$PdCl_2$ complex **4b** with a formal 16-valence electron count (this count was fulfilled by μ–chloro bridges in the dinuclear [**2a**-$PdCl_2$]$_2$ complex ($S_S$,$S_C$)-**4a**: see Scheme 1).[21] The unusual bonding features of **4b** are analyzed in detail below.

### 3.3. Analysis of electrostatic versus covalent interactions in the α-sulfinyl-ylide-Pd(II) complex 4b

The S–O bond of (*R**,*R**)-**4b** (≈1.565 Å) is strongly elongated as compared to the S–O bond of the free ligand **2b** (≈1.489 Å), and falls in the 1.50–1.60 Å range of previously reported O-bonded or $\eta^2$-S,O-bonded transition metal sulfinyl complexes.[28] In a related Pd-sulfinyl complex, the sulfinyl O-coordination has been claimed to be preferred to the alternative free sulfinyl arrangement that would result in electronic repulsion between the sulfur lone pair and the filled non-bonding $d_z^2$ orbital of the palladium atom.[28c]

AIM atomic charges[29] of the Pd complex ($S_C$,$S_C$)-**4b** have been calculated at the B3PW91/6-31G*/DZVP(Pd) level on the crystal geometry. They reveal a one-electron polarization of the S–O bond and a residual positive charge at the Pd atom (Fig. 5). Considering the quite long Pd···O distance (longer by 0.1 Å than the Pd–C distance), this charge separation suggests a strong electrostatic component of the Pd···O interaction. Recently, a related sulfinyl-Pd interaction was reported in the lowest energy transition state (denoted as **5-SN2**) of the nucleophilic substitution-determining step in a Suzuki–Miyaura cross-coupling reaction (Fig. 5).[30] On the basis of natural population analysis (NPA), the Pd-sulfinyl interaction was claimed to be of electrostatic nature and to be responsible for the stabilization of the transition state. Although ($S_C$,$S_C$)-**4b** and **5-SN2** have not been studied at the same DFT level, the geometry and atomic charges appear to be similar in both complexes (Fig. 5). These hybrid DFT calculations, which essentially differ in basis set, can thus be qualitatively compared to support a strong electrostatic component of the Pd-sulfinyl interaction.

Metal-ligand bonding in (*R**,*R**)-**4b** was further investigated using the topological electron localization function (ELF).[31] ELF analysis is indeed particularly suited for the discrimination between electrostatic and covalent interactions because it provides a selective criterion of covalent bonding through the occurence of disynaptic basins and corresponding attractors. Moreover ELF populations are also much less sensitive to the level of calculation than NBO analysis. The populations of ELF valence basins in the Pd coordination sphere of ($S_C$,$S_C$)-**4b** are shown in Figure 6.

The zero atomic contribution of Pd (namely the contribution of the corresponding AIM basin) to the disynaptic ELF valence basin V(S,O) of the S–O bond confirms the absence of a three-center π-interaction between the sulfinyl ligand and the Pd atom (the Pd···S distance of ca. 2.724 Å is indeed non-bonding: see Fig. 5). This disynaptic character is supported not only by the negligible surface

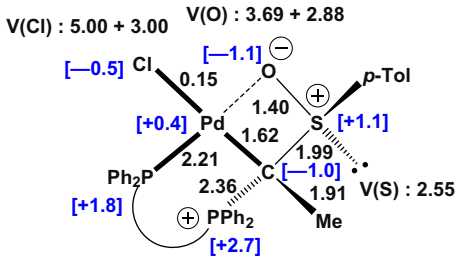



**Figure 6.** Scaled populations of selected ELF valence basins of complex ($S_C$,$S_C$)-**4b**. AIM charges in square brackets. B3PW91/6-31G*/DZVP(Pd) level of calculation.

area in common with the border of the Pd ELF basin but also by the formal 'core' character of the Pd ELF basin: the latter indeed contains the 4*d* OA population, which actually corresponds to valence electrons of a Pd(II) center (the so-called V(O) and V(Cl) basins of oxygen and chlorine lone pairs also appear formally 'disynaptic' through their large common borders with the Pd basin). This situation is clearly visible on the ELF basin partition map (Fig. 7), where the white Pd basin and the green disynaptic V(S,O) basin have a negligible common border anyway. A two-center Pd···O interaction can therefore be envisioned.

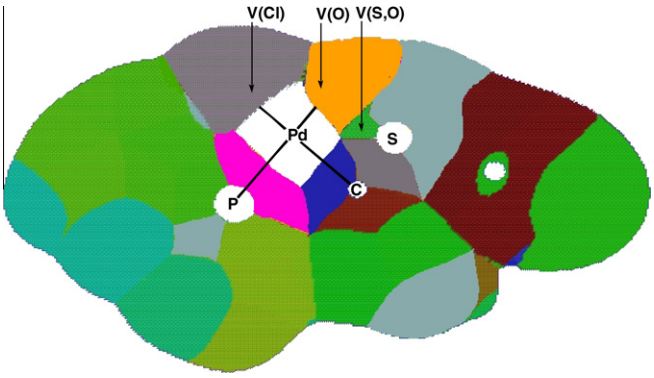



**Figure 7.** ELF basins partition map in the plane containing the palladium, sulfur and ylide carbon nuclei of complex ($S_C$,$S_C$)-**4b**. Core basins are highlighted in white. The 'monosynaptic' valence basins of chlorine and oxygen atoms are highlighted in gray and orange color, respectively (the corresponding core basins are hidden below the mapping plane). The 'disynaptic' valence basin of the S–O bond is colored in green. B3PW91/6-31G*/DZVP(Pd) level of calculation.

The absence of valence attractor between the palladium and oxygen core basins (Fig. 7), and the negligible atomic contribution of Pd to the monosynaptic valence basins of oxygen V(O) indicate that the Pd···O interaction is of electrostatic nature. This is supported by the AIM charge values (Fig. 6), showing that the S–O

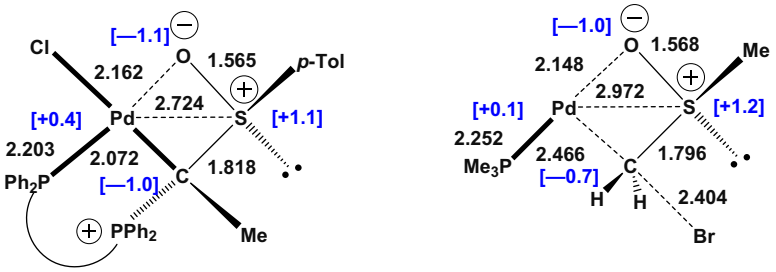



**Figure 5.** Selected experimental geometrical data (in the crystal state: see Fig. 4) and calculated AIM atomic charges (in square brackets) of the Pd complex ($S_C$,$S_C$)-**4b** at the B3PW91/6-31G*/DZVP(Pd) level (*left*). Calculated geometry and NPA charges of the analogous transition state **5-SN2** of Ref. 30 at the B3LYP/6-31+G(d,p)/SDD(Pd) level (*right*). Bond distances in Å.

bond is strongly polarized ($q_O = -q_S = -1.1$ e; $q_{Pd} = +0.4$ e). This is also in line with the analogous interaction observed in the transition state of Ref. 30 (see above). The very low population of the disynaptic basin V(Pd,Cl) is also in favor of a mostly ionic Pd–Cl bond (Fig. 6).

Beyond the $S^+\cdots O^-\cdots Pd^+\cdots Cl^-$ electrostatic interactions evidenced above, the global ionic character of the bonding in complex (*R**,*R**)-**4b** can be finally appraised by the molecular electrostatic potential (MESP), generated by the molecular charge distribution:[32]

$$V(r) = \sum_A \frac{Z_A}{|r - R_A|} - \int \frac{\rho(r')}{|r - r'|} d^3r'$$

where $Z_A$ are the nuclear charges, $R_A$ the position of the nuclei, and $\rho(r)$ the electron density.

The topological analysis of the MESP, proposed by Gadre et al.,[33] is a highly valuable tool for exploring the reactive sites of a molecule as well as their relative strengths. The minima of the MESP indicate localization of electron density and the most favorable sites for electrophilic attack, whereas the MESP textured on isodensity surfaces is convenient for exploring the regions of positive MESP and finding the most favorable sites for nucleophilic attack. Such a surface is shown in Figure 8 for the Pd complex (*R**,*R**)-**4b**. This plot shows that the most positive MESP regions (in blue) are located at the P and S nuclei, whereas the most negative MESP values (in red) are obtained at the lone pairs of the chlorine and oxygen atoms, thus illustrating the conclusion of ELF analysis.

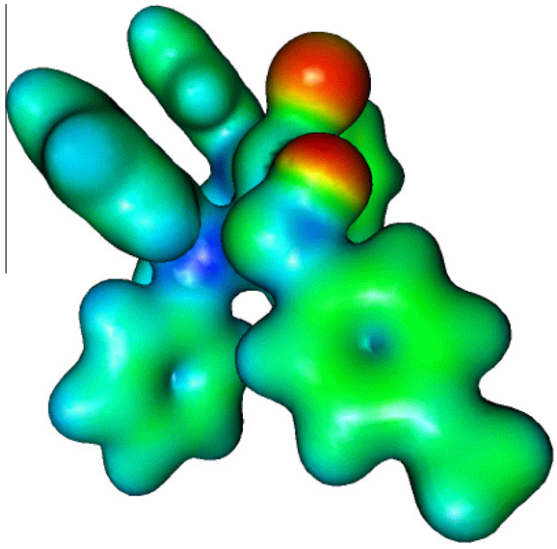


**Figure 8.** Isodensity surface (0.02 a.u.) color-coded with the MESP of the phosphonium ylide-Pd(II) complex ($S_C$,$S_C$)-**4b**. Color scale: red MESP <0.0; yellow MESP = 0.05; green MESP = 0.10; light-blue MESP = 0.20; dark-blue MESP >0.35.

### 3.4. Relevance of the $\eta^2$-P,C 'haptomeric' form in phosphonium ylide complexes

As emphasized in the introduction, the $\eta^2$-P,C coordination mode of phosphonium ylide is not known (Fig. 1). Although free ylides are classically described by two resonance structures ($R_3P^+-{}^-CHR' \leftrightarrow R_3P=CHR'$), only the zwitterionic one thus prefigures the generally assigned $\eta^1$-C 'haptomeric' form.[34] In a prebonding analysis however, the contribution of the apolar phosphoraalkene structure raises the question of the—anyway minor—exact contribution of the $\eta^2$-P,C haptomeric form. This question is quantitatively addressed for the ylide-Pd(II) complex (*R**,*R**)-**4b** from the above-described ELF analysis. As an alternative to the valence bond (VB) method for weighting resonance on the basis of the electronic wave functions,[35] the populations of the ELF valence basins can indeed be used for weighting resonance on the basis of electron density.[36] The meaning of the ELF mesomeric forms (based on the observable electron density) is however more direct (or crude) than that of VB resonance structures. In particular, as the π orbital of the P=C double bond results from the overlap of a $2p_C$ AO with a combination of the $\sigma^*_{P-C}$ localized MOs, the hypervalent resonance structure $R_3P{=}CHR'$ should be replaced by the zwitterionic structure $R^-,R_2P^+{=}CHR'$. This structure may also be invoked as a complementary ELF mesomeric form in the description of free ylides.[24] In the Pd complex (*R**,*R**)-**4b** however, the three P–C bonds are equivalent in terms of length (1.800, 1.801, 1.798 Å) and scaled ELF population (2.37). Contributions of the corresponding all-octet forms $Ph^-,Ph_2P^+{=}C$ cannot account for the calculated P–C populations higher than 2.0, and are therefore discarded from the present analysis.

Calculations show that the ELF populations of the disynaptic basins V(Pd,ylidicC) and V(P, ylidicC) of **4b** (Fig. 6) are in reliable agreement with the description of Figure 9, where the weight of the minor $\eta^2$-P,C haptomeric remains sizeable (19%), as compared to the $\eta^1$-C form (81%). Lower contributions of 6% and 11% of this $\eta^2$-P,C haptomeric form were found from ELF analysis of models of the ($S_S$,$R_C$)-**3a** rhodium phosphonium ylide complex and corresponding ($S_S$)-**5** yldiide complex, respectively.[24] To the best of our knowledge, the $\eta^2$-P,C 'haptomeric' form is suggested here for the first time on the basis of the valuable tool of ELF analysis, and might deserve to be investigated by alternative methods.

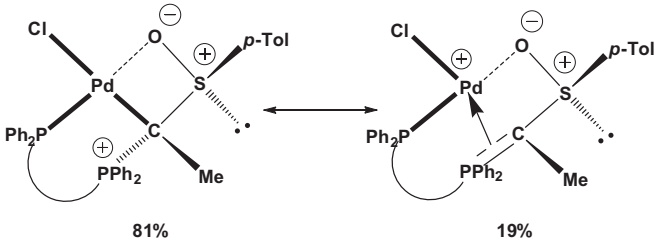



**Figure 9.** Weighted resonance forms for the description of the phosphonium ylide–Pd(II) interaction in complex ($S_C$,$S_C$)-**4b**. The weights were obtained from ELF analysis of Figure 6.[36]

## 4. Conclusion

The results show that chiral transition metal complexes (Rh(I) and Pd(II)) of (α-sulfinylethyl)phosphonium ylide ligands bearing an asymmetric trisubstituted ylidic carbon atom are chemically and configurationally stable. In spite of the racemization occurring during the complexation process, the configuration of these asymmetric ylidic centers is totally controlled by the stereogenic sulfinyl substituent. The racemic rhodium complex (*R**,*S**)-**3b** was shown to be active at a 1% catalytic ratio in the hydrogenation of (*Z*)-α-acetamidocinnamic acid (89% yield after 72 h under 15 bar $H_2$: see Experimental section). This activity is thus similar to that of the corresponding rhodium complex ($S_S$,$R_C$)-**3a** with an epimerizable ylidic center.[20] The racemic palladium complex (*R**,*R**)-**4b** was also shown to be active at a 4% catalytic ratio in allylic substitution of 3-acetoxy-1,3-diphenyl-1-propene with sodium dimethyl malonate (99% yield after 16 h at room temperature: see experimental section). The enantioselectivity of the catalysts **3b** and **4b** with a non-epimerizable asymmetric ylidic center now deserves to be investigated after achievement of their optical resolution (e.g., by semi-preparative chiral HPLC techniques).

Beyond the chemical and stereochemical results, joint experimental–theoretical insights have gained into the bonding features of phosphonium ylide ligands. ELF and MESP analyses show that electrostatics plays an important role in governing the structure of the highly polar Pd(II) complex (*R**,*R**)-**4b**. On the basis of ELF weighting of resonance in complex **4b**, a $\eta^2$-P,C haptomeric form is suggested for the first time to contribute significantly to the coordination mode of phosphonium ylide ligands (up to ca. 20%, versus 80% for the $\eta^1$-C haptomeric form).

## 5. Experimental

### 5.1. General remarks

THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane, dichloromethane, and acetonitrile over $CaH_2$. All other reagents were used as commercially available. All reactions were carried out under argon atmosphere, using schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70–200 μm). The following analytical instruments were used. $^1$H, $^{13}$C and $^{31}$P NMR: Bruker ARX 250, DPX 300, AV 500. NMR chemical shifts $\delta$ are in parts per million (ppm), with positive values to high frequency relative to the tetramethylsilane reference for $^1$H and $^{13}$C and to $H_3PO_4$ for $^{31}$P.

#### 5.1.1. [2-(Diphenylphosphino)phenyl](ethyl) diphenylphosphonium iodide 1b·I$^-$

To 1,2-bis(diphenylphosphino)benzene (2.7 g, 6.0 mmol) was added ethyl iodide (29.0 g, 0.186 mmol) and the mixture was stirred for 16 h at room temperature. Excess of ethyl iodide was evaporated under reduced pressure and the residue was washed with diethyl ether (7 mL). To remove the remaining ethyl iodide, the crude product was dissolved in dichloromethane (10 mL), the solvent was evaporated, and the residue was dried under reduced pressure (100 °C/0.005 mmHg) for 3 h. Yield: 3.60 (99%), mp = 196 °C. $^{31}$P NMR ($CDCl_3$, 293 K): $\delta$ 26.92 (d, $J_{PP+}$ = 22.6 Hz, *P+*), −14.95 (d, $J_{PP+}$ = 22.7 Hz, *P*). $^{13}$C NMR ($CDCl_3$, 293 K): $\delta$ 142.89 (dd, $J_{CP}$ = 19.0 Hz, $J_{CP+}$ = 11.3 Hz), 139.14 (d, $J_{CP+}$ = 10.9 Hz), 136.99 (dd, $J_{CP+}$ = 12.2 Hz, $J_{CP}$ = 10.0 Hz), 135.07 (d, $J_{CP+}$ = 2.9 Hz), 134.45 (d, $J_{CP+}$ = 2.9 Hz), 133.54 (d, $J_{CP}$ = 6.9 Hz), 133.27 (dd, $J_{CP+}$ = 9.7 Hz, $J_{CP}$ = 2.5 Hz), 132.96 (d, $J_{CP}$ = 19.0 Hz), 131.70 (d, $J_{CP+}$ = 12.3 Hz), 130.19 (d, $J_{CP+}$ = 12.6 Hz), 129.45, 128.84 (d, $J_{CP}$ = 7.2 Hz), 124.87 (dd, $J_{CP+}$ = 86.8 Hz, $J_{CP}$ = 35.6 Hz), 119.40 (dd, $J_{CP+}$ = 86.2 Hz, $J_{CP}$ = 3.0 Hz), 20.17 (dd, $J_{CP+}$ = 52.2 Hz, $J_{CP}$ = 13.3 Hz, *C*$H_2$), 8.09 (d, $J_{CP+}$ = 5.1 Hz, *C*$H_3$). $^1$H NMR ($CDCl_3$, 293 K): $\delta$ 8.02–7.95 (m, 1H), 7.82–7.72 (m, 6H), 7.65–7.59 (m, 2H), 7.54–7.47 (m, 5H), 7.32–7.27 (m, 2H), 7.21 (dt, $J_{HH}$ = 7.5 Hz, $J_{HP}$ = 1.6 Hz, 4H), 6.86–6.80 (m, 4H), 3.88 (dq, $J_{HH}$ = 7.5 Hz, $J_{HP+}$ = 15.0, 2H, C$H_2$), 1.35 (dt, $J_{HH}$ = 7.5 Hz, $J_{HP+}$ = 20.2 Hz, 3H, C$H_3$). IR (KBr): 3041, 2979, 2871, 2794, 1478, 1434, 1112, 996, 771, 749, 738, 718, 694 cm$^{-1}$. FAB-MS *m/z* (relative intensity): 475 (100), 369 (13). HRMS calcd for $C_{32}H_{29}OP_2^+$ 475.1738, found 475.1745. Anal. Calcd for $C_{32}H_{29}IP_2$: C, 63.80; H, 4.85; P, 10.28. Found: C, 63.71; H, 4.71; P, 10.20.

#### 5.1.2. [2-(Diphenylphosphino)phenyl](ethyl) diphenylphosphonium hexafluorophosphate 1b·$PF_6^-$

[2-(Diphenylphosphino)phenyl](ethyl)diphenylphosphonium iodide **1b**·I$^-$ (0.674 g, 1.12 mmol) in dichloromethane (50 mL) was vigorously stirred with saturated solution of potassium hexafluorophosphate (0.8 g, 4.3 mmol) in water (6 mL) for 30 min. The organic layer was separated and the procedure was repeated using the same amount of saturated aqueous solution of potassium hexafluorophosphate (0.8 g, 4.3 mmol). The layers were separated and the organic one was dried over $MgSO_4$. Evaporation of the solvent gave [2-(diphenylphosphino)phenyl]-(ethyl)diphenylphosphonium hexafluorophosphate **1b**·$PF_6^-$ as a white solid. Yield: 0.675 g (97%), mp 148–149 °C. $^{31}$P NMR ($CDCl_3$, 293 K): $\delta$ 26.53 (d, $J_{PP+}$ = 22.6 Hz, *P+*), −14.65 (d, $J_{PP+}$ = 22.6 Hz, *P*), −144.18 (septet, $J_{PF}$ = 712.9 Hz, $PF_6^-$). $^{13}$C NMR ($CDCl_3$, 293 K): $\delta$ 143.02 (dd, $J_{CP+}$ = 11.4 Hz, $J_{CP}$ = 18.8 Hz), 139.18 (d, $J_{CP+}$ = 11.5 Hz), 136.49 (dd, $J_{CP+}$ = 11.9 Hz, $J_{CP}$ = 10.0 Hz), 135.11 (d, $J_{CP+}$ = 2.9 Hz), 134.59 (d, $J_{CP+}$ = 2.9 Hz), 133.46 (d, $J_{CP}$ = 6.7 Hz), 133.00 (d, $J_{CP}$ = 19.1 Hz), 132.97 (dd, $J_{CP+}$ = 9.0 Hz, $J_{CP}$ = 2.2 Hz), 131.54 (d, $J_{CP+}$ = 12.4 Hz), 130.25 (d, $J_{CP+}$ = 12.6 Hz), 129.51, 128.88 (d, $J_{CP}$ = 7.3 Hz), 124.79 (dd, $J_{CP+}$ = 87.0 Hz, $J_{CP}$ = 35.8 Hz), 119.29 (dd, $J_{CP+}$ = 86.3 Hz, $J_{CP}$ = 2.8 Hz), 19.21 (dd, $J_{CP+}$ = 53.3 Hz, $J_{CP}$ = 15.0 Hz, *C*$H_2$), 7.84 (dd, $J_{CP+}$ = 5.3 Hz, $J_{CP}$ = 1.3 Hz, *C*$H_3$). $^1$H NMR ($CDCl_3$, 293 K): $\delta$ 7.83–7.65 (m, 3H), 7.66–7.60 (m, 6H), 7.56–7.49 (m, 5H), 7.34–7.29 (m, 2H), 7.27–7.22 (m, 4H), 6.90–6.84 (m, 4H), 3.57 (dq, $J_{HH}$ = 7.4 Hz, $J_{HP+}$ = 12.7 Hz, 2H, C$H_2$), 1.37 (dt, $J_{HH}$ = 7.5 Hz, $J_{HP+}$ = 20.2 Hz, 3H, C$H_3$). IR (KBr): 3054, 2984, 1436, 1114, 840, 694 cm$^{-1}$. FAB-MS *m/z* (relative intensity): 475 (100), 397 (5), 369 (16), 183 (17). HRMS calcd for $C_{32}H_{29}P_2^+$ 475.1745, found 475.1745. Anal. Calcd for $C_{32}H_{29}F_6P_3$: C, 61.94; H, 4.71; F, 18.37; P, 14.98. Found: C, 61.90; H, 4.77; P, 15.18.

#### 5.1.3. [2-(Diphenylphosphino)phenyl](*iso*-butyl) diphenylphosphonium hexafluorophosphate 1c·$PF_6^-$

To 1,2-bis(diphenylphosphino)benzene (0.48 g, 1.08 mmol) was added iodo-2-methylpropane (3.2 g, 17.4 mmol) in DMF (4 mL) and the mixture was stirred for 12 h at 80 °C. After evaporation of the solvent under vacuum, the crude residue was extracted with $CH_2Cl_2$ (10 mL) and the organic layer was washed with $H_2O$ (20 mL). The resulting salt dissolved in $CH_2Cl_2$ (50 mL) was then vigorously stirred with a saturated solution of potassium hexafluorophosphate (1.0 g, 5.4 mmol) in water (20 mL) for 30 min. The organic layer was separated and the procedure was repeated using the same amount of saturated aqueous solution of potassium hexafluorophosphate. The layers were separated and the organic one was dried over $Na_2SO_4$. After filtration, evaporation of the solvent gave [2-(diphenylphosphino)phenyl](*iso*-butyl)diphenylphosphonium hexafluorophosphate **1c**·$PF_6^-$ as a white solid. Yield: 0.63 g (90%). $^{31}$P NMR ($CD_2Cl_2$, 293 K): $\delta$ 22.51 (d, $J_{PP+}$ = 22.3 Hz, *P+*), −14.81 (d, $J_{PP+}$ = 22.3 Hz, *P*), −144.44 (septet, $J_{PF}$ = 710.9 Hz, $PF_6^-$). $^{13}$C NMR ($CD_2Cl_2$, 293 K): $\delta$ 143.10 (dd, $J_{CP+}$ = 12.6 Hz, $J_{CP}$ = 20.1 Hz), 139.70 (d, $J_{CP+}$ = 11.3 Hz), 135.90 (dd, $J_{CP+}$ = 11.3 Hz, $J_{CP}$ = 10.1 Hz), 135.11 (d, $J_{CP+}$ = 2.5 Hz), 134.64 (d, $J_{CP+}$ = 2.5 Hz), 133.43 (d, $J_{CP}$ = 6.3 Hz), 133.06 (dd, $J_{CP+}$ = 10.1 Hz, $J_{CP}$ = 2.5 Hz), 133.00 (d, $J_{CP}$ = 20.1 Hz), 131.18 (d, $J_{CP+}$ = 12.6 Hz), 130.14 (d, $J_{CP+}$ = 12.5 Hz), 129.54, 128.84 (d, $J_{CP}$ = 7.5 Hz), 125.75 (dd, $J_{CP+}$ = 86.8 Hz, $J_{CP}$ = 35.2 Hz), 119.69 (dd, $J_{CP+}$ = 85.6 Hz, $J_{CP}$ = 2.5 Hz), 33.06 (dd, $J_{CP+}$ = 47.8 Hz, $J_{CP}$ = 13.8 Hz, *C*$H_2$), 25.23 (dd, $J_{CP+}$ = 5.0 Hz, $J_{CP}$ = 2.5 Hz, *C*H), 23.96 (d, $J_{CP+}$ = 8.8 Hz, *C*$H_3$). $^1$H NMR ($CD_2Cl_2$, 293 K): $\delta$ 7.87–7.77 (m, 3H), 7.72–7.61 (m, 7H), 7.57–7.53 (m, 4H), 7.39–7.36 (m, 2H), 7.31–7.27 (m, 4H), 6.94–6.90 (m, 4H), 3.46 (dd, $J_{HH}$ = 6.6 Hz, $J_{HP+}$ = 13.1 Hz, 2H, C$H_2$), 2.19 (m, 1H, C*H*), 1.05 (dd, $J_{HH}$ = 6.7 Hz, $J_{HP+}$ = 1.1 Hz, 6H, C$H_3$).

#### 5.1.4. [2-(Diphenylphosphino)phenyl][1′-(*p*-tolylsulfinyl)ethyl] diphenylphosphonium hexafluorophosphate 2b·$PF_6^-$

To a stirred suspension of [2-(diphenylphosphino)phenyl](ethyl)diphenylphosphonium hexafluorophosphate **1b**·$PF_6^-$ (1.57 g, 2.53 mmol) in diethyl ether (130 mL) at −30 °C was added a solution of *n*-BuLi (1.01 mL of 2.5 M solution in hexane, 2.53 mmol). The cooling bath was removed, and the mixture was allowed to warm to room temperature. After 30 min the mixture was cooled to −5 °C and (*S*)-(−)-menthyl *p*-toluenesulfinate (0.41 g, 1.4 mmol) in diethyl ether (40 mL) was added. After stirring for 10 min at −5 °C and 30 min at room temperature a precipitate of [2-(diphenylphosphino)phenyl](ethyl)diphenylphosphonium hexafluorophosphate

was filtered off, and the reaction was quenched with a solution of ammonium hexafluorophosphate (1.5 g, 9 mmol) in THF (40 mL) at −78 °C. Then the solvents were evaporated under reduced pressure, water was added (40 mL), and the mixture was extracted with $CH_2Cl_2$ (3 × 40 mL). The organic layer was dried over $Na_2SO_4$. The solvent was evaporated, and the crude product was purified by flash column chromatography using dichloromethane–acetone (40:1) as the eluent. Yield: 0.79 g (74%), de = 89%, mp 114–123 °C (dec.). Major isomer: $^{31}$P NMR ($CDCl_3$, 213 K): $\delta$ 31.49 (d, $J_{PP+}$ = 14.2 Hz, *P+*), −10.28 (d, $J_{PP+}$ = 14.2 Hz, *P*), −144.47 (septet, $J_{PF}$ = 713.8 Hz, $PF_6^-$). $^{13}$C NMR ($CDCl_3$, 213 K): $\delta$ 143.64 (dd, $J_{CP}$ = 12.2 Hz, $J_{CP+}$ = 12.2 Hz), 143.34, 139.25 (d, $J_{CP+}$ = 11.6 Hz), 138.15 (dd, $J_{CP}$ = 10.7 Hz, $J_{CP+}$ = 10.7 Hz), 135.95, 135.77, 135.57, 135.35 (d, $J_{CP+}$ = 10.9 Hz), 134.98 (d, $J_{CP}$ = 3.7 Hz), 134.20 (d, $J_{CP}$ = 20.6 Hz), 134.12 (d, $J_{CP+}$ = 11.3 Hz), 133.93 (d, $J_{CP+}$ = 10.1 Hz), 132.04 (d, $J_{CP}$ = 14.8 Hz), 131.75 (d, $J_{CP+}$ = 12.6 Hz), 131.03, 130.83 (d, $J_{CP+}$ = 13.0 Hz), 130.37 (d, $J_{CP+}$ = 9.8 Hz), 130.27, 129.45 (d, $J_{CP+}$ = 15.3 Hz), 129.39, 129.20 (d, $J_{CP}$ = 5.6 Hz), 129.08 (d, $J_{CP}$ = 8.8 Hz), 124.55, 123.31 (dd, $J_{CP+}$ = 83.7 Hz, $J_{CP}$ = 36.6 Hz), 116.46 (d, $J_{CP+}$ = 85.8 Hz), 114.85 (d, $J_{CP+}$ = 85.1 Hz), 54.19 (dd, $J_{CP+}$ = 47.1 Hz, $J_{CP}$ = 19.6 Hz, $P^+CH$), 22.01 ($C_6H_4CH_3$), 9.17 (d, $J_{CP}$ = 3.5 Hz, $P^+CHCH_3$). $^1$H NMR ($CDCl_3$, 213 K): $\delta$ 8.62–8.53 (m, 1H), 8.03–7.96 (m, 1H), 7.94–7.78 (m, 4H), 7.73 (t, $J_{HH}$ = 6.6 Hz, 1H), 7.68–7.62 (m, 1H), 7.60–7.48 (m, 4H), 7.46 (t, $J_{HH}$ = 7.4 Hz, 1H), 7.40 (d, $J_{HH}$ = 8.1 Hz, 2H), 7.36–7.30 (m, 2H), 7.26 (t, $J_{HH}$ = 7.1 Hz, 2H), 7.18 (t, $J_{HH}$ = 7.1 Hz, 2H), 7.04 (dd, $J_{HH}$ = 7.4 Hz, $J_{HP}$ = 7.4 Hz, 2H), 6.87 (dd, $J_{HH}$ = 8.1 Hz, $J_{HP}$ = 8.1 Hz, 2H), 6.77–6.63 (m, 2H), 6.55 (dd, $J_{HH}$ = 7.6 Hz, $J_{HP+}$ = 13.3 Hz, 1H), 5.67 (dq, $J_{HH}$ = 7.2 Hz, $J_{HP+}$ = 14.0 Hz, 1H, $P^+CHCH_3$), 2.42 (s, 3H, $CH_3C_6H_4$), 1.35 (dd, $J_{HH}$ = 6.9 Hz, $J_{HP+}$ = 17.5 Hz, 3H). IR (KBr): 3056, 2924, 1482, 1438, 1185, 1108, 1088, 1045, 839, 724, 691 cm$^{-1}$. FAB-MS *m/z* (relative intensity): 613 (44), 473 (44), 397 (100), 369 (16). HRMS calcd for $C_{39}H_{35}OP_2S^+$ 613.1884, found 613.1884. Anal. Calcd for $C_{39}H_{35}F_6OP_3S$: C, 61.74; H, 4.65; P, 12.25. Found: C, 61.62; H, 4.70; P, 12.31.

### 5.1.5. Rhodium(I) complex salt 3b·$PF_6^-$

To a stirred solution of [2-(diphenylphosphino)phenyl][1′-(*p*-tolylsulfinyl)ethyl]diphenylphosphonium hexafluorophosphate **2b**·$PF_6^-$ (100 mg, 0.132 mmol) in THF (8 mL) at −30 °C was added *n*-BuLi (57 μL of 2.3 M solution in hexane, 0.132 mmol). The cooling bath was removed, and the mixture was allowed to warm to room temperature. After 15 min, bis(1,5-cyclooctadiene) rhodium(I) hexafluorophosphate (70 mg, 0.152 mmol) was added and stirring was continued for additional 3 h. The solvent was evaporated and a crude mixture was purified by flash column chromatography (dichloromethane–acetone gradient) to give complex **3b** as an orange solid. Yield: 87 mg (70%), de = 100% (only 1 diastereomer), mp 139–144 °C (dec.). $^{31}$P NMR ($CDCl_3$, 273 K): $\delta$ 31.25 (dd, $J_{PP+}$ = 25.0 Hz, $J_{RhP+}$ = 8.1 Hz, *P+*), 21.67 (dd, $J_{PP+}$ = 25.0 Hz, $J_{PRh}$ = 154.8 MHz, *P*), −144.24 (septet, $J_{PF}$ = 712.6 Hz, $PF_6^-$). $^1$H NMR ($CDCl_3$, 273 K): $\delta$ 9.26 (dd, $J_{HH}$ = 8.4 Hz, $J_{HP+}$ = 11.3 Hz, 1H), 7.97 (t, $J_{HH}$ = 7.5 Hz, 1H), 7.86 (t, $J_{HH}$ = 7.6 Hz, 1H), 7.81–7.73 (m, 5H), 7.72–7.66 (m, 2H), 7.65–7.50 (m, 5H), 7.48–7.38 (m, 2H), 7.37–7.26 (m, 6H), 7.20–7.13 (m, 4H), 6.40 (dd, $J_{HH}$ = 8.2 Hz, $J_{HP+}$ = 11.4 Hz, 1H), 4.95–4.87 (m, 1H, cod-C*H*), 3.86–3.76 (m, 2H, cod-C*H*), 3.74–3.68 (m, 1H, cod-C*H*), 2.36 (s, 3H, $C_6H_4CH_3$), 2.40–2.18 (m, 2H, cod-$CH_2$), 2.21–1.68 (m, 6H, cod-$CH_2$), 1.63 (d, $J_{HP+}$ = 19.5 Hz, 3H, $P^+CCH_3$). $^{13}$C NMR ($CDCl_3$, 273 K): $\delta$ 141.99, 138.52 (d, $J_{CP+}$ = 8.4 Hz), 138.44 (d, $J_{CP+}$ = 12.5 Hz), 137.15–136.85 (m, 2C), 136.08 (dd, $J_{CP+}$ = 7.1 Hz, $J_{CP}$ = 35.9 Hz), 135.89 (d, $J_{CP+}$ = 10.0 Hz), 135.34 (dd, $J_{CP+}$ = 2.7 Hz, $J_{CP}$ = 4.9 Hz), 135.11 (d, $J_{CP+}$ = 2.7 Hz), 133.81 (d, $J_{CP+}$ = 2.7 Hz), 133.14 (d, $J_{CP}$ = 13.0 Hz), 133.06 (d, $J_{CP}$ = 11.2 Hz), 132.37 (dd, $J_{CP+}$ = 11.9 Hz, $J_{CP}$ = 1.3 Hz), 132.13 (d, $J_{CP+}$ = 8.8 Hz), 131.37 (d, $J_{CP}$ = 45.4 Hz), 131.24 (d, $J_{CP}$ = 1.8 Hz), 131.12 (d, $J_{CP}$ = 1.9 Hz), 130.43 (d, $J_{CP+}$ = 12.4 Hz), 130.05 (d, $J_{CP}$ = 43.6 Hz), 129.91 (d, $J_{CP+}$ = 9.2 Hz), 129.67 (d, $J_{CP+}$ = 12.7 Hz), 129.39 (d, $J_{CP}$ = 9.5 Hz), 129.06 (d, $J_{CP}$ = 9.9 Hz), 128.89, 127.23, 124.83 (dd, $J_{CP+}$ = 82.2 Hz, $J_{CP}$ = 19.8 Hz), 123.78 (d, $J_{CP+}$ = 97.2 Hz), 120.85 (dd, $J_{CP+}$ = 67.4 Hz, $J_{CP}$ = 1.6 Hz), 104.35 (dd, $J_{CRh}$ = 8.2 Hz, $J_{CP}$ = 8.2 Hz, cod-C*H*), 98.58 (dd, $J_{CRh}$ = 7.4 Hz, $J_{CP}$ = 9.8 Hz, cod-C*H*), 89.92 (d, $J_{CRh}$ = 8.7 Hz, cod-C*H*), 87.12 (d, $J_{CRh}$ = 8.7 Hz, cod-C*H*), 40.57 (ddd, $J_{CRh}$ = 24.9 Hz, $J_{CP}$ = 7.7 Hz, $J_{CP+}$ = 16.9 Hz, $P^+CRh$), 31.04 (cod-$CH_2$), 30.51 (d, $J_{CP}$ = 3.4 Hz, cod-$CH_2$), 29.37 (d, $J_{CP}$ = 2.4, cod-$CH_2$), 28.66 (cod-$CH_2$), 21.54 ($CH_3C_6H_4$), 13.67 ($P^+CCH_3$). IR (KBr): 3057, 2921, 1436, 1090, 1028, 841, 744, 695, 558 cm$^{-1}$. FAB-MS *m/z* (relative intensity): 823 (16), 715 (23), 684 (15), 549 (40), 369 (20), 154 (100). HRMS calcd for $C_{47}H_{46}OP_2RhS^+$ 823.1820, found 823.1793. Anal. Calcd for $C_{47}H_{46}F_6OP_3RhS$: C, 58.27; H, 4.79; P, 9.59. Found: C, 58.305; H, 4.71, P, 9.64.

### 5.1.6. Palladium(II) complex salt 4b·$PF_6^-$

To a stirred solution of [2-(diphenylphosphino)phenyl][1′-(*p*-tolylsulfinyl)ethyl]diphenylphosphonium hexafluorophosphate (150 mg, 0.2 mmol) **2b** in THF (8 mL) at −30 °C was added *n*-BuLi (83 μL of 2.4 M solution in hexane, 0.2 mmol). The cooling bath was removed, and the mixture was allowed to warm to room temperature. After 15 min bis(acetonitrile)dichloropalladium(II) (52 mg, 0.22 mmol) was added and stirring was continued for additional 3 h. The solvent was evaporated and a crude mixture was purified by flash column chromatography (dichloromethane–acetonitrile gradient) giving complex **4b** as a yellow solid. Yield: 87 mg (70%), de = 100% (only 1 diastereomer), mp: 141–143 °C (dec.). $^{31}$P NMR ($CD_2Cl_2$, 293 K): $\delta$ 26.32 (d, $J_{PP+}$ = 30.6 Hz, *P+*), 19.33 (d, $J_{PP+}$ = 30.5 Hz, *P*), −144.47 (septet, $J_{PF}$ = 710.8 Hz, $PF_6^-$). $^1$H NMR ($CD_2Cl_2$, 293 K): $\delta$ 8.23 (ddd, $J_{HH}$ = 8.3 Hz, $J_{HP+}$ = 1.2 Hz, $J_{HP}$ = 13.8, 2H), 8.05–7.95 (m, 4H), 7.77 (ddt, $J_{HH}$ = 7.6 Hz, $J_{HP+}$ = 0.7 Hz, $J_{HP}$ = 3.6 Hz, 2H), 7.71–7.62 (m, 2H), 7.59–7.38 (m, 12H), 7.31–7.22 (m, 4H), 6.72 (br d, $J_{HH}$ = 6.1 Hz, 2H), 2.43 (s, 3H, $C_6H_4CH_3$), 1.63 (dd, $J_{HP+}$ = 3.7 Hz, $J_{HP}$ = 16.7 Hz, 3H, $CH_3$). $^{13}$C NMR ($CD_2Cl_2$, 293 K): $\delta$ 145.81, 137.82 (dd, $J_{CP+}$ = 3.3 Hz, $J_{CP}$ = 8.8 Hz), 137.03 (dd, $J_{CP+}$ = 8.3 Hz, $J_{CP}$ = 10.4 Hz), 135.97 (d, $J_{CP}$ = 2.9 Hz), 135.92 (dd, $J_{CP+}$ = 6.0 Hz, $J_{CP}$ = 2.6 Hz), 135.40 (d, $J_{CP}$ = 3.1 Hz), 134.77 (d, $J_{CP+}$ = 12.0 Hz), 134.10 (d, $J_{CP}$ = 9.8 Hz), 133.86 (d, $J_{CP}$ = 10.2 Hz), 133.85 (d, $J_{CP}$ = 12.0 Hz), 133.30 (d, $J_{CP+}$ = 11.9 Hz), 132.48 (d, $J_{CP+}$ = 3.1 Hz), 132.27 (d, $J_{CP+}$ = 3.0 Hz), 132.08 (d $J_{CP}$ = 2.0 Hz), 131.08 (d, $J_{CP}$ = 12.1 Hz), 130.96 (dd, $J_{CP+}$ = 40.7 Hz, $J_{CP}$ = 6.4 Hz), 130.83, 130.64 (d, $J_{CP}$ = 12.9 Hz), 129.27 (d, $J_{CP+}$ = 12.5 Hz), 129.09 (d, $J_{CP+}$ = 12.2 Hz), 128.45 (d, $J_{CP+}$ = 62.8 Hz), 124.29, 123.80 (d, $J_{CP+}$ = 61.4 Hz), 122.70 (dd, $J_{CP+}$ = 12.3 Hz, $J_{CP}$ = 91.7 Hz), 118.81 (dd, $J_{CP+}$ = 2.7 Hz, $J_{CP}$ = 75.9 Hz), 118.38 (d, $J_{CP}$ = 95.8 Hz), 21.48 ($C_6H_4CH_3$), 20.06 (dd, $J_{CP+}$ = 5.4 Hz, $J_{CP}$ = 54.4 Hz, $P^+CPd$), 15.20 ($P^+CCH_3$). IR (KBr): 3057, 2923, 1438, 1100, 841, 746, 691 cm$^{-1}$. FAB-MS *m/z* (relative intensity): 755 (5), 473 (20), 307 (16), 154 (100). Anal. Calcd for $C_{39}H_{34}ClF_6OP_3PdS$: C, 52.07; H, 3.81; P, 10.33. Found: C, 52.21; H, 3.88; P, 10.20.

### 5.1.7. [2-(Diphenylphosphoryl)ethyl]triphenylphosphonium hexafluorophosphate 6·$PF_6^-$

[2-(Diphenylphosphino)phenyl][1′-(*p*-tolylsulfinyl)ethyl]diphenylphosphonium hexafluorophosphate **2a**·$PF_6^-$ (70 mg, 0.092 mmol) in THF (4 mL) was heated at 50 °C for 66 h. The solvent was evaporated and the crude mixture was purified by column chromatography (dichloromethane–methanol gradient) to give [2-(diphenylphosphoryl)ethyl]triphenylphosphonium hexafluorophosphate **6** as a white solid. Yield: 35 mg (60%), mp 237 °C. $^{31}$P NMR ($CD_3CN$, 293 K): $\delta$ 29.5 (d, $J_{PP+}$ = 50.7 Hz, *P*), 25.5 (d, $J_{PP+}$ = 50.7 Hz, *P+*), −144.5 (septet, $J_{PF}$ = 706.5 Hz, $PF_6^-$). $^1$H NMR ($CD_3CN$, 293 K): $\delta$ 7.92–7.86 (m, 3H), 7.75–7.66 (m, 16H), 7.65–7.60 (m, 2H), 7.57–7.52 (m, 4H), 3.47–3.37 (m, 2H, P(O)$CH_2$), 2.65–2.55 (m, 2H, $CH_2$P+). $^{13}$C NMR ($CD_3CN$, 293 K): $\delta$ 135.36 (d,

$J_{CP+}$ = 3.0 Hz), 133.84 (d, $J_{CP+}$ = 10.1 Hz), 132.43 (d, $J_{CP}$ = 2.7 Hz), 131.28 (d, $J_{CP}$ = 100.3 Hz), 130.75 (d, $J_{CP}$ = 9.6 Hz), 130.34 (d, $J_{CP+}$ = 12.7 Hz), 128.98 (d, $J_{CP}$ = 11.9 Hz), 117.50 (d, $J_{CP+}$ = 86.8 Hz), 21.91 (dd, $J_{CP}$ = 66.7 Hz, $J_{CP+}$ = 4.5 Hz), 15.43 (d, $J_{CP+}$ = 53.8 Hz). IR (KBr): 3060, 2928, 1439, 1185, 1123, 838, 691 $cm^{-1}$. FAB-MS *m/z* (relative intensity): 491 (100), 289 (60), 147 (48). HRMS calcd for $C_{32}H_{29}OP_2^+$ 491.1694, found 491.1694. Anal. Calcd for $C_{32}H_{29}F_6OP_3$: C, 60.39; H, 4.59; P, 14.60. Found: C, 60.42; H, 4.70; P, 14.72.

### 5.1.8. 2-(Diphenylphosphino)phenyl](2′-methylpropen-1′-yl)diphenylphosphonium hexafluorophosphate 7·$PF_6^-$

2-(Diphenylphosphino)phenyl](*iso*-butyl)diphenylphosphonium hexafluorophosphate **1c**·$PF_6^-$ (0.15 g, 0.23 mmol) was dissolved in $Et_2O$ (30 mL). After treatment with *n*-BuLi (0.103 mL of 2.5 M solution in hexane, 0.256 mmol) at −60 °C, the reaction mixture was allowed to warm to room temperature. After addition of a solution of (−)-menthyl-(*S*)-*p*-toluenesulfinate (34 mg, 0.115 mmol) in $Et_2O$ (5 mL) at −60 °C, the solution was stirred at room temperature for 30 min. After filtration, the reaction was quenched by addition of a solution of $NH_4PF_6$ in THF. After evaporation of the solvent, the crude product was purified by column chromatography ($CH_2Cl_2$/acetone gradient). Recrystallization of the dried residue from THF with a few drops of $Et_3N$ afforded phosphonium **7** as a white solid. Yield: 34 mg (46%). $^{31}P$ NMR ($CD_2Cl_2$, 293 K): $\delta$ 11.07 (d, $J_{PP+}$ = 32.4 Hz, *P+*), −14.04 (d, $J_{PP+}$ = 32.4 Hz, *P*), −144.36 (septet, $J_{PF}$ = 710.9 Hz, $PF_6^-$). $^{13}C$ NMR ($CD_2Cl_2$, 293 K): $\delta$ 169.13 (dd, $J_{CP+}$ = 1.3 Hz, $J_{CP}$ = 5.0 Hz), 142.45 (dd, $J_{CP+}$ = 11.3 Hz, $J_{CP}$ = 18.9 Hz), 139.33 (d, $J_{CP+}$ = 11.3 Hz), 136.33 (dd, $J_{CP+}$ = 12.6 Hz, $J_{CP}$ = 8.8 Hz), 136.95 (d, $J_{CP+}$ = 2.5 Hz), 134.46 (d, $J_{CP+}$ = 2.5 Hz), 134.06 (d, $J_{CP}$ = 8.8 Hz), 133.10 (d, $J_{CP}$ = 20.1 Hz), 133.07 (dd, $J_{CP+}$ = 10.1 Hz, $J_{CP}$ = 1.3 Hz), 131.46 (d, $J_{CP+}$ = 12.6 Hz), 130.44 (d, $J_{CP+}$ = 12.6 Hz), 129.65, 128.96 (d, $J_{CP}$ = 6.3 Hz), 126.69 (dd, $J_{CP+}$ = 90.6 Hz, $J_{CP}$ = 35.2 Hz), 121.18 (dd, $J_{CP+}$ = 90.6 Hz, $J_{CP}$ = 1.3 Hz), 104.70 (dd, $J_{CP+}$ = 91.8 Hz, $J_{CP}$ = 8.8 Hz), 29.02 (d, $J_{CP+}$ = 18.9 Hz, *C*$H_3$), 24.28 (d, $J_{CP+}$ = 7.5 Hz, *C*$H_3$). $^1H$ NMR ($CD_2Cl_2$, 293 K): $\delta$ 7.84–7.80 (m, 1H), 7.74–7.71 (m, 3H), 7.69–7.55 (m, 10H), 7.39–7.37 (m, 2H), 7.33–7.28 (m, 4H), 6.98–6.94 (m, 4H), 6.26 (dd, $J_{HP}$ = 3.3 Hz, $J_{HP+}$ = 22.5 Hz, 1H, C*H*), 1.84 (d, $J_{HP}$ = 2.3 Hz, 3H, C$H_3$), 1.55 (pseudo t, $J_{HP}$ = $J_{HP+}$ = 2.4 Hz, 3H, C$H_3$). FAB-MS *m/z* 501 $[M]^+$.

### 5.1.9. Hydrogenation of (*Z*)-α-acetamidocinnamic acid catalyzed by (*R**,*S**)-3b

To a mixture of (*Z*)-α-acetamidocinnamic acid (0.1 g, 0.49 mmol) and racemic rhodium complex (*R**,*S**)-**3b** (4.7 mg, 0.005 mmol, 1 mol %) was added methanol (4 mL), and the mixture was stirred under a 15 bar of hydrogen for 72 h. The solution was evaporated to dryness. The conversion determined by $^1H$ NMR spectroscopy was 89%.

### 5.1.10. Allylic substitution of 3-acetoxy-1,3-diphenylpropene by dimethyl malonate catalyzed by (*R**,*R**)-4b

To a stirred solution of the racemic complex (*R**,*R**)-**4b** (10 mg, 0.011 mmol) in THF (4 mL) at −78 °C, allylmagnesium bromide (11 μl of 1 M solution in diethyl ether, 0.011 mmol) was added. After 20 min, 3-acetoxy-1,3-diphenyl-1-propene (70 mg, 0.275 mmol) in THF (2 mL) was added, and the reaction mixture was allowed to warm to room temperature. A THF solution of an anion generated from dimethyl malonate (0.54 mg, 0.41 mmol) and NaH (9.8 mg, 0.41 mmol) was transferred to the reaction mixture and the stirring was continued for additional 16 h. After a usual workup the yield determined by $^1H$ NMR was 99%.

### 5.2. Computational details

AIM[29] and ELF[31] analyses of the experimental structure of the Pd(II) complex ($S_C$,$S_C$)-**4b** of the phosphino-(sulfinylethyl)phosphonium ylide ligand were performed with the TOPMOD program[37] at the B3PW91/6-31G*/DZVP(Pd)[38] level of calculation.[39]

The gas phase molecular electrostatic potential (MESP) was computed for the experimental geometries at the same level as mentioned above using GAUSSIAN03.[39] Visualization of the isodensity surfaces colour coded with the MESP was performed using Molden.[40]

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### References

1. Wittig, G.; Schöllkopf, U. *Ber. Dtsch. Chem. Ges.* **1954**, *87*, 1318–1330.
2. Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863–927.
3. Robiette, R.; Richardson, J.; Aggarwal, V. K.; Harvey, J. N. *J. Am. Chem. Soc.* **2006**, *128*, 2394–2409.
4. Bestmann, H. J.; Vostrowsky, O. *Top. Curr. Chem.* **1983**, *109*, 85–163.
5. Bachrach, S. M. *J. Org. Chem.* **1992**, *57*, 4367–4373.
6. Barnhardt, R. G., Jr.; McEwen, W. E. *J. Am. Chem. Soc.* **1967**, *89*, 7009–7014.
7. Armstrong, D. R.; Davidson, M. G.; Moncrieff, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 478–481.
8. Pauling, L. *Nature of the Chemical Bond*; Cornell University Press, 1960.
9. (a) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907; (b) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1; (c) Belluco, U.; Michelin, R. A.; Mozzon, M.; Bertani, R.; Facchin, G.; Zanotto, L.; Pandolfo, L. *J. Organomet. Chem.* **1998**, *557*, 37; (d) Bricklebank, N.. In *Organophosphorus Chemistry*; The Royal Society of Chemistry, 1999; Vol. 29. Chapter 6; (e) Urriolabeitia, E. P. *Dalton Trans.* **2008**, *42*, 5673; (f) Canac, Y.; Lepetit, C.; Abdalilah, M.; Duhayon, C.; Chauvin, R. *J. Am. Chem. Soc.* **2008**, *130*, 8406–8413.
10. (a) Canac, Y.; Lepetit, C.; Chauvin, R. In *Transition Metal Complexes of Neutral η1-Carbon Ligands*; Canac, Y., Chauvin, R., Eds.; Topics in Organomet. Chem.; Springer: Berlin/Heidelberg, 2010; 30, pp 1–12; (b) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612; (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.
11. For few early examples, see: (a) Grey, R. A.; Anderson, L. R. *Inorg. Chem.* **1977**, *16*, 3187; (b) Alexander, K.; Starzewsky, O.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 599; (c) Canac, Y.; Duhayon, C.; Chauvin, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6313–6315.
12. Ohta, T.; Fujii, T.; Kurahashi, N.; Sasayama, H.; Furukawa, I. *Sci. Eng. Rev. Doshisha Univ.* **1998**, *39*, 133. C.A.130: 139441r.
13. Ohta, T.; Sasayama, H.; Nakajima, O.; Kurahashi, N.; Fujii, T.; Furukawa, I. *Tetrahedron: Asymmetry* **2003**, *14*, 537.
14. Canal, C.; Lepetit, C.; Soleilhavoup, M.; Chauvin, R. *Afinidad* **2004**, *61*, 298–303.
15. (a) Leglaye, P.; Donnadieu, B.; Brunet, J.-J.; Chauvin, R. *Tetrahedron Lett.* **1998**, *39*, 9179–9182; (b) Viau, L.; Lepetit, C.; Commenges, G.; Chauvin, R. *Organometallics* **2001**, *20*, 808–810.
16. Canac, Y.; Chauvin, R. *Eur. J. Inorg. Chem.* **2010**, *16*, 2325–2335.
17. Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429–6433.
18. Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946–5952.
19. Abdellah, I.; Debono, N.; Canac, Y.; Duhayon, C.; Chauvin, R. *Dalton Trans.* **2009**, 7196–7202.
20. Zurawinski, R.; Donnadieu, B.; Mikolajczyk, M.; Chauvin, R. *Organometallics* **2003**, *22*, 4810–4817.
21. Zurawinski, R.; Donnadieu, B.; Mikolajczyk, M.; Chauvin, R. *J. Organomet. Chem.* **2004**, *689*, 380–386.
22. Mikolajczyk, M.; Perlikowska, W.; Omelanczuk, J.; Cristau, H.-J.; Peyraud-Darcy, A. *J. Org. Chem.* **1998**, *63*, 9716.
23. (a) Bowmaker, G. A.; Herr, R.; Schmidbaur, H. *Chem. Ber.* **1983**, *116*, 3567; (b) Abdalilah, M.; Zurawinski, R.; Canac, Y.; Laleu, B.; Lacour, J.; Lepetit, C.; Magro, G.; Bernadinelli, G.; Donnadieu, B.; Duhayon, C.; Mikolajczyk, M.; Chauvin, R. *Dalton Trans.* **2009**, 8493–8508.
24. Zurawinski, R.; Lepetit, C.; Canac, Y.; Mikolajczyk, M.; Chauvin, R. *Inorg. Chem.* **2009**, *48*, 2147–2155.

25. CCDC 773289 (**2b**), CCDC 773287 (**3b**), and CCDC-773288 (**4b**) 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.
26. Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933–938.
27. Mikolajczyk, M. *Phosphorus Sulfur* **1986**, *27*, 31–42.
28. (a) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1978**, *17*, 2134; (b) Alcock, N. W.; Brown, J. M.; Evans, P. L. *J. Organomet. Chem.* **1988**, *356*, 233; (c) Leung, P.-H.; Quek, G. H.; Lang, H.; Liu, A. M.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1639; (d) Kung, I.; Schweitzer, D.; Shearer, J.; Taylor, W. D.; Jackson, H. L.; Lovell, S.; Kovacs, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 8299.
29. Bader, R. F. W. *Atoms in Molecules*; Clarendon Press: Oxford, UK, 1990.
30. Gourlaouen, C.; Ujaque, G.; Lledos, A.; Medio-Simon, M.; Asensio, G.; Maseras, F. *J. Org. Chem.* **2009**, *74*, 4049.
31. (a) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5379; (b) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.
32. (a) Sorocco, E.; Tomasi, J. *Adv. Quantum Chem.* **1978**, *11*, 116; (b) Sorocco, E.; Tomasi, J. In *Chemical Applications of Atomic and Molecular Electrostatic potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; (c) Politzer, P.; Murray, J. S. *Theor. Chem. Acc.* **2002**, *108*, 134.
33. (a) Gadre, S. R.; Kulkarni, S. A.; Shrivastava, I. H. *J. Chem. Phys.* **1992**, *96*, 5253; (b) Gadre, S. R.. In Leczynski, J., Ed.; Comp. Chem., Reviews in Current Trends; World Scientific: Singapore, 2000; Vol. 4, p 1; (c)*Electrostatics of Atoms and Molecules*; Gadre, S. R., Shirsat, R. N., Eds.; Universities Press: Hyderabad, India, 2000.
34. Chauvin, R. *Eur. J. Inorg. Chem.* **2000**, 577–591.
35. *A Chemist Guide to Valence Bond Theory*; Shaik, S. S., Hiberty, P. C., Eds.; Wiley-Interscience, 2007.
36. (a) Lepetit, C.; Silvi, B.; Chauvin, R. *J. Phys. Chem. A* **2003**, *107*, 464; (b) Silvi, B. *Phys. Chem. Chem. Phys.* **2004**, *6*, 256.
37. Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. *Comput. Chem.* **1999**, *23*, 597.
38. Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560; Feller, D. *J. Comput. Chem.* **1996**, *17*, 1571; Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. *J. Chem. Inf. Model.* **2007**, *47*, 1045. doi:10.1021/ci600510j.
39. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. GAUSSIAN *03, Revision C.02*, Gaussian, Wallingford, CT, 2004.
40. Molden software, Schaftenaar, G., CMBI: http://www.cmbi.ru.nl/molden/molden.html.