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Ligands with cycloalkane backbones II. Chelate ligands from 2-(diphenylphosphinyl)cyclohexanol: syntheses and transition metal complexes [1]

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Abstract

Starting from PPh_3 ($Ph = C_6H_5$), lithium metal, and epoxicyclohexane, (±)-2-(diphenylphosphinyl)cyclohexanol (**1**) was obtained in about 80% yield in a one-pot reaction. Oxidation of the phosphine moiety, either with elemental sulfur or with hydrogen peroxide, gave the corresponding phosphine sulfide **3** resp. oxide **2**. The latter compound forms dimers in the solid state. Reaction of the OH fragment of **1** and **3** with chlorodiphenyl phosphine led to new chiral bidentate ligands, bearing a phosphinite donor fragment. Several new transition metal complexes of these ligands were characterized spectroscopically and by X-ray structure analysis. © 1997 Elsevier Science S.A.

Keywords: Phosphine ligands; Phosphinite ligands; Chelate ligands; Transition metal complexes

1. Introduction

The development of methods for stereoselective synthesis of chiral compounds made rapid progress during the last decades. Parallel to synthetic routes, starting with precursor molecules from the so-called 'chiral pool', enantioselective catalyses have been worked out [2]. Enzymes as well as chiral transition metal catalysts now allow stereoselective transformations of achiral compounds. One of the first examples for stereoselective reactions catalyzed by transition metal complexes is the synthesis of (L)-DOPA, performed with a chiral rhodium phosphine complex [3]. Starting in the early 1970s, the evolution of new chiral ligands, particularly chelate phosphines, for catalytic applications is still a challenge in chemical research. Modification of the first generation of chelate ligands, mostly bearing a C_2-symmetric arrangement of donor fragments, led to chelate phosphines equipped with two differently substituted phosphorus atoms, giving electronically different donor sites. Recently Takaya reported on highly enantioselective hydroformylations and propene/CO copolymerisations with phosphine/phosphite substituted binaphthyl derivatives [4]. A common structural feature for all ligands giving high enantioselectivities is a relatively rigid backbone, which decreases the coordinative flexibility of the system.

Such rigid backbones can easily be generated by the ring-opening of achiral epoxides of cyclic olefins with various nucleophiles, giving racemic mixtures of *trans*-2-substituted cycloalkanols. We recently reported the synthesis and kinetic resolution of 2-(1-pyrazolyl)cyclohexanol [1]. This 1,3-amino alcohol is now available in amounts of several grams as an enantiomerically pure precursor for ligand and complex syntheses. The corresponding phosphorus substituted cycloalkanols were first described by Issleib in 1965, and picked up again in 1995 by Muller [5], who used lithium phosphides $LiPR_2$ as nucleophiles. These reagents were either achieved commercially or generated from HPR_2 and butyl lithium. We here describe a simple 'one-pot' synthesis of (±)-2-(diphenylphosphinyl)cyclohexanol (**1**), starting from triphenyl phosphine. **1** turned out to be an ideal precursor for a new class of chelate ligands bearing one phosphinite donor fragment in combination

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[1] Dedicated to Professor Gottfried Huttner for the occasion of his 60th birthday. For Part I of this series see Ref. [1].

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with a phosphine or a phosphine sulfide moiety. The coordination chemistry of these ligands was worked out on molybdenum, rhodium, and palladium complexes.

2. Results and discussion

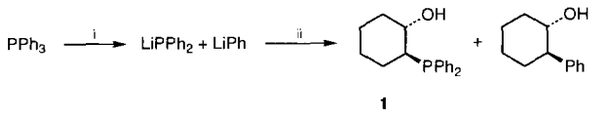
2.1. Syntheses

Starting from PPh_3 instead of isolated $LiPPh_2$ or $HPPh_2$ for the synthesis of 2-(diphenylphosphinyl)cyclohexanol (**1**) allows to carry out large scale reactions (up to 100 g of PPh_3). The in-situ generation of $LiPPh_2$ from PPh_3 and lithium metal gives phenyl lithium as a second product [6]. As any attempts to destroy phenyl lithium with *t*-butyl bromide, according to the published method [6], decreased the yields of **1**, the whole mixture was reacted with epoxicyclohexane giving both, the desired phosphino alcohol **1** and 2-(phenyl)cyclohexanol in a one to one ratio (Scheme 1).

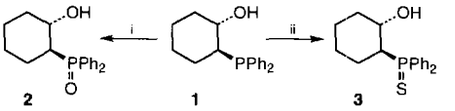
Simple recrystallization of the reaction mixture from ethanol led to pure **1** in excellent yields (ca. 80%, with respect to PPh_3).

The separation of the enantiomers of 2-(1-pyrazolyl)cyclohexanol bases on different solid state structures of the racemic (dimers) and the enantiomerically pure form (helices) [1]. Both structures are determined by strong hydrogen bridges between the OH group and the pyrazole moiety. An analogous resolution of the enantiomers of **1** would require a basic group in the molecule. Hydrogen bridges between alcohols and phosphines are usually much weaker than those between alcohols and amines. For that reason, we synthesized the corresponding phosphine oxide **2** and sulfide **3**. This concept was confirmed by the X-ray structure analysis of **2**, which showed that the structural features of racemic **2** are almost compatible to those of racemic 2-(1-pyrazolyl)cyclohexanol (see structural part; Scheme 2). (The determination of the crystal structure of **1** failed due to the notoriously low quality of the crystals.)

The OH stretching frequencies of alcohols depend strongly on the strength of inter (or intra) molecular hydrogen bridges. IR investigations on the alcohols **1–3** (KBr; **1**: 3412 cm^{-1}, **2**: 3287 cm^{-1}, **3**: 3415 cm^{-1}) demonstrate the high basicity of the phosphine oxide **2**, compared to **1** and **3**. The low basicity of the P=S



Scheme 1. i: THF, 2 equiv. of Li, 2 h; ii: 2 equiv. of epoxicyclohexane, reflux, 2 h; the other enantiomer of the products is omitted (Ph=C_6H_5).



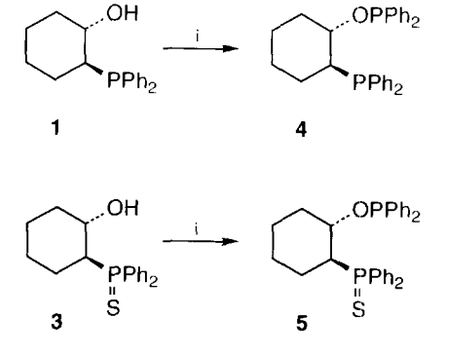
Scheme 2. i: THF, H_2O_2, reflux, 1 h; ii: toluene, S_8, reflux, 15 min; the other enantiomers are omitted (Ph=C_6H_5).

fragment of **3** is compensated by one molecule of water per formula unit in the solid state (elemental analysis). ^1H NMR spectroscopic investigations prove a chair conformation for the *trans*-disubstituted cyclohexane ring with a diequatorial orientation of the donor sites in **1–3**. The coupling constants $^3J_{H1,H2}$ are found within a range of 10–16 Hz, typical for a diaxial arrangement of the vicinal protons. Due to the asymmetrically substituted carbon centers C1 and C2, the phenyl rings of the phosphorus containing moiety are diastereotopic. The chemical shifts of the phosphorus resonances (**1**: $\delta = -10.7$ ppm, **2**: $\delta = 39.7$ ppm, **3**: $\delta = 46.4$ ppm) and the coupling constants (**1**: $^1J_{P,Ci} = 10.6/12.6$ Hz, **2**: $^1J_{P,Ci} = 95.9/94.9$ Hz, **3**: $^1J_{P,Ci} = 78.4/77.5$ Hz) are characteristic for such alkyldiaryl substituted phosphorus centers [7].

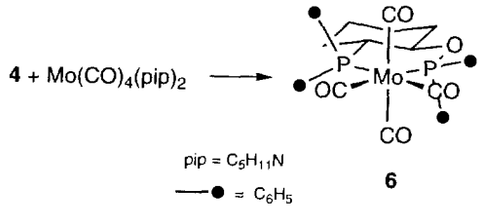
The kinetic resolution of **1**, **2**, and **3**, which was carried out analogously to 2-(1-pyrazolyl)cyclohexanol with lipase B of *candida antarctica*, failed. We assume that the bulky diphenylphosphinyl fragment avoids an interaction of the substrate and the enzyme. Only a slow and non-enantioselective esterification of the OH function is observed. However, sterically demanding cycloalkanols have been successfully derivatized with other enzymes [8], so an enzymatic resolution of our phosphorus ligands may be possible.

Deprotonation of **1** and **3** with butyl lithium, followed by the addition of chlorodiphenyl phosphine, leads to the corresponding bidentate chelate ligands **4** and **5**, with both a phosphine/phosphine sulfide and a phosphinite donor site, in high yields (Scheme 3).

^{31}P NMR spectroscopy clearly proves the chemical constitution of the chelate ligands [7]. While the resonances of the phosphine (**4**: $\delta = -12.0$ ppm) and the



Scheme 3. i: THF, *n*-BuLi, $ClP(C_6H_5)_2$, room temperature; the other enantiomers are omitted (Ph=C_6H_5).



Scheme 4. i: CH_2Cl_2, $(pip)_2Mo(CO)_4$ (pip = piperidine, $C_5H_{11}N$), room temperature; the other enantiomer of the product is omitted.

phosphine sulfide (**5**: $\delta = 47.7$ ppm) are found at almost the same δ values as in the precursor molecules **1** and **3**, new resonances for the diphenyl phosphinite moieties are observed at about 105 ppm. As the $OPPh_2$ unit is attached to an asymmetrically substituted carbon center, we now obtain complex ^1H and ^{13}C NMR spectra, showing the resonances of two pairs of diastereotopic phenyl rings.

The phosphine/phosphinite ligand **4** reacts almost quantitatively with labile precursor complexes like $(pip)_2Mo(CO)_4$ (pip = piperidine, $C_5H_{11}N$), $[(CO)_2Rh(\mu\text{-}Cl)]_2$, and $(C_6H_5CN)_2PdCl_2$ to give the chelate complexes **6**, **7**, and **8**.

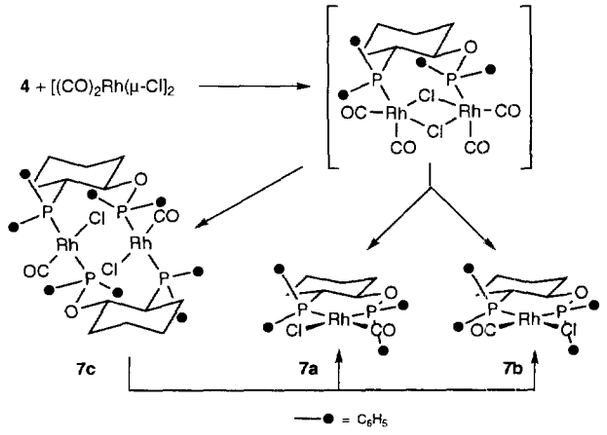
$(pip)_2Mo(CO)_4$ (pip = piperidine, $C_5H_{11}N$) reacts with **4** by exchange of the monodentate ligands (Scheme 4).

Coordination of **4** to the $Mo(CO)_4$ fragment shifts the ^{31}P NMR resonances of the ligand to lower field ($\delta = 145.1$, 35.9 ppm) and now allows coupling of the two different phosphorus centers ($^2J_{PP} = 35.8$ Hz). The absolute value of the coupling constant was not determined. For complexes of the type $(dppp)M(CO)_4$ (M = Cr, Mo, W; dppp = bisdiphenylphosphinopropane), with a corresponding diphosphametalla six ring, negative coupling constants $^2J_{PP}$ (−33.7 to −21.5 Hz) were found by multiple resonance techniques [9]. In the ^{13}C NMR spectrum of **6**, resonances of four different carbonyl ligands are observed in addition to the signals of the chelate ligand. In combination with the chemical shift of the *CO* resonances, the coupling constants $^2J_{PC}$ enabled an assignment of the axial and equatorial carbonyl ligands (axial: $\delta = 213.5$ ppm, $^2J_{PC} = 9.7/9.7$ Hz; $\delta = 206.0$ ppm, $^2J_{PC} = 8.7/8.7$ Hz; equ.: $\delta = 216.6$ ppm, $^2J_{PC} = 21.4/8.7$ Hz; $\delta = 215.6$ ppm, $^2J_{PC} = 29.2/8.7$ Hz). Due to its characteristic coupling constant of 21.4 Hz, the resonance at 216.6 ppm can be assigned to the carbonyl ligand in *trans* position to the phosphine moiety [9]. While the resonance of one of the axial CO ligands is found at a typical δ value ($\delta = 206.0$ ppm), the resonance of the second axial CO ligand is shifted to lower field ($\delta = 213.5$ ppm), probably due to different shielding effects of the asymmetric ligand (see structural part). Combination of one- and two-dimensional NMR techniques allowed the assignment of all proton and carbon resonances.

Table 1
^{31}P NMR spectroscopic data of **7a–c**

Compound	δ(P-1)	$^1J_{Rh,P-1}$ [Hz]	δ(P-2)	$^1J_{Rh,P-2}$ [Hz]	$^2J_{P-1,P-2}$ [Hz]
7a	29.8	139.6	108.5	151.5	17.8
7b	27.9	121.8	105.2	139.6	17.8
7c	20.6	121.8	129.9	169.3	56.4

Reaction of **4** with $[(CO)_2Rh(\mu\text{-}Cl)]_2$ results in the formation of three new compounds **7a–c**, each giving two doublets of doublets in the ^{31}P NMR spectrum of the reaction mixture. One of these species (**7c**) was only observed in solution. It is an intermediate of the formation of **7a** and **7b**, leading finally to a 1:1 mixture of these complexes. IR and NMR data for **7a** and **7b** (Table 1) suggest a *cis*-coordination of the chelate ligand to one rhodium atom, which is quite unusual for bisphosphinecarbonylchlororhodium(I) complexes. The only reported example in the α,ω-bis-diphenylphosphinoalkane series, showing this mode of coordination, is (dppe)Rh(CO)Cl (dppe = bisdiphenylphosphinoethane) [10]. All other α,ω-bisdiphenylphosphinoalkane ligands give rise to a *trans* arrangement of the phosphorus donors, e.g. by a bridging coordination, resulting in a dinuclear geometry. Alternatively, long chain ligands are able to coordinate to a single rhodium center in *trans* configuration. In the case of **7a** and **7b**, *cis*-coordination is proved by a CO stretching frequency of 2021 cm^{-1} (in CH_2Cl_2; (dppe)Rh(CO)Cl: 2010 cm^{-1}), while the typical values for *trans* configurated complexes are found at 1960–1950 cm^{-1}. Additionally, small P–P coupling constants ($^2J_{PP} \sim 18$ Hz) are characteristic for this type of complex geometry. The unsymmetrical, *cis*-coordinating ligand leads to two isomeric structures for **7a** and **7b**, one with the CO ligand in *trans* position to the phosphine moiety, the other with the CO ligand in *trans* position to the phosphinite group (Scheme 5). Both ^{31}P NMR and IR data point out that the energetic features



Scheme 5. Reaction of **4** with $[(CO)_2Rh(\mu\text{-}Cl)]_2$; the other enantiomers of **7a–c** are omitted.

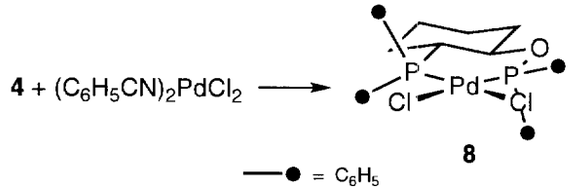
of **7a** and **7b** should be almost identical. Attempts at the separation of the isomers by crystallization failed. Crystals obtained from CH_2Cl_2 solution were disordered and thus not suitable for a single crystal structure determination. We assume that both isomers **7a** and **7b** are statistically incorporated in the crystals [11].

A larger P–P coupling constant ($^2J_{PP} = 56.4$ Hz, Table 1), which is observed for **7c**, indicates a *trans* configuration of the phosphorus atoms at rhodium, leading to a dinuclear complex bearing two chelate ligands coordinated in a bridging mode. As there are two different phosphorus donor centers in **4**, and the synthesis was carried out with the racemic ligand, the specific formation of one single dinuclear complex is quite remarkable. If we assume that the first attack of **4** on $[(CO)_2Rh(\mu\text{-}Cl)]_2$ will lead to $[(CO)_2Rh(\mu\text{-}Cl)]_2(\mu\text{-}\mathbf{4})$ [12], the regioselectivity of the second attack (phosphine versus phosphinite) can be determined by this intermediate. However, the stability of the reaction product must depend on the stereochemistry of both chelate ligands. If the reaction product contains both enantiomers of **4**, a centrosymmetric, dimeric structure, comparable to the solid state structures of **2** or racemic 2-(1-pyrazolyl)cyclohexanol (linear O–H · · · O=P resp. O–H · · · N arrangement), can be formed, which enables a (stable) *trans* arrangement of the two P · · · Rh · · · P fragments. In contrast, if two molecules of the same enantiomer coordinate to the rhodium centers, a dimeric structure would be impossible for stereochemical reasons. In the case of enantiomerically pure 2-(1-pyrazolyl)cyclohexanol, this leads to the formation of a helical structure, which was proved by means of IR spectroscopy to be less stable than the dimeric structure of the racemic compound [1]. In our case, an attack of a second chelate ligand with identical stereochemistry would rapidly lead to the formation of **7a** and **7b** (Scheme 5).

Ligand **4** enables for the first time the observation of both geometries, *cis*-coordination to one Rh(CO)Cl fragment and bridging coordination resulting in a dinuclear species, with one particular chelate ligand. The steric properties of **4** coordinating to a Rh(CO)Cl fragment may therefore be located somewhere between dppe and dppp. For the examination of possible catalytical applications, a mixture of **7a,b** was tested in the catalytic hydrosilylation of acetophenone with triethylsilane, where it showed moderate activity [13].

Analogous to the formation of **6**, ligand exchange reaction with the labile palladium compound $(C_6H_5\text{–}CN)_2PdCl_2$ yields the dichloro complex **8** in an almost quantitative reaction (Scheme 6).

In contrast to the related complexes **6** and **7a,b**, the coupling between the two phosphorus centers is weak ($^2J_{PP} < 1$ Hz), while the chemical shifts of the ^{31}P NMR resonances are observed at normal δ values. We assign this to the *trans* influence of the two chloro ligands (**6**: 2 × CO, $^2J_{PP} = 35.6$ Hz, **7a,b**: 1 × CO, 1 × Cl, $^2J_{PP} = 17.8$ Hz). ^{13}C and ^1H NMR spectra of **8** could be assigned by means of 2D techniques (HH-COSY, H,H-J resolved spectra and C,H-correlation). An X-ray structure analysis finally proved the square planar geometry of the palladium complex **8**.



Scheme 6. Reaction of **4** with $(C_6H_5\text{–}CN)_2PdCl_2$; the other enantiomer is omitted.

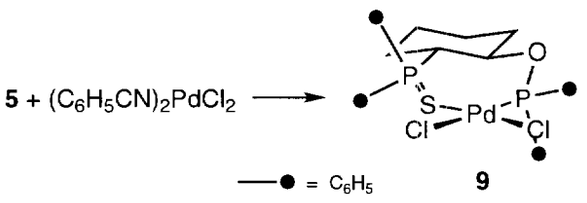
$(C_6H_5\text{–}CN)_2PdCl_2$ also reacts with the phosphane sulfide/phosphinite ligand **5** to give the chelate complex **9**. The additional sulfur atom leads to the formation of a seven-membered ring system bearing one palladium, one sulfur, one oxygen atom, and two phosphorus and two carbon atoms (Scheme 7).

While the previously discussed phosphine/phosphinite complexes are well soluble in organic solvents, the solubility of **9** is low, due to the increased polarity of the chelate ligand. However, crystallization from CH_2Cl_2 solution gave crystals suitable for the determination of the solid state structure.

2.2. Crystal structures

(±)-*trans*-(2-Diphenylphosphinoyl)cyclohexanol (**2**) crystallizes from ethylacetate as colorless bricks in the monoclinic space group $P2_1/n$ (Int. Tab. No. 14 [14]). The unit cell contains two dimers, each of them formed by one (1R,2R) and one (1S,2S) enantiomer. Fig. 1 shows the dimeric structure of **2** in the solid state. The crystal data and collection parameters are summarized in Table 2.

As expected, the four substituents at the phosphorus atom are arranged in an almost tetrahedral mode and the cyclohexane ring is found to be in the energetically favorable chair conformation with a *cis*-diequatorial arrangement of the OH and the $OPPh_2$ group. The monomeric units are linked by two intermolecular hydrogen bonds between the OH group (donor) and the



Scheme 7. Reaction of **5** with $(C_6H_5\text{–}CN)_2PdCl_2$; the other enantiomer is omitted.

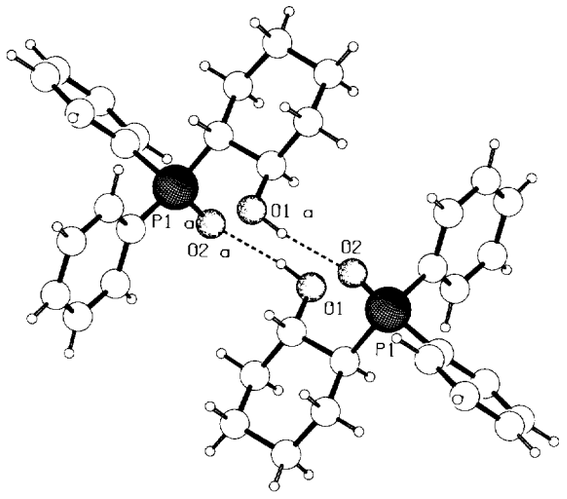


Fig. 1. PLUTON [15] plot of the molecular structure of dimeric **2**. Selected bond lengths [Å], angles [°], and torsion angles [°]: P(1)–O(2) 1.4916(12), P(1)–C(2) 1.8252(19), P(1)–C(11) 1.8098(17), P(1)–C(21) 1.8037(18), O(1)–C(1) 1.421(2), O(1)–H(31) 0.89(2), O(1) · · · O(2a) 2.7359(18), O(2) · · · H(31a) 1.87(2); O(2)–P(1)–C(2) 112.95(7), O(2)–P(1)–C(11) 110.26(7), O(2)–P(1)–C(21) 112.96(8), C(2)–P(1)–C(11) 104.88(8), C(2)–P(1)–C(21) 110.15(8), C(11)–P(1)–C(21) 105.03(9), C(1)–O(1)–H(31) 106.6(16), O(1)–H(31) · · · O(2a) 167(2); O(1)–C(1)–C(2)–P(1) 59.31(15).

P=O fragment (acceptor), leading to a center of inversion in the dimeric structure. An analogous arrangement was found in the solid state structure of (±)-*trans*-(2-pyrazolyl)cyclohexanol [1] and seems to be a general feature for the solid state structure of such compounds.

Dichloro{(±)-*trans*-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinicacidester}palladium(II) (**8**) crystallizes from CH_2Cl_2 by slow diffusion of diethylether as bright yellow plates in the monoclinic space group $P2_1/c$ (Int. Tab. No. 14 [14]) with one additional molecule of CH_2Cl_2 per formula unit. Fig. 2 shows the molecular structure of **8**. The crystal data and collection parameters are summarized in Table 2.

Due to the stereoelectronic requirements of the *cis*-coordinating chelate ligand, the palladium center is found in a distorted square planar coordination. The distance Pd–P1 (phosphine) is about 4.6 pm longer than Pd–P2 (phosphinite), which has already been observed for analogous compounds [16]. This can be explained by an increasing s-character of the lone pair at the latter donor fragment, induced by the electronegative oxo substituent. Corresponding to that, the distance Pd–Cl2 (*trans* to P2) is about 1.2 pm longer than Pd–Cl1 (*trans* to P1). As the cyclohexane ring of the chelate ligand is

Table 2
Crystallographic data and parameters of the crystal structure determinations

	2	**8** · CH_2Cl_2	**9**
Formula	$C_{18}H_{21}O_2P$	$C_{31}H_{32}Cl_4OP_2Pd$	$C_{30}H_{30}Cl_2OP_2PdS$
M [g mol^{-1}]	300.34	730.71	677.91
a [Å]	11.158(1)	15.775(3)	9.112(1)
b [Å]	9.451(1)	9.585(1)	15.692(1)
c [Å]	15.252(1)	20.926(5)	20.681(1)
β [°]	98.58(1)	100.69(1)	101.89(1)
V [Å^3]	1590.4(2)	3109.2(10)	2893.6(4)
ρ_{calc} [g cm^{-3}]	1.254	1.561	1.556
Z	4	4	4
Crystal system	monoclinic	monoclinic	monoclinic
Space group (Int. Tab. No.)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)
F(000) [e]	640	1480	1376
μ(Mo Kα) [cm^{-1}]	1.7	10.7	10.3
Radiation	λ = 0.71073 Å (Mo Kα), graphite monochromator		
Diffractometer	STOE-IPDS	MACH 3	STOE-IPDS
Crystal size [mm^3]	0.2 × 0.2 × 0.2	0.89 × 0.51 × 0.43	0.43 × 0.38 × 0.13
Temperature [°C]	0	−80	−80
Data collecting mode	oscillation	ω-scan	oscillation
Scan range (2Θ) [°]	3–49.83	2–52.6	3–49.42
hkl Range	−13/13, −11/11, −17/17	0/19, −13/0, −25/25	−10/10, −18/18, −23/24
Measured refl.	12956	5932	35935
Unique refl.	2750	4824	4468
Observed refl.	2750	4824	4468
$F_0 >$	0.01$\sigma(I)$	0.01$\sigma(I)$	0.01$\sigma(I)$
Refined param.	274	480	454
R_1	0.0469	0.0528	0.0313
wR_2	0.0992	0.0863	0.0684
GoF	1.09	1.03	1.00
$\Delta\rho$(max/min) [e Å^{-3}]	0.13/−0.29	1.38/−1.30	0.53/−0.34

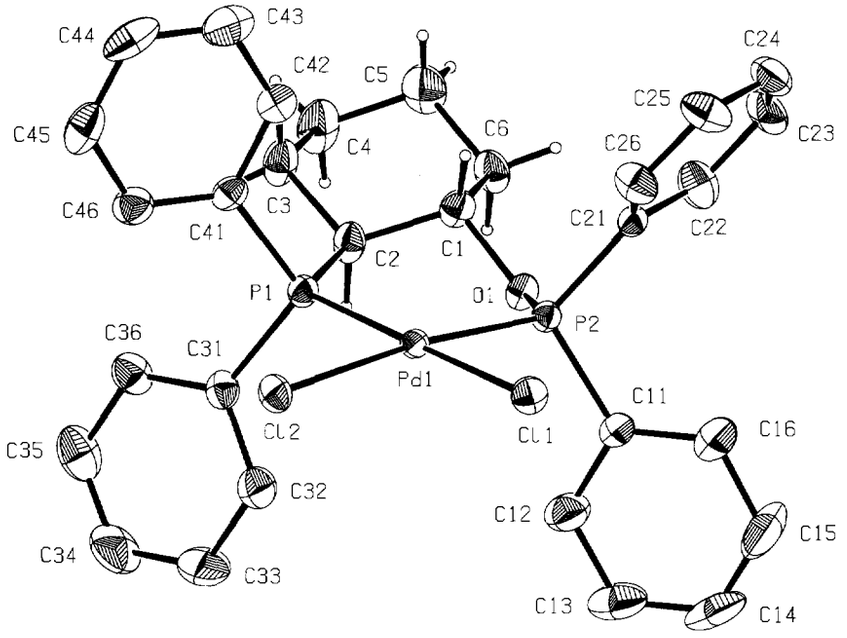


Fig. 2. PLATON [15] plot (50% probability ellipsoids) of the molecular structure of **8** (the additional solvent molecule is omitted). Selected bond lengths [Å], angles [°], and torsion angles [°]: Pd(1)–Cl(1) 2.3482(12), Pd(1)–Cl(2) 2.3605(13), Pd(1)–P1 2.2495(12), Pd(1)–P(2) 2.2033(13), P(1)–C(2) 1.863(5), P(2)–O(1) 1.606(3), O(1)–C(1) 1.456(5); Cl(1)–Pd(1)–Cl(2) 93.43(4), Cl(1)–Pd(1)–P(1) 178.33(4), Cl(1)–Pd(1)–P(2) 85.62(4), Cl(2)–Pd(1)–P(1) 86.04(4), Cl(2)–Pd(1)–P(2) 173.14(4), P(1)–Pd(1)–P(2) 95.10(4), Pd(1)–P(2)–O(1) 115.19(12), P(2)–O(1)–C(1) 119.3(3); O(1)–C(1)–C(2)–P(1) 62.0(4).

again found in the chair conformation (*cis*-diequatorial arrangement of OPh_2 and PPh_2), the new six-membered ring (Pd, P1, C1, C2, O, P2), generated by the coordination of **4** to the Pd center, is forced into an envelope conformation, which leads to a pseudo C_2-symmetrical arrangement of the phenyl substituents.

Dichloro{(±)-*trans*-diphenyl[(2-diphenylthiophosphinoyl)cyclohexyl]phosphinicacidester}palladium(II)

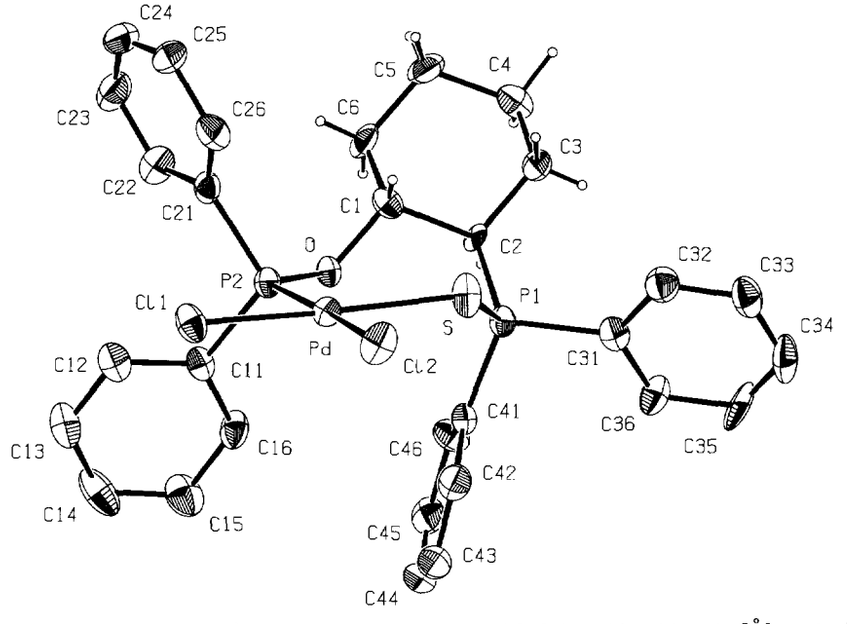


Fig. 3. PLATON [15] plot (50% probability ellipsoids) of the molecular structure of **9**. Selected bond lengths [Å], angles [°], and torsion angles [°]: Pd–Cl(1) 2.3152(9), Pd–Cl(2) 2.3610(9), Pd–S 2.3112(9), Pd–P(2) 2.2188(9), S–P(1) 2.0220(12), P(1)–C(2) 1.826(3), P(2)–O 1.620(2), O–C(1) 1.461(4); Cl(1)–Pd–Cl(2) 90.64(3), Cl(1)–Pd–S 172.24(3), Cl(1)–Pd–P(2) 84.77(3), Cl(2)–Pd–S 82.58(3), Cl(2)–Pd–P(2) 175.41(3), S–Pd–P(2) 101.98(3), Pd–S–P(1) 116.26(4), Pd–P(2)–O 117.49(8), P(2)–O–C(1) 119.46(19); O–C(1)–C(2)–P(1) −52.5(3).

(**9**) crystallizes from CH_2Cl_2 by slow diffusion of diethylether as orange colored plates in the monoclinic space group $P2_1/n$ (Int. Tab. No. 14 [14]). Fig. 3 shows the molecular structure of **9**. The crystal data and collection parameters are summarized in Table 2.

While a multitude of transition metal complexes bearing phosphine or phosphine sulfide ligands are known, only few examples with chelating ligands showing that combination of donor centers have been structurally characterized [17]. The combination of a phosphinite and a phosphine sulfide donor coordinating to one metal center, either in a monodentate or chelating mode, was yet unknown [18].

Chelating coordination of **5** to $PdCl_2$ leads to the formation of a seven-membered ring system including the atoms Pd, P1, S, C2, C1, O and P2. While S, Pd, P2, O and C2 are found in an almost planar arrangement, C1 and P1 are located above and below that plane. This special geometry is forced by the steric demand of two rigid fragments: first the square planar coordinated Pd center, second, the cyclohexane ring (carbon atoms C1 and C2), which is again found to occupy a chair conformation. Corresponding to **8**, the phenyl substituents of the phosphinite/phosphine sulfide ligand of **9** are, as expected, arranged in a pseudo C_2-symmetrical way.

Bond lengths Pd–S of 2.28–2.35 Å have been observed for phosphine sulfides coordinating to Pd(II) [19], which are comparable to the distance Pd–S (2.3112 Å) in **9**. The other relevant bond lengths and angles of **8** and **9** are almost similar.

3. Conclusion

(±)-2-(Diphenylphosphinyl)cyclohexanol (**1**) and the corresponding phosphine sulfide **3**, which are available by simple syntheses and in large quantities, can be used as starting materials for the synthesis of new chelating phosphinite ligands. Attempts for an enzymatic separation of the stereoisomers of these compounds failed, in contrast to the analogous 2-(1-pyrazolyl)cyclohexanol. We assume that the bulky PPh_2 fragment prevents the interaction of the substrates with the enzyme (lipase B from *candida antarctica*). However, the application of other enzymes might allow stereospecific reactions with **1–3** and enable the separation of the enantiomers.

We therefore used the racemic chelate ligands **4** and **5** for the syntheses of new transition metal complexes. X-ray structure analyses of the palladium complexes **8** and **9** prove some general structural features of chelate complexes with a 1,2-*cis* substituted cyclohexane backbone. As expected, the rigid backbone leads to a pseudo C_2-symmetrical arrangement of the four phenyl rings of the ligand, like is known for example for C_2-symmetrical binaphthyl derivatives.

Reaction of **4** with the rhodium precursor complex $[(CO)_2Rh(\mu\text{-}Cl)]_2$ results in the formation of three new chelate complexes **7a–c**. Two of them (**7a,b**) are isomers with a *cis*-coordinated chelate ligand, differing only in the orientation of the carbonyl resp. the chloro ligand. The third complex (**7c**), which was observed only by ^{31}P NMR spectroscopy, has a centrosymmetric, dimeric structure, with two enantiomeric ligands bridging two Rh(Cl)CO fragments. **7c** is an intermediate in the formation of **7a,b**.

4. Experimental part

The synthesis of all compounds was carried out under an inert gas atmosphere of nitrogen and with dried solvents. The starting materials $(pip)_2Mo(CO)_4$ (pip = piperidine, $C_5H_{11}N$) and $(C_6H_5\text{–}CN)_2PdCl_2$ were prepared according to procedures described in the literature [20], $[(CO)_2Rh(\mu\text{-}Cl)]_2$ (STREM: 45-0450) was achieved commercially. The NMR (Bruker DPX 400), mass (gas chromatograph Hewlett-Packard HP 5890 coupled with a mass selective detector HP 5970, Finnigan MAT 90), and infrared spectra (Perkin–Elmer 1600 Series FTIR), the X-ray structure analyses, and all elemental analyses were carried out at the Anorganisch-chemisches Institut der Technischen Universität München. The numbering of the NMR data (cyclohexane ring) corresponds to the numbering of the X-ray structures.

4.1. (±)-trans-(2-Diphenylphosphinyl)cyclohexanol (1)

To 100.0 g (381 mmol) of triphenylphosphine and 6.0 g (864 mmol, 2.3 equiv.) of lithium metal mixed in a 2 l flask, equipped with a reflux condenser, 1 l of THF is added within a period of 10 min. During the addition of THF, the color of the solution turns to orange and the mixture starts to boil. After 1 h of stirring the solution is transferred to another 2 l flask by a cannula to remove excess of lithium. 74.9 g (763 mmol) of epoxicyclohexane are added dropwise and the solution is refluxed for 2 h. After cooling to room temperature, 100 ml of a concentrated NH_4Cl solution are added and about 600 ml of the THF are removed in vacuo. The product precipitates as colorless crystals, which are filtered off and recrystallized from ethanol. Yield: 84.5 g (78%). M.p. 136 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3413 vs [ν(OH)], 3069 m, 3056 m, 3018 w, 2944 s, 2923 vs, 2848 s, 1583 w, 1482 m, 1458 w, 1446 s, 1429 vs, 1294 m, 1227 w, 1194 w, 1182 w, 1120 s, 1067 s, 1058 vs, 1028 s, 998 w, 958 w, 734 vs, 697 vs, 511 s, 489 s. ^1H NMR (400.13 MHz, 25 °C, $CDCl_3$): δ = 7.50 (dt, $^3J_{P,o\text{-}H} = {}^3J_{o\text{-}H,m\text{-}H}$ = 7.3 Hz, $^4J_{o\text{-}H,p\text{-}H}$ = 1.0 Hz, o-H), 7.42 (dt, $^3J_{P,o'\text{-}H} = {}^3J_{o'\text{-}H,m'\text{-}H}$ = 7.3 Hz, $^4J_{o'\text{-}H,p'\text{-}H}$ = 1.0 Hz, o'-H), 7.36–7.28 (m, 6H, ar-H), 3.47 (dddd, $^3J_{P,1\text{-}H} = {}^3J_{1\text{-}H,2\text{-}H}$ = 10.0 Hz,

$^3J_{1\text{-}H,6_{ax}\text{-}H}$ = 7.5 Hz, $^3J_{1\text{-}H,6_{eq}\text{-}H}$ = 4.5 Hz, 1-H), 2.30 (br, OH), 2.26 (dd, $^3J_{2\text{-}H,3_{ax}\text{-}H}$ = 11.6 Hz, $^3J_{2\text{-}H,3_{eq}\text{-}H}$ = 3.5 Hz, $^4J_{P,2\text{-}H}$ < 1.0 Hz, 2-H), 2.08, 1.71, 1.62, 1.40, 1.20, 0.90 (6 × m, 8H, al-H). $^{13}C\{^1H\}$ NMR (100.25 MHz, 25 °C, $CDCl_3$): δ = 136.3 (d, $^1J_{P,C\text{-}i}$ = 10.6 Hz, C-i), 135.2 (d, $^1J_{P,C\text{-}i'}$ = 12.6 Hz, C-i'), 134.6 (d, $^2J_{P,C\text{-}o}$ = 20.3 Hz, C-o), 132.7 (d, $^2J_{P,C\text{-}o'}$ = 17.5 Hz, C-o'), 129.1 (s, C-p), 128.4 (d, $^3J_{P,C\text{-}m}$ = 6.7 Hz, C-m), 128.3 (s, C-p'), 128.2 (d, $^3J_{P,C\text{-}m'}$ = 7.7 Hz, C-m'), 71.9 (d, $^2J_{P,C-1}$ = 14.5 Hz, C-1), 43.6 (d, $^1J_{P,C\text{-}2}$ = 12.6 Hz, C-2), 35.1 (d, $^3J_{P,C\text{-}6}$ = 6.8 Hz, C-6), 27.1 (d, $^2J_{P,C\text{-}3}$ = 3.9 Hz, C-3), 25.8 (d, $^3J_{P,C\text{-}4}$ = 4.9 Hz, C-4), 24.2 (s, C-5). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): δ = −10.7. MS (EI), *m/e* (%): 284 (54) [M^+], 186 (66) [$M^+ - C_6H_9OH$], 108 (100) [$M^+ - C_6H_9OH - C_6H_6$], 77 (6) [$C_6H_5^+$]. Anal. Found: C, 75.61; H, 7.59. $C_{18}H_{21}OP$ (284.34) Calc.: C, 76.04; H, 7.44%.

4.2. (±)-trans-(2-Diphenylphosphinoyl)cyclohexanol (2)

2.84 g (10 mmol) of **1** are dissolved in 100 ml of THF and 8 ml (10.1 mmol) of 30% H_2O_2 are added. The solution is refluxed for 1 h, and after the addition of 50 ml of H_2O the THF is removed in vacuo. The precipitated product is removed by filtration and recrystallized from ethanol/H_2O (3:1), giving an ethanol adduct, or from ethylacetate. Yield: 2.90 g (97%) of colorless crystals. M.p. 151 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3288 vs [ν(OH)], 3076 m, 3056 m, 2952 m, 2919 s, 2848 m, 1484 m, 1462 m, 1450 s, 1437 s, 1358 s, 1322 s, 1179 vs [ν(P=O)], 1150 s, 1118 s, 1101 s, 1072 s, 1064 s, 1032 m, 896 m, 801 s, 740 s, 717 vs, 701 s, 690 vs, 562 vs, 549 s, 532 vs, 453 m. IR (toluene, cm^{-1}): $\tilde{\nu}$ = 3357 s [ν(OH), associated]. ^1H NMR (400.13 MHz, 25 °C, $CDCl_3$): δ = 7.75 (ddd, $^3J_{P,o\text{-}H}$ = 8.5 Hz, $^3J_{o\text{-}H,m\text{-}H}$ = 7.0 Hz, $^4J_{o\text{-}H,p\text{-}H}$ = 1.6 Hz, o-H), 7.67 (ddd, $^3J_{P,o'\text{-}H}$ = 11.0 Hz, $^3J_{o'\text{-}H,m'\text{-}H}$ = 7.5 Hz, $^4J_{o'\text{-}H,p'\text{-}H}$ = 1.5 Hz, o'-H), 7.56–7.42 (m, 6H, ar-H), 3.81 (dddd, $^3J_{P,1\text{-}H}$ = $^3J_{1\text{-}H,2\text{-}H}$ = 10.2 Hz, $^3J_{1\text{-}H,6_{ax}\text{-}H}$ = 7.0 Hz, $^3J_{1\text{-}H,6_{eq}\text{-}H}$ = 4.5 Hz, 1-H), 2.50 (dddd, $^3J_{2\text{-}H,3_{ax}\text{-}H}$ = 13.0 Hz, $^3J_{2\text{-}H,3_{eq}\text{-}H}$ = 3.5 Hz, $^4J_{P,2\text{-}H}$ = 10.2 Hz, 2-H), 2.18 (s, OH), 2.06, 1.70, 1.61, 1.38, 1.20, 1.16, 0.95 (7 × m, 8H, al-H). $^{13}C\{^1H\}$ NMR (100.25 MHz, 25 °C, $CDCl_3$): δ = 132.2 (d, $^2J_{P,C\text{-}o}$ = 8.7 Hz, C-o), 132.1 (d, $^4J_{P,C\text{-}p}$ = 4.8 Hz, C-p), 132.0 (d, $^4J_{P,C\text{-}p'}$ = 2.9 Hz, C-p'), 131.9 (d, $^1J_{P,C\text{-}i}$ = 95.9 Hz, C-i), 131.0 (d, $^2J_{P,C\text{-}o'}$ = 9.7 Hz, C-o'), 129.7 (d, $^1J_{P,C\text{-}i}$ = 94.9 Hz, C-i'), 128.7 (d, $^3J_{P,C\text{-}m}$ = 11.7 Hz, C-m), 128.3 (d, $^3J_{P,C\text{-}m}$ = 11.7 Hz, C-m'), 69.5 (d, $^2J_{P,C\text{-}1}$ = 5.8 Hz, C-1), 43.8 (d, $^1J_{P,C\text{-}2}$ = 69.7 Hz, C-2), 35.3 (d, $^3J_{P,C\text{-}6}$ = 10.6 Hz, C-6), 26.4 (d, $^2J_{P,C\text{-}3}$ = 1.9 Hz, C-3), 25.5 (d, $^3J_{P,C\text{-}4}$ = 13.6 Hz, C-4), 24.0 (s, C-5). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): δ = 39.7. MS (EI), *m/e* (%): 300 (6) [M^+], 272 (43) [$M^+ - C_2H_4$], 257 (24) [$M^+ - C_3H_7$], 229 (100) [$M^+ - C_4H_7O$], 202 (64) [$M^+ - C_6H_9OH$], 125 (13) [$M^+ - C_6H_9OH - C_6H_6$], 77 (37) [$C_6H_5^+$], 47 (41) [PO^+]. Anal. Found: C, 70.70; H, 7.01. $C_{18}H_{21}O_2P \cdot 1/2(C_2H_5OH)$ (323.38) Calc.: C, 70.58; H, 7.43%.

4.3. (±)-trans-(2-Diphenylthiophosphinoyl)cyclohexanol (3)

2.84 g (10 mmol) of **1** and 0.35 g (10.9 mmol) of sulfur are dissolved in 100 ml of toluene. The solution is refluxed for 15 min and the solvent is removed in vacuo. The resulting colorless solid is dissolved in ethanol to remove excess sulfur, the solvent is removed and the product is recrystallized from ethylacetate giving **3** · H_2O. Yield: 3.0 g (95%) of colorless needles. M.p. 180 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3416 vs [ν(OH)], 3049 m, 2920 s, 2854 m, 1480 m, 1447 w, 1435 s, 1260 m, 1180w, 1097 vs, 1052 s, 1025 m, 988 w, 962 w, 800 m, 761 m, 745 vs, 706 vs, 691 vs, 624 vs, 610 vs, 523 vs, 504 s. ^1H NMR (400.13 MHz, 25 °C, $CDCl_3$): δ = 7.98 (ddd, $^3J_{P,o\text{-}H}$ = 10.5 Hz, $^3J_{o\text{-}H,m\text{-}H}$ = 7.5 Hz, $^4J_{o\text{-}H,p\text{-}H}$ = 2.0 Hz, o-H), 7.80 (ddd, $^3J_{P,o'\text{-}H}$ = 10.5 Hz, $^3J_{o'\text{-}H,m'\text{-}H}$ = 7.5 Hz, $^4J_{o'\text{-}H,p'\text{-}H}$ = 1.5 Hz, o'-H), 7.47–7.38 (m, 6H, ar-H), 4.10 (dddd, $^3J_{1\text{-}H,2\text{-}H}$ = 16.0 Hz, $^3J_{P,1\text{-}H}$ = $^3J_{1\text{-}H,6_{ax}\text{-}H}$ = 8.0 Hz, $^3J_{1\text{-}H,6_{eq}\text{-}H}$ = 4.0 Hz, 1-H), 2.70 (m, 2-H), 2.68 (d, $^4J_{P,H}$ = 3.0 Hz, OH), 2.03, 1.77, 1.64, 1.50, 1.10–1.36 (5 × m, 8H, al-H). $^{13}C\{^1H\}$ NMR (100.25 MHz, 25 °C, $CDCl_3$): δ = 134.0 (d, $^1J_{P,C\text{-}i}$ = 78.4 Hz, C-i), 131.8 (d, $^2J_{P,C\text{-}o}$ = 9.7 Hz, C-o), 131.4 (d, $^2J_{P,C\text{-}o'}$ = 10.7 Hz, C-o'), 131.2 (d, $^1J_{P,C\text{-}i'}$ = 77.5 Hz, C-i'), 131.2 (d, $^4J_{P,C\text{-}p}$ = 2.9 Hz, C-p), 131.2 (d, $^4J_{P,C\text{-}p'}$ = 2.9 Hz, C-p'), 128.4 (d, $^3J_{P,C\text{-}m}$ = 9.7 Hz, C-m), 128.3 (d, $^3J_{P,C\text{-}m'}$ = 9.7 Hz, C-m'), 70.6 (d, $^2J_{P,C\text{-}1}$ = 4.8 Hz, C-1), 45.1 (d, $^1J_{P,C\text{-}2}$ = 54.2 Hz, C-2), 35.0 (d, $^3J_{P,C\text{-}6}$ = 10.7 Hz, C-6), 25.9 (d, $^2J_{P,C\text{-}3}$ = 1.1 Hz, C-3), 25.6 (d, $^3J_{P,C\text{-}4}$ = 13.6 Hz, C-4), 24.4 (s, C-5). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): δ = 46.4. MS (EI), *m/e* (%): 316 (2) [M^+], 218 (100) [$M^+ - C_6H_9OH$], 185 (20) [$M^+ - C_6H_9O\text{–}S$], 183 (20) [$M^+ - C_6H_9OH\text{–}SH$], 140 (26) [$M^+ - C_6H_9OH - C_6H_6$], 63 (10) [PS^+]. Anal. Found: C, 63.84; H, 6.17. $C_{18}H_{21}OPS \cdot H_2O$ (334.42) Calc.: C, 64.65; H, 6.93%.

4.4. (±)-trans-Diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinicacidester (4) and (±)-trans-Diphenyl[(2-diphenylthiophosphinoyl)cyclohexyl]-phosphinicacidester (5)

10 mmol of **1** or **3** are dissolved in 100 ml of toluene and 6.3 ml (10 mmol) of a 1.6 M *n*-BuLi solution in *n*-hexane are added dropwise. Then 2.20 g (10 mmol) of freshly distilled chlorodiphenyl phosphine are added dropwise and the mixture is stirred for 2 h at room temperature while LiCl precipitates. After removing the solvent in vacuo, the residue is dissolved in CH_2Cl_2 and filtered over a short column filled with degassed

SiO_2. The solvent is removed in vacuo leading to highly viscous oils, which can be used for the following preparations of transition metal complexes without further purification. Yields: **4**: 3.1 g (66%); **5**: 3.5 g (70.0%). **4**: $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): $\delta = 104.8$ (s, P-2), -12.0 (s, P-1). **5**: $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): $\delta = 105.8$ (s, P-2), 47.7 (s, P-1).

*4.5. Syntheses of tetracarbonyl{(±)-trans-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinicacidester}-molybdenum(0) (**6**), carbonylchloro{(±)-trans-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinic-acidester}rhodium(I) (**7a,b**), dichloro{(±)-trans-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinic-acidester}palladium(II) (**8**), and dichloro{(±)-trans-diphenyl[(2-diphenylthiophosphinoyl)cyclohexyl]phosphinicacidester}palladium(II) (**9**)*

A solution of 3.0 mmol of the ligand **4** or **5** in 20 ml of CH_2Cl_2 is added to a solution of 3.0 mmol of the corresponding precursor compound $(pip)_2Mo(CO)_4$, $[(CO)_2Rh(\mu\text{-}Cl)]_2$, or $(C_6H_5CN)_2PdCl_2$ in 30 ml CH_2Cl_2 and the mixture is stirred for 1 h. After filtration to remove small amounts of insoluble byproducts, the solvent is removed in vacuo and the solid residues are recrystallized as described below.

6: Bright yellow crystals from diethylether, containing one molecule of the solvent per formula unit. Yield: 1.58 g (70%). IR (KBr, cm^{-1}): $\tilde{\nu} = 3074$ w, 3055 w, 2932 m, 2900 w, 2856 m, 2021 vs, 1927 vs, 1896 vs, 1880 vs [$4 \times \nu$(C=O)], 1480 m, 1448 m, 1435 s, 1183 w, 1114 m, 1094 s, 1071 m, 1025 s, 991 w, 967 m, 817 m, 794 m, 746 m, 695 s, 607 s, 589 s, 577 s, 553 s, 520 s, 512 s, 496 m, 421 m. IR (toluene, cm^{-1}): $\tilde{\nu} = 2025$ s, 1936 vs, 1903 vs, 1895 vs [$4 \times \nu$(C=O)]. ^1H NMR (400.13 MHz, 25 °C, C_6D_6): $\delta = 8.15$ (dd, $^3J_{P,o\text{-}H} = 9.8$ Hz, $^3J_{o\text{-}H,m\text{-}H} = 7.3$ Hz, o-H), 7.68 (dd, $^3J_{P,o'\text{-}H} = 9.0$ Hz, $^3J_{o'\text{-}H,m'\text{-}H} = 8.0$ Hz, o'-H), 7.60–7.50 (m, 4H, o''-H, o'''-H), 7.15–6.82 (m, 12H, ar-H), 4.02 (ddddd, $^3J_{P\text{-}2,1\text{-}H} = 15.3$ Hz, $^3J_{P\text{-}1,1\text{-}H} = {}^3J_{1\text{-}H,2\text{-}H} = 10.2$ Hz, $^3J_{1\text{-}H,6_{ax}\text{-}H} = {}^3J_{1\text{-}H,6_{eq}\text{-}H} = 5.1$ Hz, 1-H), 3.26 (q, $^3J_{H,H} = 7.0$ Hz, OCH_2CH_3), 2.42 (m, 2-H), 1.80, 1.61, 1.19 (3 × m, 3H, al-H), 1.12 (t, OCH_2CH_3), 1.01, 0.80–0.60 (2 × m, 5H, al-H). $^{13}C\{^1H\}$ NMR (100.25 MHz, 25 °C, C_6D_6): $\delta = 216.6$ (dd, $^2J_{P\text{-}1,C} = 21.4$ Hz, $^2J_{P\text{-}2,C} = 8.7$ Hz, CO-eq.), 215.6 (dd, $^2J_{P\text{-}21,C} = 29.2$ Hz, $^2J_{P\text{-}1,C} = 8.7$ Hz, CO-eq.), 213.5 (dd, $^2J_{P\text{-}1,C} = {}^2J_{P\text{-}2,C} = 9.7$ Hz, CO-ax.), 206.0 (dd, $^2J_{P\text{-}1,C} = {}^2J_{P\text{-}2,C} = 8.7$ Hz, CO-ax.), 142.0 (d, $^1J_{P\text{-}2,C\text{-}i''} = 46.5$ Hz, C-i''), 140.7 (d, $^1J_{P\text{-}2,C\text{-}i'''} = 34.9$ Hz, C-i'''), 140.2 (d, $^1J_{P\text{-}1,C\text{-}i} = 21.3$ Hz, C-i), 135.5 (d, $^2J_{P\text{-}2,C\text{-}o''} = 13.6$ Hz, C-o''), 134.2 (dd, $^1J_{P\text{-}1,C\text{-}i'} = 21.3$ Hz, $^3J_{P\text{-}1,C\text{-}i'} = 3.9$ Hz, C-i'), 132.8 (d, $^2J_{P\text{-}2,C\text{-}o'''} = 15.5$ Hz, C-o'''), 131.8 (d, $^2J_{P\text{-}2,C\text{-}o} = 10.6$ Hz, C-o), 131.3, 130.3, 129.5, 129.1 (4 × s, C-p, C-p', C-p'', C-p'''), 129.2 (d, $^2J_{P\text{-}2,C\text{-}o'} = 13.6$ Hz, C-o''), 128.6–127.9 (m, C-m, C-m', C-m'', C-m'''), 80.5 (s, $^2J_{P\text{-}2,C\text{-}1} < 2$ Hz, $^2J_{P\text{-}1,C\text{-}1} < 2$ Hz, C-1), 65.9 (s, OCH_2CH_3), 42.2 (d, $^1J_{P\text{-}1,C\text{-}2} = 16.5$ Hz, C-2), 35.5 (s, $^3J_{P\text{-}2,C\text{-}6} < 2$ Hz, $^3J_{P\text{-}1,C_36} < 2$ Hz, C-6), 29.4 (s, $^3J_{P\text{-}1,C\text{-}3} < 2$ Hz, C-3), 26.4 (d, $^3J_{P\text{-}1,C\text{-}4} = 6.8$ Hz, C-4), 24.9 (s, C-5), 15.5 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, C_6D_6): $\delta = 145.1$ (d, $^2J_{P\text{-}1,P\text{-}2} = 35.8$ Hz, P-2), 35.9 (d, P-1). Anal. Found: C, 60.62; H, 5.32. $C_{34}H_{30}MoO_5P_2 \cdot C_4H_{10}O$ (750.62) Calc.: C, 60.81; H, 5.37%.

7a,b: Yellow crystals from CH_2Cl_2 by slow diffusion of diethylether, containing one molecule of the solvent per formula unit. Yield: 1.24 g (65%) of a 1:1 mixture of **7a,b**. IR (KBr, cm^{-1}): $\tilde{\nu} = 3069$ w, 3052 w, 2931 m, 2850 m, 2013 vs [ν(C=O)], 1481 m, 1435 s, 1101 s, 1022 s, 974 m, 830 m, 748 m, 693 s, 572 s, 545 m, 5245 s, 473 m. IR (CH_2Cl_2, cm^{-1}): $\tilde{\nu} = 2021$ vs [ν(C=O)]. $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): **7a**: $\delta = 108.5$ (dd, $^1J_{Rh,P\text{-}2} = 151.5$ Hz, $^2J_{P\text{-}1,P\text{-}2} = 17.8$ Hz, P-2), 29.8 (dd, $^1J_{Rh,P\text{-}1} = 139.6$ Hz, P-1); **7b**: $\delta = 105.2$ (dd, $^1J_{Rh,P\text{-}2} = 139.6$ Hz, $^2J_{P\text{-}1,P\text{-}2} = 17.8$ Hz, P-2), 27.9 (dd, $^1J_{Rh,P\text{-}1} = 121.8$ Hz, P-1). MS (FAB), *m/e* (%): 571 (80) [$M^+ - CO - Cl$]. Anal. Found: C, 58.39; H, 4.86; P, 10.22. $C_{31}H_{30}ClO_2P_2Rh$ (634.89) Calc.: C, 58.65; H, 4.76; P, 9.76%.

NMR spectroscopic data of **7c**: $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): $\delta = 129.9$ (dd, $^1J_{Rh,P\text{-}2} = 169.3$ Hz, $^2J_{P\text{-}1,P\text{-}2} = 56.4$ Hz, P-2), 20.6 (dd, $^1J_{Rh,P\text{-}1} = 121.8$ Hz, P-1).

8: Bright yellow crystals from CH_2Cl_2 by slow diffusion of diethylether, containing one molecule of CH_2Cl_2 per formula unit. Yield: 1.67 g (76%). IR (KBr, cm^{-1}): $\tilde{\nu} = 3052$ m, 3015 w, 2946 w, 2924 m, 2885 w, 2860 m, 2839, 1481 m, 1436 s, 1308 w, 1270 m, 1185 w, 1160 w, 1129 w, 1101 vs, 1011 vs, 998 m, 974 vs, 902 m, 876 w, 834 s, 747 s, 732 s, 690 vs, 568 s, 512 vs. ^1H NMR (400.13 MHz, 25 °C, $CDCl_3$, protons x and x' belong to phenyl groups at P1, protons x'' and x''' belong to phenyl groups at P2): $\delta = 8.21$ (ddd, $^3J_{P\text{-}2,o''\text{-}H} = 12.6$ Hz, $^3J_{o''\text{-}H,m''\text{-}H} = 8.6$ Hz, $^4J_{o''\text{-}H,p''\text{-}H} = 1.5$ Hz, o''-H), 8.06 (ddd, $^3J_{P\text{-}2,o'''\text{-}H} = 11.5$ Hz, $^3J_{o'''\text{-}H,m'''\text{-}H} = 8.5$ Hz, $^4J_{o'''\text{-}H,p'''\text{-}H} = 1.5$ Hz, o'''-H), 7.70 (ddd, $^3J_{P\text{-}1,o\text{-}H} = 12.6$ Hz, $^3J_{o\text{-}H,m\text{-}H} = 8.6$ Hz, $^4J_{o\text{-}H,p\text{-}H} = 1.5$ Hz, o-H), 7.63 (ddd, $^3J_{P\text{-}1,o'\text{-}H} = 12.6$ Hz, $^3J_{o'\text{-}H,m'\text{-}H} = 8.0$ Hz, $^4J_{o'\text{-}H,p'\text{-}H} = 1.5$ Hz, o'-H), 7.61 (ttd, $^3J_{p''\text{-}H,m''\text{-}H} = 7.5$ Hz, $^5J_{P\text{-}2,p''\text{-}H} = 3.0$ Hz, p''-H), 7.55 (td, $^4J_{P\text{-}2,m''\text{-}H} = 3.0$ Hz, m''-H), 7.52 (ttd, $^3J_{p''\text{-}H,m''\text{-}H} = 7.3$ Hz, $^5J_{P\text{-}2,p'''\text{-}H} = 2.0$ Hz, p'''-H), 7.47 (td, $^4J_{P\text{-}2,m'''\text{-}H} = 3.0$ Hz, m'''-H), 7.47 (ttd, $^5J_{P\text{-}1,p\text{-}H} = 3.7$ Hz, $^3J_{p\text{-}H,m\text{-}H} = 7.4$ Hz, p-H), 7.43 (ttd, $^5J_{p'\text{-}H} = 3.7$ Hz, $^3J_{p'\text{-}H,m'\text{-}H} = 7.4$ Hz, p'-H), 7.40 (td, $^4J_{P\text{-}1,m\text{-}H} = 4.4$ Hz, m-H), 7.35 (td, $^4J_{P\text{-}1,m'\text{-}H} = 4.4$ Hz, m'-H), 3.78 (ddddd, $^3J_{P\text{-}1,1\text{-}H} = {}^3J_{P\text{-}2,1\text{-}H} = {}^3J_{1\text{-}H,6_{ax}\text{-}H} = {}^3J_{1\text{-}H,2\text{-}H} = 10.0$ Hz, $^3J_{1\text{-}H,6_{eq}\text{-}H} = 5.0$ Hz, 1-H), 2.33 (m, 2-H), 1.94 (m, 6_{eq}-H), 1.72–1.53 (m, 3_{eq}-H, 4_{eq}-H, 5_{eq}-H, 6_{ax}-H), 1.20 (m, 5_{ax}-H), 1.05 (m, 1H, 4_{ax}-H), 0.75 (m, 1H, 3_{ax}-H). $^{13}C\{^1H\}$ NMR (100.25 MHz, 25 °C, $CDCl_3$, nuclei x and x' belong to

phenyl groups at P1, nuclei x″ and x‴ belong to phenyl groups at P2): δ = 134.9 (d, $^{2}J_{P\text{-}2,C\text{-}o''}$ = 11.6 Hz, C-o″$_2$), 134.6 (d, $^{2}J_{P\text{-}2,C\text{-}o'''}$ = 12.6 Hz, C-o‴), 134.1 (d, $^{2}J_{P\text{-}1,C\text{-}o}$ = 9.7 Hz, C-o), 132.9 (d, $^{4}J_{P\text{-}2,C\text{-}p''}$ = 2.9 Hz, C-p″), 132.4 (d, $^{1}J_{P\text{-}2,C\text{-}i''}$ = 43.5 Hz, C-i″), 132.4 (d, $^{2}J_{P\text{-}1,C\text{-}o''}$ = 11.6 Hz, C-o′), 131.8 (d, $^{4}J_{P\text{-}1,C\text{-}p'}$ = 2.9 Hz, C-p′), 131.8 (d, $^{1}J_{P\text{-}2,C\text{-}i'''}$ = 25.1 Hz, C-i‴), 131.7 (d, $^{4}J_{P\text{-}2,C\text{-}p'''}$ = 2.9 Hz, C-p‴), 131.5 (d, $^{4}J_{C\text{-}p}$ = 2.9 Hz, C-p), 128.9 (d, $^{3}J_{P\text{-}2,C\text{-}m''}$ = 11.7 Hz, C-m″), 128.7 (d, $^{3}J_{P\text{-}2,C\text{-}m'''}$ = 11.8 Hz, C-m‴), 128.3 (d, $^{3}J_{P\text{-}1,C\text{-}m}$ = 11.6 Hz, C-m), 128.1 (d, $^{3}J_{P\text{-}1,C\text{-}m'}$ = 11.6 Hz, C-m′), 127.3 (d, $^{1}J_{P\text{-}1,C\text{-}i}$ = 57.1 Hz, C-i), 127.2 (d, $^{1}J_{P\text{-}1,C\text{-}i'}$ = 55.2 Hz, C-i′), 77.2 (d, $^{2}J_{P\text{-}2,C\text{-}1}$ = 21.4 Hz, C-1), 36.9 (dd, $^{1}J_{P\text{-}1,C\text{-}2}$ = 30.9 Hz, $^{3}J_{P\text{-}1,C\text{-}2}$ = 4.8 Hz, C-2), 35.0 (t, $^{3}J_{P\text{-}1,C\text{-}6}$ = 6.8 Hz, $^{3}J_{P\text{-}2,C\text{-}6}$ = 6.8 Hz, C-6), 28.2 (d, $^{2}J_{P\text{-}1,C\text{-}3}$ = 5.8 Hz, C-3), 25.8 (d, $^{3}J_{P\text{-}1,C\text{-}4}$ = 8.8 Hz, C-4), 24.0 (C-5). ^{31}P{^{1}H} NMR (161.98 MHz, 25 °C, $CDCl_3$): δ = 105.2 (s, P-2), 23.9 (s, P-1). MS (CI), *m/e* (%): 391 (100) [$M^+ - PdCl_2 - C_6H_5$], 285 (12) [$M^+ - PdCl_2 - P(C_6H_5)_2$]. Anal. Found: C, 50.93; H, 4.44; Cl, 19.02. $C_{30}H_{30}Cl_2OP_2Pd \cdot CH_2Cl_2$ (730.77) Calc.: C, 50.95; H, 4.41; Cl, 19.40%.

9: Orange colored crystals from CH_2Cl_2 by slow diffusion of diethylether. Yield: 1.79 g (88%). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055 m, 2940 m, 2908 w, 2885 w, 2850 m, 1586 w, 1482 m, 1437 vs, 1375 m, 1314 w, 1186 w, 1160 w, 1104 vs, 1025 m, 1013 s, 998 m, 969 s, 908 m, 878 m, 831 s, 799 m, 755 m, 742 s, 716 m, 702 s, 687 s, 578 s, 553 s, 534 vs, 522 vs, 508 m, 476 m, 450 m. ^{1}H NMR (400.13 MHz, 25 °C, CD_2Cl_2, protons x and x′ belong to phenyl groups at P1, protons x″ and x‴ belong to phenyl groups at P2): δ = 8.05 (ddd, $^{3}J_{P\text{-}2,o''\text{-}H}$ = 13.0 Hz, $^{3}J_{o''\text{-}H,m''\text{-}H}$ = 8.0 Hz, $^{4}J_{o''\text{-}H,p''\text{-}H}$ = 1.5 Hz, o″-H), 7.87 (ddd, $^{3}J_{P\text{-}2,o'''\text{-}H}$ = 12.6 Hz, $^{3}J_{o'''\text{-}H,m'''\text{-}H}$ = 7.8 Hz, $^{4}J_{o'''\text{-}H,p'''\text{-}H}$ = 1.5 Hz, o‴-H), 7.59 (ddd, $^{3}J_{P\text{-}1,o\text{-}H}$ = 12.6 Hz, $^{3}J_{o\text{-}H,m\text{-}H}$ = 8.3 Hz, $^{4}J_{o\text{-}H,p\text{-}H}$ = 1.5 Hz, o-H), 7.52 (ddd, $^{3}J_{P\text{-}1,o'\text{-}H}$ = 15.1 Hz, $^{3}J_{o'\text{-}H,m'\text{-}H}$ = 8.0 Hz, $^{4}J_{o'\text{-}H,p'\text{-}H}$ = 2.0 Hz, o′-H), 7.50–7.32 (m, 10H, p″-H, p‴-H, m-H, m′-H, m″-H, m‴-H), 7.23 (2 × td, 2H, $^{3}J_{p\text{-}H,m\text{-}H} = {}^{3}J_{p'\text{-}H,m'\text{-}H}$ = 8.0 Hz, $^{5}J_{P\text{-}1,p\text{-}H} = {}^{5}J_{p'\text{-}H}$ = 3.0 Hz, p-H, p′-H), 4.72 (ddddd, $^{3}J_{P\text{-}1,1\text{-}H}$ = 13.0 Hz, $^{3}J_{P\text{-}2,1\text{-}H} = {}^{3}J_{1\text{-}H,6ax\text{-}H}$ = 9.0 Hz, $^{3}J_{1\text{-}H,2\text{-}H_2}$ = 10.5 Hz, $^{3}J_{1\text{-}H,6eq\text{-}H}$ = 4.5 Hz, 1-H), 3.07 (dddd, $^{2}J_{P,2\text{-}H}$ = 14.0 Hz, $^{3}J_{2\text{-}H,3eq\text{-}H} = {}^{3}J_{2\text{-}H,3ax\text{-}H}$ = 3.5 Hz, 2-H), 1.71–0.80 (m, 3_{ax}-H, 3_{eq}-H, 4_{ax}-H, 4_{eq}-H, 5_{ax}-H, 5_{eq}-H, 6_{ax}-H). ^{13}C{^{1}H} NMR (100.25 MHz, 25 °C, CD_2Cl_2, nuclei x and x′ belong to phenyl groups at P1, nuclei x″ and x‴ belong to phenyl groups at P2): δ = 135.3 (d, $^{1}J_{P\text{-}2,C\text{-}i''}$ = 56.0 Hz, C-i″), 133.6 (d, $^{2}J_{P\text{-}2,C\text{-}o''}$ = 13.5 Hz, C-o″$_2$), 133.6 (d, $^{4}J_{P\text{-}2,C\text{-}p''}$ = 2.9 Hz, C-p″), 133.4 (d, $^{2}J_{P\text{-}2,C\text{-}o'''}$ = 11.6 Hz, C-o‴), 133.3 (d, $^{4}J_{P\text{-}2,C\text{-}p'''}$ = 2.9 Hz, C-p‴), 132.6 (d, $^{4}J'_{P\text{-}1,C\text{-}p}$ = 1.9 Hz, C-p′), 132.5 (d, $^{2}J_{P\text{-}1,C\text{-}o}$ = 8.7 Hz, C-o), 132.0 (d, $^{4}J_{P\text{-}1,C\text{-}p}$ = 2.9 Hz, C-p), 132.0 (d, $^{2}J_{P\text{-}1,C\text{-}o'}$ = 11.0 Hz, C-o′), 129.6 (d, $^{3}J_{P\text{-}2,C\text{-}m''}$ = 12.6 Hz, C-m″), 129.5 (d, $^{3}J_{P\text{-}2,C\text{-}m'''}$ = 12.5 Hz, C-m‴), 129.0 (d, $^{1}J_{P\text{-}2,C\text{-}i'''}$ = 53.9 Hz, C-i‴), 128.7 (d, $^{3}J_{P\text{-}1,C\text{-}m}$ = 10.6 Hz, C-m), 128.4 (d, $^{3}J_{P\text{-}1,C\text{-}m'}$ = 11.6 Hz, C-m′), 127.1 (d, $^{1}J_{P\text{-}1,C\text{-}i}$ = 73.3 Hz, C-i), 125.1 (d, $^{1}J_{P\text{-}1,C\text{-}i'}$ = 83.1 Hz, C-i′), 78.3 (d, $^{2}J_{P\text{-}2,C\text{-}1}$ = 4.8 Hz, C-1), 43.5 (dd, $^{1}J_{P\text{-}1,C\text{-}2}$ = 47.3 Hz, $^{3}J_{P\text{-}1,C\text{-}2}$ = 4.8 Hz, C-2), 32.9 (d, $^{3}J_{P\text{-}1,C\text{-}6}$ = 10.6 Hz, C-6), 26.4 (s, C-3), 25.3 (d, $^{3}J_{P\text{-}1,C\text{-}4}$ = 13.5 Hz, C-4), 24.3 (C-5). ^{31}P{^{1}H} NMR (161.98 MHz, 25 °C, $CDCl_3$): δ = 120.7 (s, P-2), 48.9 (s, P-1). Anal. Found: C, 52.60; H, 4.50; Cl, 10.88; P, 9.01; Pd, 15.2; S, 5.11. $C_{30}H_{30}Cl_2OP_2PdS$ (677.90) Calc.: C, 53.15; H, 4.46; Cl, 10.46; P, 9.14; Pd, 15.70; S, 4.73%.

4.6. Structure determination of 2, 8, and 9

X-ray diffraction data for **2** and **9** were collected on a STOE IPDS, for **8** on an Enraf–Nonius MACH3 diffractometer. The diffraction data were corrected for Lorentz and polarisation effects. The structures were solved by direct (**2**, **8**) or Patterson methods (**9**) and refined by the full-matrix least-squares method using the programs SHELXS-86 resp. SHELXL-93 [21]. All non-H atoms were refined anisotropically and all H atoms were located in the difference Fourier maps and refined with isotropic thermal parameters. The weighting scheme was calculated to $w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.2527P]$ for **2**, to $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 4.6755P]$ for **8**, and to $w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 0.3775P]$ for **9**, where $P = (F_o^2 + 2F_c^2)/3$. Further crystal data and collection parameters are summarized in Table 2.

5. Supplementary material available

Complete lists of crystal structure data, bond lengths and angles, and tables of hydrogen atom coordinates and thermal parameters are available on request from the Cambridge Crystallographic Data Centre on quoting the names of the authors and the journal citation.

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