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Palladium complexes of a chiral P,C-chelating phosphino-(sulfinylmethyl)phosphonium ylide ligand

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Abstract

A new type of phosphino-phosphonium ylide ligand bearing a chiral sulfinyl center affords a P,C-chelated palladium(II) complex with a resolved asymmetric ylidic carbon atom. According to ^{31}P NMR analysis of the crude material, the diastereoselectivity of the complexation at room temperature is ca. 7:1. In the crystal state, an X-ray diffraction analysis of one epimer reveals a quasi C_2-symmetric chloro-bridged dinuclear structure, where the (*S*) configuration of the sulfur atom induces a (*S*) configuration of the ylidic carbon atom. A in situ Pd(0) catalyst generated from the phosphino-ylide and $Pd(PPh_3)_4$ promotes allylic substitution of 3-acetoxy-1,3-diphenylpropene by sodium malonate in 70% yield and 5% e.e.
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Keywords: Chiral palladium complexes; Ylide complexes; Phosphoniophosphines; Chiral sulfoxides; Allylic substitution

1. Introduction

The diagonal least-change pass relating phosphorus to carbon in the periodic table has been widely recognized [1]. In organometallic chemistry, phosphinidene ligands were thus early regarded as phosphorus versions of carbene ligands [2]. Conversely, the persistency and related catalytic properties of phosphorus ligands in metal complexes could be smoothly varied by passing to carbon versions. The diagonal periodicity thus formally underlies the catalytic properties of persistent carbene complexes [3]. In particular, palladium complexes with Arduengo-type diaminocarbene ligands do catalyze Heck reactions as efficiently as do the corresponding complexes with phosphine ligands [4]. Nonetheless, while the phosphorus atom of phosphines is sp^3 hybridized, the carbon atom of amino- [3] (and phosphino- [5]) carbenes is sp^2 hybridized, with partial vinylic character. Non-conjugated sp^3 carbyls (alkyls) are generally quite reactive and should not behave as phosphine-like persistent ligands. Phosphonium ylides, however, act as peculiar stable η^1-sp^3 carbyl ligands [6], but their catalytic properties were practically not explored until recently. In the achiral version, two examples involve a rhodium-diylide complex for the hydrogenation of 1-hexene [7], and a nickel-ylide complex for the polymerization of olefins [8]. In the chiral version, ylides derivatives of (*R*)-"methylbinapium" [9,10] ("yliphos" [11a]) provided rhodium complexes **1** (Scheme 1), with significant catalytic activity but low enantioslectivity [12]. As we were writing this report, efficient asymmetric allylic substitution was shown to be promoted by a catalyst in situ generated from $Pd(dba)_2$ and yliphos [11b]. Simultaneously, a second generation of phosphine-phosphonium ylide ligands bearing an appending chiral sulfinyl center was designed [13], and both epimers of the rhodium complex **2** (Scheme 1) were shown to catalyze the hydrogenation of acetamidocinnamic acid and the hydrosilylation of acetophenone [13]. The coordination chemistry of the latter type of ligands is here extended in the palladium series. In this series, related chiral, but racemic, complexes of P,C-chelated phosphine-phosphonium ylide ligands of type **3** were

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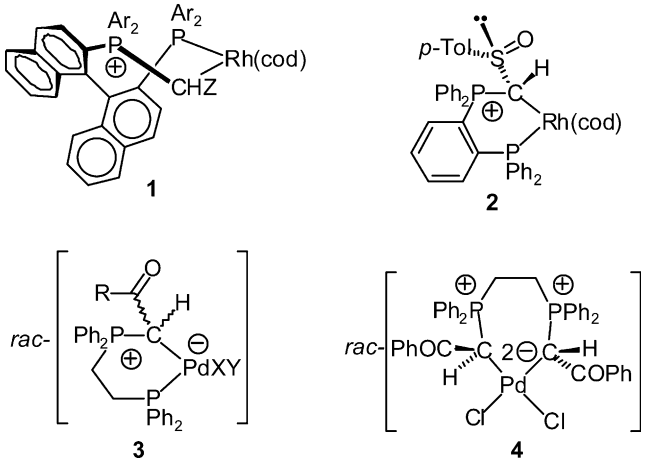


Scheme 1. Known chiral P,C- and C,C-chelated phosphonium ylide complexes in the enantiomerically pure rhodium(I) series and in the racemic palladium(II) series.

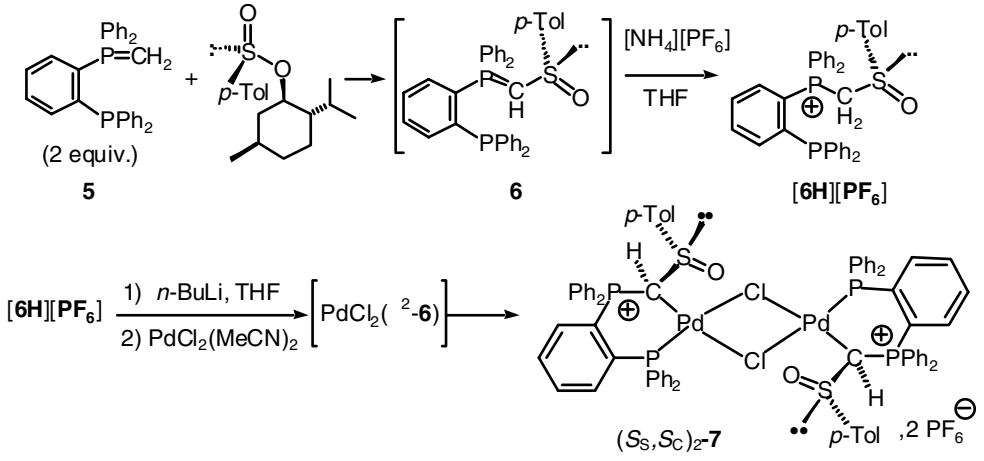
described [14]. It is also worth mentioning the racemic doubly zwitterionic C,C-chelated palladium(II) complex **4**, where the relative configuration of two ylidic carbons was spontaneously controlled during the complexation of the achiral stabilized bisphosphonium diylide ligand at the $PdCl_2$ center [15].

2. Results and discussion

2.1. Stereoselective preparation of complex 7

Monomethylation of *o*-bis(diphenylphosphino)benzene and subsequent deprotonation give the ylide **5**. Reaction of **5** with optically pure menthyl-(*S*)-*p*-toluenesulfinate followed by quenching with NH_4PF_6 affords the (sulfinylmethyl)phosphonium salt [(S_S)-**6H**][PF_6] [13,16]. Deprotonation of (S_S)-**6H**$^+$ in THF regenerates the ylide (S_S)-**6**, which in situ reacted with $PdCl_2(MeCN)_2$. The ^{31}P NMR spectrum of the crude reaction mixture in THF displays two pairs of doublets in a 7:1 ratio which could be assigned to (S_S, S_C) and (S_S, R_C) diastereoisomeric units O=S*–C*H–Pd. The major pattern takes place at $\delta_{P:} = 21.89$ ppm, $\delta_{P^+} = 17.56$ ppm, $J_{PP^+} = 40.7$ Hz, and the minor pattern at: $\delta'_{P:} = 23.52$ ppm, $\delta'_{P^+} = 19.00$ ppm, $J'_{PP^+} = 30.6$ Hz. The P–P$^+$ coupling constant of the major species is almost equal to that of the (S_S, S_C) epimer of the mononuclear rhodium complex **2**, whereas the P–P$^+$ coupling constant of the minor species is close to that of the (S_S, R_C) epimer of **2** [17]. This suggests the respective assignment of the configuration of each epimeric palladium species. After evaporation of THF and extraction in dichloromethane, selective crystallization from chloroform, afforded a single complex in 42% yield. Its purity was indicated by clean NMR spectra and a sharp melting point (m.p. = 184–185 °C). A μ-dichloro dinuclear structure $(S_S, S_C)_2$-**7** (Scheme 2) was revealed by an X-ray diffraction analysis of a single crystal (see below). The ^{31}P NMR spectrum of $(S_S, S_C)_2$-**7** consists in a septet and a pair of doublets at: $\delta_{PF_6} = -141.82$ ppm, $\delta_{P^+} = 18.43$ ppm, $\delta_P = 27.03$ ppm, $J_{PP^+} = 44.5$ Hz. These data are different from those of the main species observed in the crude material (see above), suggesting that the latter is the corresponding mononuclear zwitterionic complex [$PdCl_2(\eta^2$-**6**)]. Whereas mononuclear $PdCl_2$ complexes of phosphonium ylides proved to be stable under zwitterionic forms such as **3** and **4** (Scheme 1), the anionic charge of the putative palladate intermediate [$PdCl_2(\eta^2$-**6**)] is here slowly expelled with a leaving chloride ligand. A 16-electron count is then restored by dimerization of the resulting electron-deficient species (formally: [$PdCl(\eta^2$-**6**)]$^+$) through the bridging remaining chloride.

The complexation reaction carried out at −60 °C resulted in a lower 5:1 diastereoisomeric ratio (^{31}P NMR assay), but the major epimer remained the same. The



Scheme 2. Stereoselective synthesis of ligand **6** and complex **7**.

Table 1
Summary for crystallographic data for compound $(S_S,S_C)_2$-**7**

Empirical formula	$C_{80}H_{68}Cl_{14}F_{12}O_2P_6S_2Pd_2$
Formula weight	2248.38
Temperature (K)	160(2)
Wavelength, λ (Å)	0.71073
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	13.683(5)
b (Å)	13.718(5)
c (Å)	13.877(5)
α (°)	94.600(5)
β (°)	104.023(5)
γ (°)	115.316(5)
Volume (Å^3)	2233.7(14)
Z	1
Calculated density, ρ_{calcd} (g cm^{-3})	1.671
Absorption coefficient, μ (mm^{-1})	1.047
$F(000)$	1124
Crystal size (mm^{-3})	$0.35 \times 0.27 \times 0.10$
2θ range (°)	3.3–52.1
d_{hkl} range (Å)	12.453–0.809
Range for data collection (°)	2.23–26.06
Index ranges	$-16 \leqslant h \leqslant 16$, $-16 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 17$
Reflections collected/unique	21400/15531 [$R_{int} = 0.0608$]
Completeness to $2\theta = 52.12°$	89.7%
Data/restraints/parameters	15531/3/1065
T_{min}–T_{max}	0.464–0.825
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0389$, $wR_2 = 0.1028$
R indices (all data)	$R_1 = 0.0391$, $wR_2 = 0.1030$
Absolute structure parameter	−0.010(15)
Largest diffraction peak and hole (e Å^{-3})	0.715 and −0.824

effect of temperature on the stereoselectivity of the complexation is therefore less pronounced than in the rhodium series, where opposite kinetic and thermodynamic complexation stereoselectivities were observed [13].

2.2. Structural analysis of complex 7

As in the case of the rhodium complex (S_S, R_C)-**2**, the X-ray diffraction analysis of $(S_S, S_C)_2$-**7** (Table 1, Fig. 1) shows that, in spite of the well established coordinating and chelating ability of sulfinyl groups [18], both the sulfur and oxygen atoms occur at non-bonding distances from the palladium center. The (*S*)-*p*-tolylsulfinyl group thus just serves to control the (*S*) configuration of the adjacent ylidic carbon, and then remains bystanding. This ylidic carbon is substituted by an unusual set of substituents H, P$^+$, S, Pd. To the best of our knowledge, the complex $(S_S, S_C)_2$-**7** is the first example of a palladium-ylide complex containing an asymmetric ylidic carbon of definite absolute configuration (Table 2).

The palladium atom lies close to the mean plane of the six-membered metalacycle (Pd-⟨Pd1,C1,P2,C9, C14,P1⟩ ≈ 0.08 Å). The latter is however not planar: both the palladium atom and the ylidic carbon atom are on the same side of the mean plane defined by the phosphorus atoms and the phenylene carbon atoms (rms deviation: 0.0589 Å): Pd1–(P1,C14,C9,P2) = +0.91 Å, C1–(P1,C14,C9,P2) = +1.35 Å. The ring conformation in $(S_S, S_C)_2$-**7** is quite different from that observed in the rhodium(I) complex (S_S, R_C)-**2**. The ligands of either

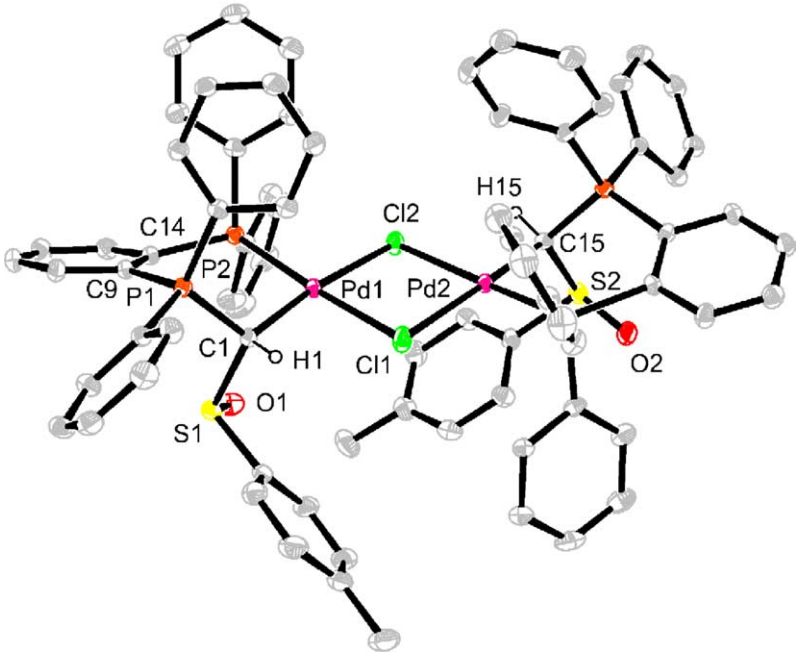


Fig. 1. ORTEP view of the X-ray crystal structure of complex (S_S,S_C)-**7**, with 50% probability displacement ellipsoids for non-hydrogen atoms (see Tables 1 and 2).

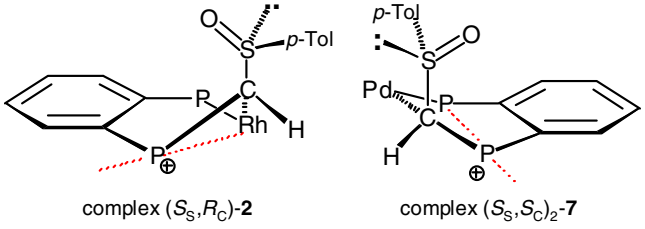
Table 2
Selected bond lengths (Å) and angles (°) for compound (S_S,S_C)-**7** (see Fig. 1)

Pd(1)–C(1)	2.031(4)	Pd(2)–C(15)	2.040(4)
Pd(1)–P(2)	2.2256(12)	Pd(2)–P(3)	2.2330(13)
Pd(1)–Cl(1)	2.3845(14)	Pd(2)–Cl(1)	2.3874(13)
Pd(1)–Cl(2)	2.3887(12)	Pd(2)–Cl(2)	2.4295(13)
S(1)–O(1)	1.486(4)	S(2)–O(2)	1.491(4)
S(1)–C(1)	1.851(4)	S(2)–C(15)	1.830(4)
P(1)–C(1)	1.783(4)	P(4)–C(15)	1.792(4)
C(1)–Pd(1)–P(2)	93.01(13)	C(15)–Pd(2)–P(3)	95.01(13)
C(1)–Pd(1)–Cl(1)	87.68(13)	C(15)–Pd(2)–Cl(1)	171.42(12)
C(1)–Pd(1)–Cl(2)	172.73(12)	C(15)–Pd(2)–Cl(2)	88.37(13)
Cl(1)–Pd(1)–Cl(2)	85.87(4)	Cl(1)–Pd(2)–Cl(2)	84.90(4)
P(2)–Pd(1)–Cl(1)	174.98(5)	P(3)–Pd(2)–Cl(1)	92.12(4)
P(2)–Pd(1)–Cl(2)	93.71(4)	P(3)–Pd(2)–Cl(2)	174.39(4)
O(1)–S(1)–C(1)	107.4(2)	O(2)–S(2)–C(15)	106.8(2)
Pd(1)–Cl(1)–Pd(2)	94.90(5)	Pd(1)–Cl(2)–Pd(2)	93.70(5)
P(1)–C(1)–Pd(1)	115.1(2)	P(4)–C(15)–Pd(2)	113.7(2)
P(1)–C(1)–S(1)	109.7(2)	P(4)–C(15)–S(2)	111.2(2)
S(1)–C(1)–Pd(1)	113.0(2)	S(2)–C(15)–Pd(2)	116.3(2)

complexes exhibit epimeric configurations at the level of the ylidic carbon atom. In (S_S, R_C)-**2**, a folding of the hexagonal ring occurs along the 1,3-P+···Rh axis, while in $(S_S, S_C)_2$-**7**, the folding occurs along the 1,4-P+···P axis (Scheme 3). In both conformations, the cumbersome sulfinyl group occupies a pseudo-axial (*endo*) position.

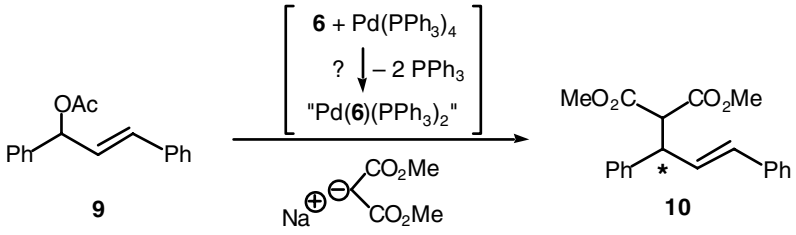
2.3. Preliminary catalytic results

Noticing that various P,X heterochelating ligands (X = N, S) provide efficient palladium catalysts for allylic substitution by either hard or soft nucleophiles [19], the P,C-chelating ligand **6** was tested for allylic alkylation and amination of 3-acetoxy-1,3-diphenylpropene **9**. The pre-formed palladium(II) complex $(S_S, S_C)_2$-**7** failed to catalyze allylation of either dimethyl malonate (in the presence of BSA) or *p*-tolylmethyl amine. In an attempt to generate a palladium(0) species, in situ reductive pretreatment of $(S_S, S_C)_2$-**7** with DIBAL [20], did not improve the catalytic results. To the best of our knowledge, β-zwitterionic palladate(0) complexes of phosphonium ylide C-ligands are not known [21]. Nevertheless, a coordinatively stabilized zwitterionic palladate(0) complex of the phosphino-phosphonium ylide ligand **6** might be generated by reaction of ylide with the palladiun(0) precursor $Pd(PPh_3)_4$. It is indeed known that the latter precursor dissociates in solution to $Pd(PPh_3)_3$ and irreversibly reacts with various chelating ligands [22]. Although no well defined complex could be identified, a in situ-generated complex, (formally "Pd(η²-**6**)$(PPh_3)_n$", $n = 2$, 1) in 3% catalytic ratio was found to promote allylic substitution of **9** by sodium dimethyl malonate (Scheme 4).



Scheme 3. Schematic conformational preferences of the six-membered metallacycle of Pd(II) and Rh(I) complexes of the P,C-chelating ligand (*S*)-**6**. The dotted lines indicate the main folding axes of the metalacycles.

No information about the stereoselectivity of the carbon complexation of (S_S)-**6** at a $Pd^0(PPh_3)_2$ center has been available, but it might be different from that occuring at a $Pd^{II}Cl_2$ center (ca. 75% d.e.: see above). A



Scheme 4. Allylic substitution catalyzed by a in situ-formed Pd(0) complex of the chiral phosphino-phosphonium ylide ligand (S_S)-**6**.

lower stereoselectivity might here afford a pseudo-racemic catalyst and account for the low enantioselectivity observed (5% e.e.). According to the X-ray-crystal structure, the stereogenic sulfur atom indeed occupies a bystanding place in the coordination sphere of the metal, and thus of the catalytic center. Nonetheless, the catalytic activity enlarges horizons to the use of ylides complexes in catalysis. Along the same line, Ohta et al. very recently reported on highly efficient asymmetric allylic substitution of **9** in situ catalyzed by $Pd(dba)_2$ + stabilized yliphos (namely the binap-based ligand of complex **1** with Z = 3D CN, CO_2R, Scheme 1) [11b,23].

3. Conclusion

The reported stereochemical and catalytic properties of a chiral phosphino-(sulfinylmethyl)phosphonium ylide ligand of palladium appear within the context of a recent interest in $PdCl_2$ complexes of α-, β-, and γ-phosphoniocarbyl ligands [24]. The low catalytic enantioselectivity might be due to a low stereoselectivity of the in situ P,C complexation at a $Pd(PPh_3)_2$ center, and efforts will be undertaken to improve enantioselectivity by tuning the structure (symmetry, substitution, rigidity) of chiral (sulfinylmethyl)triarylphosphonium ylide ligands. More generally, the propensity of (chiral) phosphonium ylide complexes to catalyze selective transformations of organic substrates certainly deserve further investigations.

4. Experimental

4.1. General

Reactions were carried out under a nitrogen atmosphere using Schlenk tube and vacuum line technics. THF was distilled over Na/benzophenone. Dichloromethane was distilled over P_2O_5. $[PdCl_2(MeCN)_2]$ was purchased from Fluka. (+)-Phosphonium salt **[6H][PF$_6$]** was prepared from 1,2-diphenylphosphinobenzene and menthyl (*S*)-*p*-tolysulfinate as described in reference [13]. 3-Acetoxy-1,3-diphenylpropene **9** was prepared in two steps from benzylidene acetophenone according to the described method [25]. $Pd(PPh_3)_4$ was prepared according to the described method [26].

NMR spectra were recorded in $CDCl_3$ solution, on Bruker AC 200 and AMX 400 spectrometers. Positive chemical shifts at low field are expressed in ppm by internal reference to TMS for ^1H and ^{13}C, and by external reference to 85% H_3PO_4 in D_2O for ^{31}P. Optical rotations were measured in a 1 dm cell with a Perkin–Elmer 241 photopolarimeter.

4.2. Crystallographic study of 7

Data were collected at low temperature ($T = 160$ K) on a STOE diffractometer using a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryosystems Cryostream Cooler Jet Cooler Device. The final unit cell parameters were obtained by means of a least-squares refinement performed on a set of 8000 well measured reflections. A crystal decay was monitored; no significant fluctuations of intensities were observed during the data collection. Structure was solved by direct methods using SIR-92 [27], and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL-97 [28] included in WINGX version 1.63 [29]. The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography [30]. Hydrogens atoms were located on a difference Fourier maps, but introduced in the procesus of the refinement in idealized positions using a riding model. The C–H distances were fixed at 0.93 Å for Csp^2 atoms and 0.96 Å for Csp^3 atoms, which an isotropic parameter at 20% higher than the U_{eq} value of the Csp^2 atoms to with they were attached, and 50% higher for the Csp^3 atom. Concerning specifically methyl groups they were refined by using a rigid group with the torsion angle refined as a free variable. All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[2(F_o^2) + (0.0675P)^2 + 2.388P]$, where $P = (F_o^2 + 2F_c^2)/3$. The absolute configuration was assigned on the basis of the refinement of the Flack's enantiopole parameter, x, which is the fractional contribution of $F(-h)$ to the observed structure amplitude [31], as depicted in the following formula: $F_o^2 = (1-x)F(h)^2 + xF(-h)^2$; this parameter is sensitive to the polarity of the structure. The Flack's parameter was found close to 0, which clearly indicated the good choice of the enantiomer refined. Least-squares refinements were carried out by minimizing the function: $w(F_o - F_c)^2$, where F_o and F_c are the observed and calculated factor structure. The criteria for a satisfactory complete analysis were the ratios of root mean square shift standard deviation being less than 0.1 and no significant features in final difference Fourier maps. The drawings of the molecule are performed by using the program ORTEP3 with 50% probability displacement ellipsoids for non-hydrogen atoms [32].

4.3. Palladium complex 7

To a stirred solution of **[6H][PF$_6$]** (100 mg, 0.134 mmol) in THF (8 ml) at −20 °C *n*-BuLi (84 μl of 1.6 M solution in hexane, 0.134 mmol) was added. The cooling bath was removed and the mixture was allowed to warm

up to room temperature (orange solution). After 15 min bis(acetonitrile)dichloropalladium(II) (35 mg, 0.134 mmol) was added and the stirring was continued for additional 2 h. The solvent was evaporated and the residue was dissolved in dichloromethane (6 ml). The organic layer was washed with water (2×5 ml) and dried over Na_2SO_4. After filtration the solvent was evaporated in vacuo and the crude product was crystallized from chloroform to afford the hexafluorophosphate of complex **7** as a yellow crystalline solid. Yield: 50 mg (42%).

M.p.: 184–185 °C. $[\alpha]_D^{22} = +282.5$ ($c = 1.8$, CH_2Cl_2). ^{31}P NMR (162 MHz, CD_2Cl_2, $T = 253$ K): δ 27.03 (d, $J_{PP^+} = 44.5$ Hz, *P*), 18.43 (d, $J_{PP^+} = 44.5$ Hz, P^+), −141.82 (septet, $J_{PF} = 711.2$ Hz, PF_6^-). ^1H NMR (400 MHz, CD_2Cl_2, $T = 253$ K): δ 8.16–7.02 (m, 56 H), 4.35 (dd, $J_{HP^+} = 7.8$ Hz, $J_{HP} = 1.6$ Hz, 2 H, P^+CH), 2.41 (s, 6 H, CH_3). $^{13}C\{^1H,^{31}P\}$NMR (100.6 MHz, CD_2Cl_2, $T = 253$ K): δ 142.93, 140.34, 138.40, 136.50, 136.30, 136.21, 135.64, 135.09, 134.66, 134.54, 134.01, 133.54, 133.34, 133.07, 132.99, 131.13, 130.96, 130.22, 129.65, 129.51, 127.05, 126.44, 124.88, 121.46, 120.25, 119.72, 49.83 (P^+CH), 22.25 (CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, $T = 253$ K): δ 142.96, 140.40 (d, $J_{CP^+} = 12.2$ Hz), 138.46 (dd, $J_{CP^+} = 9.7$ Hz, $J_{CP} = 8.8$ Hz), 136.56 (dd, $J_{CP} = 8.6$ Hz, $J_{CP^+} = 2.7$ Hz), 136.24, 136.22, 135.66 (d, $J_{CP^+} = 9.5$ Hz), 135.12 (d, $J_{CP} = 11.5$ Hz), 134.68 (d, $J_{CP^+} = 6.3$ Hz), 134.59 (d, $J_{CP} = 8.6$ Hz), 134.00 (dd, $J_{CP} = 54.9$ Hz, $J_{CP^+} = 7.6$ Hz), 133.60 (d, $J_{CP^+} = 14.7$ Hz), 133.40 (d, $J_{CP^+} = 10.0$ Hz), 133.07, 132.99, 131.11 (d, $J_{CP^+} = 13.1$ Hz), 130.98 (d, $J_{CP^+} = 12.4$ Hz), 130.26, 129.65 (d, $J_{CP} = 12.3$ Hz), 129.53 (d, $J_{CP} = 12.7$ Hz), 127.13 (d, $J_{CP} = 57.6$ Hz), 126.48 (d, $J_{CP} = 59.8$ Hz), 124.92, 121.46 (dd, $J_{CP^+} = 90.3$ Hz, $J_{CP} = 14.6$ Hz), 120.28 (dd, $J_{CP^+} = 78.9$ Hz, $J_{CP} = 2.8$ Hz), 119.84 (d, $J_{CP^+} = 93.9$ Hz), 49.83 (d, $J_{CP^+} = 34.9$ Hz, P^+CH), 22.24 (CH_3). IR (KBr): 3056, 2921, 1637, 1483, 1438, 1099, 837, 744, 688, 557 cm^{-1}. FAB-MS *m*/*z* (relative intensity): 741 (10), 459 (100). HRMS calcd for $C_{38}H_{32}OSClPdP_2^+$ 739.0364, found 739.0381.

Single crystals of **7** suitable for X-ray diffraction analysis were obtained by slow crystallization from $CDCl_3$.

4.4. Catalytic allylic susbtitution of 3-acetoxy-1,3-diphenylpropene by dimethyl malonate

To a stirred solution of (*S*)-[2-(diphenylphosphino)phenyl]methyldiphenylphosphonium hexafluorophosphate [**6H**][PF_6] (0.024 g, 0.032 mmol) in THF (1 ml) at −20 °C *n*-BuLi (13 μl of 2.5 M solution in hexane, 0.032 mmol) was added. The cooling bath was removed and the mixture was allowed to warm up to room temperature. After 15 min the temperature was lowered to −20 °C and $Pd(PPh_3)_4$ (0.027 g, 0.023 mmol) was added. Stirring was continued at room temperature for 20 min and then, after cooling to −20 °C, 3-acetoxy-1,3-diphenyl-1-propene **9** (0.2 g, 0.79 mmol) was added. A THF solution of an anion generated from dimethyl malonate (0.21 g, 1.59 mmol) and NaH (0.038 g, 1.59 mmol) was transferred to the reaction mixture and the stirring was continued for additional 12 h at room temperature. After usual workup, crude product **10** was purified by column chromatography using hexane:dichloromethane (1:1) as the eluent. Yield: 0.18 g (70%). $[\alpha]_D^{23} = -0.9°$ ($c = 1.5$, EtOH); e.e. ≈ 5% (determined from ^1H NMR ($CDCl_3$) recorded in the presence of Eu(hfc)$_3$).

5. Supplementary material

Crystallographic data for structural analysis of compound **7** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 216575. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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