Chiral Bisphosphanes, III[◇]

P-Alkylated (1*S*,2*S*)-Cyclopentane-1,2-diylbisphosphanes with Four Stereogenic Centers and Some Group 10 Metal(II) Complexes Containing the (1*S*,2*S*)-$C_5H_8[P(CH_3)C_8H_{15}$-*cyclo*$]_2$ Ligand

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Radical-initiated P−H addition of (1*S*,2*S*)-$C_5H_8(PH_2)_2$ to cycloalkenes gave bis(secondary phosphanes), (1*S*,2*S*)-$C_5H_8[P(H)C_nH_{2n-1}$-*cyclo*$]_2$ (n = 5−8), as mixtures of $R_P,R_{P'}$, $S_P,S_{P'}$, and $R_P,S_{P'}$ diastereomers. The three diastereomers of the peralkylated chiral P_2 ligand (1*S*,2*S*)-$C_5H_8[P(CH_3)C_8H_{15}$-*cyclo*$]_2$ and its complexes with $NiCl_2$, PdI_2, and PtI_2 were prepared. The structures of [(1*S*,2*S*)-$C_5H_8\{P(CH_3)C_8H_{15}$-*cyclo*-(*R*)$\}_2NiCl_2$]·[(1*S*,2*S*)-$C_5H_8\{P(CH_3)C_8H_{15}$-*cyclo*-(*S*)$\}_2NiCl_2$], (1*S*,2*S*)-$C_5H_8\{P(CH_3)C_8H_{15}$-*cyclo*-(*R*)$\}_2PdI_2$, and (1*S*,2*S*)-$C_5H_8\{P(CH_3)C_8H_{15}$-*cyclo*-(*R*)$\}_2PtI_2$ were determined by X-ray diffraction.

The development of novel chiral ligands for applications in catalysis continues to be an important field of synthetic organic and organometallic chemistry[3]. Optically stable bidentate phosphanes exhibiting C_2 chirality in their carbon frameworks are among the most successful ligands employed in a variety of transition metal-catalyzed enantioselective hydrogenations[4]. In many of these widely used chelating bisphosphanes the phosphorus atoms bear two aryl substituents. The correct orientation of these aryl substituents in the coordination sphere has been identified as a stereochemically important feature contributing to the "recognition ability" of the metal complex[5]. The traditional route to this class of compounds involves the nucleophilic substitution with alkali metal diarylphosphides of enantiopure ditosylates derived from optically active natural precursors. This approach suffers the disadvantage that it cannot be applied to the preparation of *P*-alkylated analogs. Attempted replacement reactions using alkali metal dialkylphosphides thus resulted in products originating from P−P coupling and elimination rather than substitution[6]. Our objective has been the development of more variable methods for the synthesis of chiral bidentate phosphorus ligands, starting from the *resolved enantiomers* of chiral bis(primary phosphanes)[1], $H_2P{\cap}PH_2$, and bis(phosphonous dichlorides)[7], $Cl_2P{\cap}PCl_2$, respectively. In this report we describe how the radical-chain addition of the P−H bonds of (1*S*,2*S*)-cyclopentane-1,2-diylbis(phosphane), (1*S*,2*S*)-$C_5H_8(PH_2)_2$ (**1**)[1], across the >C=C< double bonds of several cycloalkenes can conveniently be exploited for the high-yield synthesis of bis(secondary) and bis(tertiary) P_2 ligands (1*S*,2*S*)-$C_5H_8[P(R')R]_2$ (R = cycloalkyl, R′ = H, Me) having chiral phosphorus centers supported on an asymmetric carbon backbone.

Results and Discussion

The AIBN-initiated addition of the $-PH_2$ functions of optically pure **1** across the carbon−carbon double bonds of cycloalkenes C_nH_{2n-2} [AIBN = α,α′-azobis(isobutyronitrile); n = 5−8] in the absence of a diluting solvent (Scheme 1) was employed as a method for the synthesis of (1*S*,2*S*)-cyclopentane-1,2-diyl-linked bis(secondary phosphanes) (1*S*,2*S*)-$C_5H_8[P(H)R]_2$, where R = *cyclo*-C_5H_9 (**2**), *cyclo*-C_6H_{11} (**3**), *cyclo*-C_7H_{13} (**4**), or *cyclo*-C_8H_{15} (**5**). Formation of higher alkylated by-products resulting from consecutive P−H/>C=C< addition steps did not occur in any of the preparations leading to **3**−**5**. We note, however, the observation of threefold and/or completely alkylated derivatives in reactions between **1** and cyclopentene if the latter was employed in a higher than 30-fold excess.

As anticipated for a free-radical-initiated reaction, no diastereoselectivity was observed in any of the examples studied; i. e., a more or less statistical mixture of $R_P,R_{P'}$, $R_P,S_{P'}$ (= $S_P,R_{P'}$), and $S_P,S_{P'}$ diastereomers was obtained in each case. Those compounds with like chirality at phosphorus ($R_P,R_{P'}$ and $S_P,S_{P'}$) are C_2-symmetric and, hence, show ^{31}P-NMR singlet signals; the presence of unlike configurations at the phosphorus atoms of the $R_P,S_{P'}$ isomers renders the two ^{31}P nuclei inequivalent, thus giving rise to AB doublets. For example, the stereoisomeric mixture of bisphosphanes **5** displayed ^{31}P-NMR singlets at δ = −29.30

[◇] Parts I and II: Refs.[1][2]

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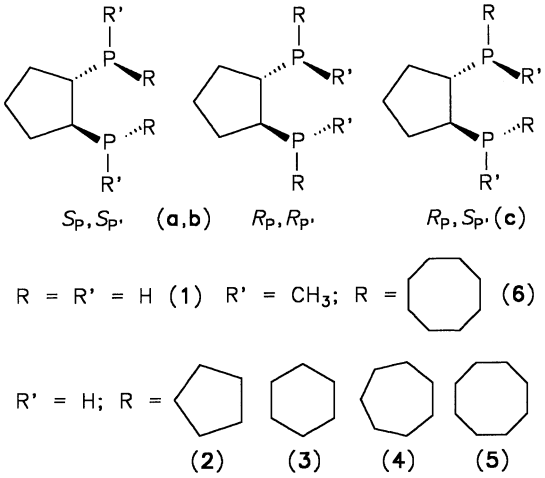
Scheme 1



(C_2-symmetric diastereomer **5a**; 31%) and δ = −22.79 (C_2-symmetric diastereomer **5b**, 19%), together with an AB spectrum characterized by $\delta(P_A)$ = −22.45, $\delta(P_B)$ = −29.52, and $^3J(P_A,P_B)$ = 6.8 Hz ($R_P,S_{P'}$ diastereomer **5c**; 50%).

While the >PH signals of compound **2** suffered from spectral overlap, the >PH groups of one of the two C_2-symmetric diastereomers of bisphosphanes **3**−**5** emerged as (deceptively simple) AA′ subspectra of AMNXX′N′M′A′ spin systems, as expected for $H_AP_X(CH_M<)$-$CH_NCH_{N'}P_{X'}(CH_{M'}<)H_{A'}$ building blocks of symmetry C_2 [$\delta(^1H) \approx 3.3$; $^1J(P,H) \approx 195$, $^3J(H,H) \approx 5$ Hz]. Two-dimensional $\delta(^{31}P\{^1H\})-\delta(^1H\{^{31}P\})$-correlated NMR spectroscopy showed the resonating protons H_A and $H_{A'}$ to be associated with those ^{31}P nuclei that gave rise to the "lower frequency"-singlets, assigned to stereoisomers "**3a**"−"**5a**" [−36 < $\delta(^{31}P)$ < −29]. Furthermore, chemical shift correlation was evident for the "diastereomer **b**"-^{31}P singlet resonances located at higher frequencies [−28 < $\delta(^{31}P)$ < −22] and >P*H* multiplets centered at $\delta(^1H) \approx 3.0$. The contour map demonstrated that the latter proton resonances are also associated with ^{31}P doublets resulting from those phosphorus nuclei P_A of $R_P,S_{P'}$-configurated diastereomers **3c**−**5c**, which were found to resonate at high frequencies, close to the mutually equivalent nuclei of diastereomers **3b**−**5b**. Finally, the correlation spectra enabled the chemical shifts $\delta(P_B)$ of diastereomers **3c**−**5c**, having values similar to those of diastereomers **3a**−**5a**, to be associated with >P*H* multiplets centered around δ = 3.5.

Deprotonation of **5** using 2 equiv. of methyllithium in diethyl ether, followed by hydrolysis of the dilithio derivative so generated, caused the diastereomeric distribution to change in favor of the one diastereomer, **5b**, having its ^{31}P chemical shift at δ = −22.79; diastereomeric distribution after de- and re-protonation: **5a** (16%), **5b** (40%), **5c** (44%). An even more pronounced diastereoselectivity was encountered if the diastereomeric mixture of the dilithiated phosphanes (1*S*,2*S*)-$C_5H_8[P(Li)C_8H_{15}$-*cyclo*$]_2$ was allowed to interact with methyl iodide as an electrophile. The bis(tertiary phosphane) (1*S*,2*S*)-$C_5H_8[P(CH_3)C_8H_{15}$-*cyclo*$]_2$ (**6**) obtained in this way gave ^{31}P-NMR singlets at δ = −11.82 (C_2-symmetric diastereomer **6a**; 72%) and δ = −10.02 (C_2-symmetric diastereomer **6b**; 4%), along with two AB doublets at $\delta(P_A)$ = −6.01 and $\delta(P_B)$ = −14.04 [$^3J(P_A,P_B)$ = 6.2 Hz] originating from the $R_P,S_{P'}$-configurated donor atoms of diastereomer **6c** (24%).

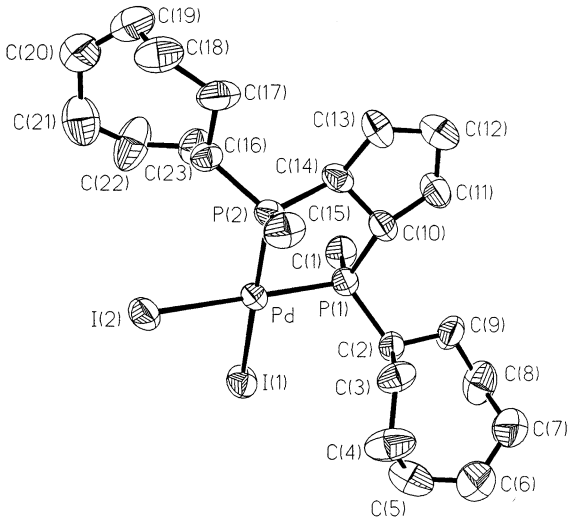
While unequivocal assignment of $R_P,R_{P'}$ or $S_P,S_{P'}$ configuration was not feasible for the C_2-symmetric isomers **a** and **b** in the family of bisphosphanes **2**−**5**, differentiation between the $R_P,R_{P'}$ and $S_P,S_{P'}$ diastereomers was achieved for the bis(tertiary) ligand **6** by structural characterization of three of its nickel, palladium, and platinum complexes [**6**·MX_2] (X = Cl, I). Stirring the diastereomeric mixture **6a**−**c** with $NiCl_2 \cdot 6\,H_2O$ in ethanol or with (1,5-C_8H_{12})PdI_2 or (1,5-C_8H_{12})PtI_2 in dichloromethane cleanly produced the MX_2 adducts (1*S*,2*S*)-$C_5H_8\{P(CH_3)C_8H_{15}$-*cyclo*$\}_2NiCl_2$ (**7**), (1*S*,2*S*)-$C_5H_8\{P(CH_3)C_8H_{15}$-*cyclo*$\}_2PdI_2$ (**8**), and (1*S*,2*S*)-$C_5H_8P(CH_3)C_8H_{15}$-*cyclo*$\}_2PtI_2$ (**9**). The diastereomeric distributions of metal complexes **7**−**9** were found to be largely identical with those of the free ligand **6**. For example, the isomeric mixture of palladium complex **8** contained the C_2-symmetric stereoisomers **8a** [$\delta(^{31}P)$ = 42.83] and **8b** [$\delta(^{31}P)$ = 43.93] accompanied by the $R_P,S_{P'}$-configurated diastereomer **8c** [$\delta(P_A)$ = 47.66, $\delta(P_B)$ = 40.97; $J(P_A,P_B)$ = 20.7 Hz] in proportions of 70%, 3%, and 27%, respectively, suggesting that non-selective coordination rather than preferential binding of one particular stereoisomer **6a**, **6b**, or **6c** had occurred during complex formation.

For the platinum complex, selective precipitation of the prevalent isomer **9a** [$\delta(^{31}P)$ = 24.94] from solution was observed upon crystallzing the mixture of diastereomers **9a**−**c** from chloroform. Column chromatography on silica gel was used to separate the predominant stereoisomers of the nickel and palladium homologues **7a** [$\delta(^{31}P)$ = 42.28] and **8a** [$\delta(^{31}P)$ = 42.83] from their isomeric mixtures. Elution with ethyl acetate/acetone and dichloromethane provided palladium complex **8a** as diastereomerically pure crystals. For the nickel compound, on the other hand, the overall separation remained somewhat unsatisfactory as ^{31}P-NMR spectroscopy showed the predominant diastereomer **7a** to persistently contain ca. 5% of its minor C_2-symmetric diastereomer **7b** [$\delta(^{31}P)$ = 41.17], even after repeated attempts at chromatographic purification.

The configuration at phosphorus in **8a** (= [**6a**·PdI_2]) was established by X-ray diffraction as $R_P,R_{P'}$ (Figure 1), indicating that the uncoordinated bisphosphane diastereomer **6a** has to be assigned $S_P,S_{P'}$ stereochemistry. According to the results of an X-ray structure determination, platinum complex **9a** also has the $R_P,R_{P'}$ configuration (Figure 2). Moreover, crystals of **8a** and **9a** showed isotypism, both belonging to the same tetragonal space group $P4_1$ with virtually identical lattice constants and atomic positions. Samples of (1*S*,2*S*)-C_5H_8 $\{P(CH_3)C_8H_{15}$-*cyclo*$\}_2NiCl_2$ (**7**), largely enriched in diastereomer **7a** (vide supra) by chromatographic work-up, were found to crystallize with difficulty. Eventually, an X-ray diffraction study of a suitable speci-

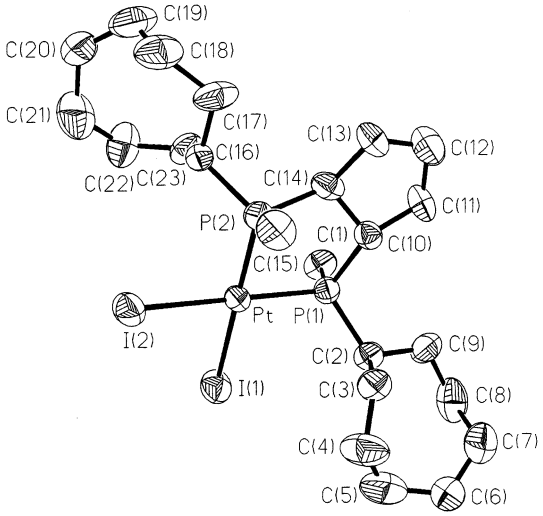
men grown from acetone revealed that **7a** and its minor C_2-symmetric stereoisomer **7b** tend to co-crystallize, forming $[(1S,2S)\text{-}C_5H_8\{P(CH_3)C_8H_{15}\text{-}cyclo\text{-}(R)\}_2NiCl_2]\cdot[(1S,2S)\text{-}C_5H_8\{P(CH_3)C_8H_{15}\text{-}cyclo\text{-}(S)\}_2NiCl_2]$, **7a·7b** (see Figures 3 and 4), irrespective of their divergent concentrations present in solution.

Figure 1. Molecular Structure of $(1S,2S)\text{-}C_5H_8\{P(CH_3)C_8H_{15}\text{-}cyclo\text{-}(R)\}_2PdI_2$ (**8a**)[a]



[a] Selected bond lengths [Å] and angles [°]: Pd−P(1), 2.257(2); Pd−P(2), 2.256(2); Pd−I(1), 2.6483(9); Pd−I(2), 2.6442(9). P(1)−Pd−P(2), 87.22(7); P(1)−Pd−I(1), 89.81(5); P(1)−Pd−I(2), 175.71(6); P(2)−Pd−I(1), 175.54(6); P(2)−Pd−I(2), 89.75(5); I(1)−Pd−I(2), 93.38(2).

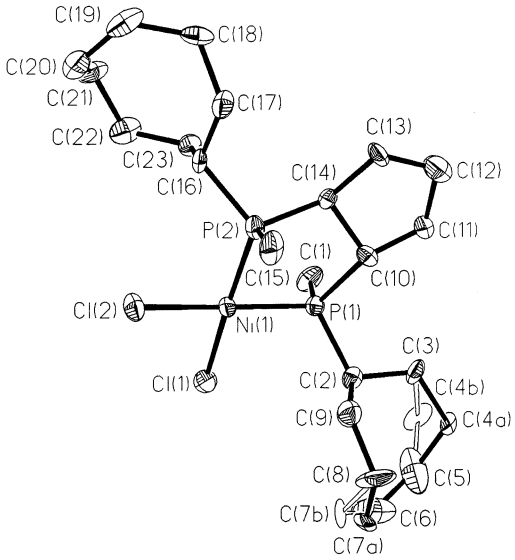
Figure 2. Molecular Structure of $(1S,2S)\text{-}C_5H_8\{P(CH_3)C_8H_{15}\text{-}cyclo\text{-}(R)\}_2PtI_2$ (**9a**)[a]



[a] Selected bond lengths [Å] and angles [°]: Pt−P(1), 2.236(3); Pt−P(2), 2.237(3); Pt−I(1), 2.6480(9); Pt−I(2), 2.6481(9). P(1)−Pt−P(2), 87.7(1); P(1)−Pt−I(1), 90.39(7); P(1)−Pt−I(2), 176.63(8); P(2)−Pt−I(1), 176.74(8); P(2)−Pt−I(2), 90.38(8); I(1)−Pt−I(2), 91.62(3).

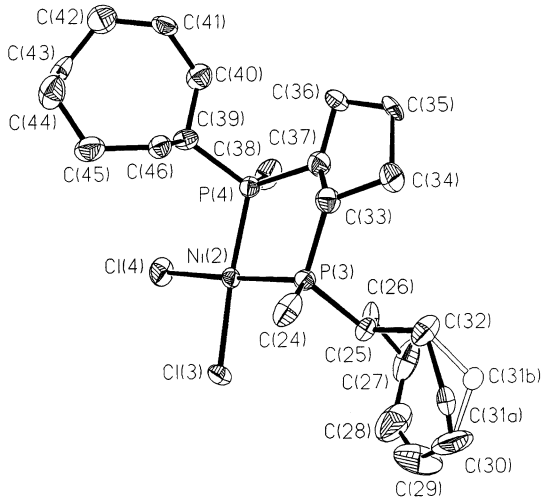
The three X-ray structure analyses revealed the expected presence of square planar molecules, as evidenced (i) from the sum of the four interligand *cis* angles, 360.1°, and (ii) from the angles between the normals to the two planes de-

Figure 3. Molecular Structure of $(1S,2S)\text{-}C_5H_8\{P(CH_3)C_8H_{15}\text{-}cyclo\text{-}(R)\}_2NiCl_2$ (**7a**)[a]



[a] Selected bond lengths [Å] and angles [°]: Ni(1)−P(1), 2.161(3); Ni(1)−P(2), 2.158(3); Ni(1)−Cl(1), 2.214(3); Ni(1)−Cl(2), 2.215(3). P(1)−Ni(1)−P(2), 88.4(1); P(1)−Ni(1)−Cl(1), 87.9(1); P(1)−Ni(1)−Cl(2), 175.8(1); P(2)−Ni(1)−Cl(1), 175.7(1); P(2)−Ni(1)−Cl(2), 88.5(1); Cl(1)−Ni(1)−Cl(2), 95.3(1).

Figure 4. Molecular Structure of $(1S,2S)\text{-}C_5H_8\{P(CH_3)C_8H_{15}\text{-}cyclo\text{-}(S)\}_2NiCl_2$ (**7b**)[a]



[a] Selected bond lengths [Å] and angles [°]: Ni(2)−P(1), 2.157(3); Ni(2)−P(2), 2.166(3); Ni(2)−Cl(3), 2.216(3); Ni(2)−Cl(4), 2.208(3). P(3)−Ni(2)−P(4), 89.0(1), P(3)−Ni(2)−Cl(3), 87.7(1); P(3)−Ni(2)−Cl(4), 177.3(1); P(4)−Ni(2)−Cl(3), 175.4(1); P(4)−Ni(2)−Cl(4), 88.6(1); Cl(3)−Ni(2)−Cl(4), 94.7(1).

fined by the MX_2 and MP_2 fragments. These dihedral angles amount to only 3.5° in molecules **7a** and **7b** of the nickel compound, the values for the palladium and platinum complexes **8a** and **9a** being 4.4° and 3.8°, respectively. The P−M−P bite-angle of the chelate ligand is almost the same in **8a** [87.22(7)°] and **9a** [87.7(1)°] and increases only slightly to 88.4(1)° and 89.0(1)° on going to structures **7a** and **7b**. The M−P distances range from 2.157(3) to 2.166(3) Å for *d*(Ni−P) in **7a·7b**, but are 2.256(3) and 2.257(3) Å

for *d*(Pd−P) in molecule **8a**. The M−P bonds of platinum complex **9a**, with lengths of 2.236(3) and 2.237(3) Å, are somewhat shorter than those of its lower homologue **8a**, whereas the lengths of the M−I bonds in the two molecules, 2.649(1) Å (M = Pd) and 2.648(1) Å (M = Pt), are equal within their standard deviations. While the torsion angle between the two planes through P(1), C(10), C(14) and C(10), C(14), P(2) within the chelate back-bones of the three $R_P,R_{P'}$-configurated diastereomers decreases marginally from 50.8° to 50.5° and 48.8° on going from **7a** to **8a** and **9a**, the corresponding value for the P(3)−C(33)−C(37)−P(4) framework of $S_P,S_{P'}$ diastereomer **7b** amounts to only 39.0°. Front views of the complexes, shown schematically for **7b** and **8a** in Figures 5 and 6, identify the puckering of the chelate rings in the λ,δ notation as δ. In the $R_P,R_{P'}$-configurated diastereomers the methyl substituents occupy axial positions with respect to the coordination plane, the torsion angles P−M−P−CH_3 being close to −105° in all three molecules **7a**, **8a**, and **9a**. The orientation of the equatorial pairs of cyclooctyl groups (torsion angles P−M−P−CH<, 130.1−132.5°) can be described as approximately "face-on" (Figure 6), similar to the alignment of the equatorial aryl groups in a variety of structurally characterized transition metal complexes containing perphenylated chelating bisphosphane ligands[5]. The $S_P,S_{P'}$ form of nickel complex **7b**, on the other hand, displays little differentiation between axially and equatorially oriented substituents, the torsion angles being −115.0° and −119.0° for the P−M−P−CH_3 fragments P(4)−Ni(2)−P(3)−C(25) and P(3)−Ni(2)−P(4)−C(39) and 125.8° and 120.7° for the two P−M−P−CH< chains of atoms P(4)−Ni(2)−P(3)−C(24) and P(3)−Ni(2)−P(4)−C(38). The conformation of the cyclooctyl rings can be approximated as "boat-chair"-like in the palladium and platinum complexes, and thus corresponds to the lowest-energy conformation of cycloctane[8][9]. In the two nickel complexes, on the other hand, the C_8H_{15} conformation comes close to "boat-only" if conformational disorder is neglected.

Figure 5. Schematic front view of (1*S*,2*S*)-C_5H_8{P(CH_3)C_8H_{15}-*cyclo*-(*S*)}$_2$$NiCl_2$ (**7b**)

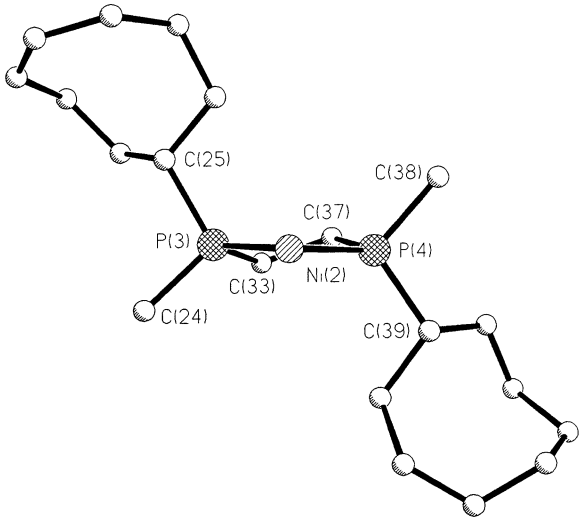
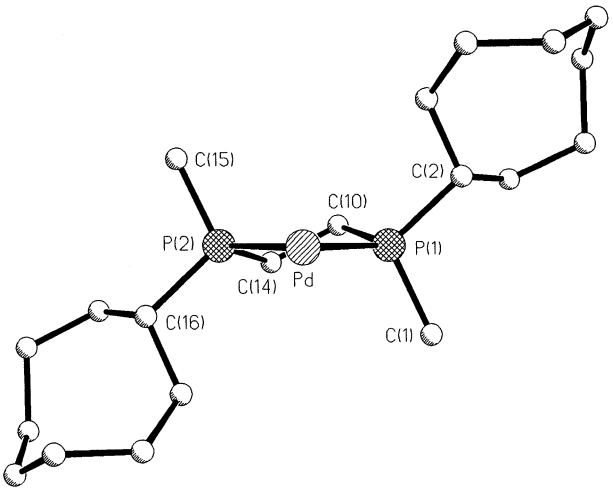


Figure 6. Schematic front view of (1*S*,2*S*)-C_5H_8{P(CH_3)C_8H_{15}-*cyclo*-(*R*)}$_2$$PdI_2$ (**8a**)



Conclusions

This work has shown that the free-radical-initiated P−H addition of enantiomerically pure bis(primary phosphanes), e.g. (1*S*,2*S*)-$C_5H_8(PH)_2$[1], across the carbon−carbon double bonds of cycloalkenes containing five to eight ring atoms provides an attractive method for the synthesis of the preparation of asymmetric bis(secondary phosphanes). The latter can be derivatized further by metalation and alkylation to give bis(tertiary) P_2 ligands, such as (1*S*,2*S*)-C_5H_8[P(CH_3)C_8H_{15}-*cyclo*]$_2$ (**6**), combining phosphorus-based asymmetry with backbone chirality. Only a few bisphosphanes with asymmetric phosphorus atoms connected to a chiral carbon framework have been reported before[10][11][12][13][14][15]. None of these contains peralkylated phosphanyl substituents −P(R′)R. It was therefore a challenge to isolate the $S_P,S_{P'}$-configurated diastereomer **6a**, observed to predominate in the isomeric mixture of bisphosphanes **6a**−**c**, in optically pure form. Attempts to liberate **6a** from its palladium or platinum complexes **8a** and **9a** were hampered, however, by extensive epimerization at phosphorus, which occurred upon reacting **8a** with excess sodium cyanide in the two-phase system toluene/water. Configurational inversion at phosphorus appears to be facile due to the fact that cyanolysis of **8a** under the conditions outlined before resulted in the liberation of **6** as an isomeric mixture containing 52% of the desired **6a** accompanied by 27% of **6b** and, 21% of **6c**.

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Experimental Section

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. − IR: Mattson Polaris. − NMR: Bruker

DPX 300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P) and Jeol FT-JNM-EX 270 (109.4 MHz for ^{31}P; for compounds **2**−**4** only) at 20 ± 2°C with TMS as internal or with H_3PO_4 as external standard (downfield positive). − Mass spectra: Jeol MS 700.

(1S,2S)-C_5H_8[P(H)C_5H_9-cyclo]$_2$ (**2**): A suspension of 0.2 g of AIBN in 1.63 g (23.9 mmol) of cyclopentene was added in two portions within 2 h to a gently refluxing solution of 0.64 g (4.77 mmol) of **1**[1] in 1.63 g (23.9 mmol) of cyclopentene. The mixture was stirred at reflux temperature for 4 d. Excess cyclopentene was then removed at room temperature under reduced pressure, and any remaining volatile material was removed from the product by heating at 60°C under a dynamic vacuum. The yield was 1.10 g (85%) of a colorless liquid, which was characterized as the desired bis(secondary phosphane) **2** on the basis of its spectroscopic properties. − MS (FD; toluene, 35 mA, 10 kV): *m*/*z* = 270 [M$^+$]. − IR (film): $\tilde{\nu}$ = 2295 (PH) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 1.1−2.3 (m, 26 H, C_5H_8 and C_5H_9), 2.86 [dm, ^1J(P,H) = 191 Hz; PH of C_2-symmetric diastereomer **2b** superimposed by P_AH of $R_P,S_{P'}$ diastereomer **2c**], 3.21 [dm, ^1J(P,H) = 193 Hz; PH of C_2-symmetric diastereomer **2a**], 3.45 [dm, ^1J(P,H) = 192 Hz; P_BH of $R_P,S_{P'}$ diastereomer **2c**]. − ^{31}P NMR (C_6D_6): δ = −41.2 (br; C_2-symmetric diastereomer **2a** overlapped by P_B of $R_P,S_{P'}$ diastereomer **2c**), −34.0 (br; C_2-symmetric diastereomer **2b** overlapped by P_A of $R_P,S_{P'}$ diastereomer **2c**); ^3J(P,P) not resolved.

(1S,2S)-C_5H_8[P(H)C_6H_{11}-cyclo]$_2$ (**3**): The preparation of this compound was carried out as described for **2** by reacting 0.68 g (5.07 mmol) of **1** with a total of 3.50 g (42.6 mmol) of cyclohexene, in the presence of a catalytic amount of AIBN (0.2 g), at 60°C for 3 d; yield 1.35 g (89%) of a colorless, viscous liquid. − IR (film): $\tilde{\nu}$ = 2263 (PH) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 1.1−2.2 (m, 30 H, C_5H_8 and C_6H_{11}), 3.0 [dm (br), ^1J(P,H) = 194 Hz; PH of C_2-symmetric diastereomer **3b** superimposed by P_AH of $R_P,S_{P'}$ diastereomer **3c**], 3.32 ["ddd", ^1J(P,H) = 194, ^3J(H,H) = 3.4, 5.9 Hz; PH of C_2-symmetric diastereomer **3a**], 3.4 [dm (br), ^1J(P,H) = 196 Hz; P_BH of $R_P,S_{P'}$ diastereomer **3c**]. − ^{31}P NMR (C_6D_6): −35.9 [AB-d, ^3J(P,P) = 5 Hz; P_B of $R_P,S_{P'}$ diastereomer **3c**], −35.5 (s; C_2-symmetric diastereomer **3a**), −28.4 (s; C_2-symmetric diastereomer **3b**), −28.2 [AB-d, ^3J(P,P) = 5 Hz; P_A of $R_P,S_{P'}$ diastereomer]; diastereomeric distribution: **3a**, 38%; **3b**, 20%; **3c**, 42%.

(1S,2S)-C_5H_8[P(H)C_7H_{13}-cyclo]$_2$ (**4**): The preparation of this compound was carried out as described for **2** and **3**, by reacting 0.30 g (2.24 mmol) of **1** with 3.00 g (31.2 mmol) of cycloheptene, in the presence of 0.2 g of AIBN, at 60°C for 3 d; yield 0.65 g (89%) of a colorless oil. − MS (FD; toluene, 35 mA, 10 kV): *m*/*z* = 326 [M$^+$]. − IR (film): $\tilde{\nu}$ = 2263 (PH) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 1.3−2.1 (m, 34 H, C_5H_8 and C_7H_{13}), 3.0 [dm (br), ^1J(P,H) = 194 Hz; PH of C_2-symmetric diastereomer **4b** superimposed by P_AH of $R_P,S_{P'}$ diastereomer **4c**], 3.35 ["ddd", ^1J(P,H) = 194, ^3J(H,H) = 3.4, 6.1 Hz; PH of C_2-symmetric diastereomer **4a**], 3.5 [dt (br), ^1J(P,H) = 196, ^3J(H,H) = 6 Hz; P_BH of $R_P,S_{P'}$ diastereomer **4c**]. − ^{31}P NMR (C_6D_6): −32.7 [AB-d, ^3J(P,P) = 7 Hz; P_B of $R_P,S_{P'}$ diastereomer **4c**], −32.4 (s; C_2-symmetric diastereomer **4a**), −26.4 (s; C_2-symmetric diastereomer **4b**), −26.0 [AB-d, ^3J(P,P) = 7 Hz; P_A of $R_P,S_{P'}$ diastereomer **4c**]; diastereomeric distribution: **4a**, 30%; **4b**, 27%; **4c**, 43%.

(1S,2S)-C_5H_8[P(H)C_8H_{15}-cyclo]$_2$ (**5**): This material was prepared as described above by stirring 0.50 g (3.73 mmol) of **1** in 4.00 g (36. 3 mmol) of cyclooctene, containing AIBN (0.2 g), at 60°C for 3 d; yield 1.12 g (85%) of colorless liquid **5**. MS (FD; toluene, 35 mA, 10 kV): *m*/*z* = 354 [M$^+$]. − IR (film): $\tilde{\nu}$ = 2265 (PH) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 1.3−2.2 (m, 38 H, C_5H_8 and C_8H_{15}), 3.0 [dm (br), ^1J(P,H) = 192 Hz; PH of C_2-symmetric diastereomer **5b** superimposed by P_AH of $R_P,S_{P'}$ diastereomer **5c**], 3.32 ["ddd", ^1J(P,H) = 194, ^3J(H,H) = 3.4, 5.3 Hz; PH of C_2-symmetric diastereomer **5a**], 3.46 [dt (br), ^1J(P,H) = 196, ^3J(H,H) = 5 Hz; P_BH of $R_P,S_{P'}$ diastereomer **5c**]. − ^{31}P NMR (C_6D_6): −29.52 [AB-d, ^3J(P,P) = 6.8 Hz; P_B of $R_P,S_{P'}$ diastereomer **5c**], −29.30 (s; C_2-symmetric diastereomer **5a**), −22.79 (s; C_2-symmetric diastereomer **5b**), −22.45 (AB-d; P_A of $R_P,S_{P'}$ diastereomer **5c**); diastereomeric distribution: **5a**, 31%; **5b**, 19%; **5c**, 50%.

(1S,2S)-C_5H_8[P(CH_3)C_8H_{15}-cyclo]$_2$ (**6**): A solution of **5** (0.72 g, 2.03 mmol) in 25 ml of THF was treated with 2.60 ml of a 1.6 M hexane solution of *n*-butyllithium (4.16 mmol) at room temperature. The resulting orange solution was stirred for 10 min and then cooled to −25°C. Methyl iodide (7.6 ml of a 0.54 M solution in THF, 4.10 mmol) was then added and the decolorized mixture was evaporated to dryness in vacuo at −25°C. The oily residue was allowed to warm to room temperature, dissolved in toluene, and washed with degassed water. After separation of the organic layer and removal of solvent, the product was extracted from the residue into boiling hexane. Removal of all volatile material from the extracts left ligand **6** as a clear viscous oil; yield 0.73 g (94%). − ^{1}H NMR (C_6D_6): δ = 0.84 ("t", ^2J(P,H) + ^5J(P′,H) = 3.5 Hz; PCH_3 of predominating $S_P,S_{P'}$ diastereomer **6a**), 0.94 ("d", ^2J(P,H) + ^5J(P′,H) = 3.7 Hz; PCH_3 of minor $R_P,R_{P'}$ diastereomer **6b**), 0.81, 1.19 (both "d", ^2J(P,H) + ^5J(P,H) = 3.5 Hz; both PCH_3 of $R_P,S_{P'}$ diastereomer **6c** present in intermediate concentration), 1.3−2.0 (m; 38 H, C_5H_8 and C_8H_{15}). − ^{31}P NMR (C_6D_6): δ = −14.04 [AB-d, ^3J(P_A,P_B) = 6.2 Hz; P_B of $R_P,S_{P'}$ diastereomer **6c**], −11.82 (s; $S_P,S_{P'}$ diastereomer **6a**), −10.02 ($R_P,R_{P'}$ diastereomer **6b**), −6.01 (AB-d; P_A of $R_P,S_{P'}$ diastereomer **6c**); diastereomeric distribution: **6a**, 72%; **6b**, 4%; **6c**, 24%.

(1S,2S)-C_5H_8[P(CH_3)C_8H_{15}-cyclo]$_2$NiCl$_2$ (**7**): To a stirred solution of **6** (0.58 g, 1.52 mmol) in 20 ml of CH_2Cl_2 was added a solution of $NiCl_2 \cdot 6\,H_2O$ (0.37 g, 1.56 mmol) in 30 ml of ethanol. The resulting red-brown mixture was stirred for 8 h and then the solvent was evaporated to give a quantitative yield (0.78 g) of **7** as a brown powder. − $C_{23}H_{44}Cl_2NiP_2$ (512.13): calcd. C 53.9, H 8.7; found C 54.00, H 8.87. − MS (EI, 70 eV, 180°C): *m*/*z* (%) = 512 (21%) [M$^+$], 475 (58) [M$^+$ − Cl], 438 (9%) [M$^+$ − 2Cl], 364 (61%) [M$^+$ − Cl − C_8H_{15}]. − ^{31}P NMR ($CDCl_3$): 38.51 [AB-d, J(P_A,P_B) = 84.6 Hz; P_B of $R_P,S_{P'}$ diastereomer **7c**], 41.17 (s; $S_P,S_{P'}$ diastereomer **7b**), 42.28 (s; $R_P,R_{P'}$ diastereomer **7a**), 45.23 (AB-d; P_A of $R_P,S_{P'}$ diastereomer **7c**); diastereomeric distribution: **7a**, 75%; **7b**, 4%; **7c**, 21%.

The $R_P,S_{P'}$ diastereomer **7c** was removed by chromatography on a column containing silica gel/acetone, which was charged with 0.78 g (1.52 mol) of **7** as a suspension in acetone. Elution with 5% ethyl acetate in acetone, followed by elution with dichloromethane, gave a yellow fraction, which on evaporation of solvent yielded 0.12 g (22%) of microcrystalline **7a**, contaminated by ca. 5% of **7b** (diastereomeric purity estimated by ^{31}P NMR). − ^{13}C{^{31}P,^{1}H} NMR ($CDCl_3$): 3.41 (CH_3), 23.39, 25.44, 25.55, 26.18, 26.89, 27.13, 27.97, 30.53, 31.52 (all CH_2), 34.02 (C_8H_{15}-CH), 44.03 (C_5H_8-CH); the CH_3 and CH resonances showed deceptively simple AA′*X* triplet splitting in the ^{31}P-coupled spectrum: J(P,C) + J(P′,C) = 23.4 Hz (CH_3), 30.2 Hz (C_8H_{15}-CH), and 45.3 Hz (C_5H_8-CH), respectively.

(1S,2S)-C_5H_8[P(CH_3)C_8H_{15}-cyclo]$_2$PdI$_2$ (**8**): To a solution of **6** (1.77 g, 4.65 mmol) in 100 ml of CH_2Cl_2 was added 1.52 g (5.34 mmol) of solid (1,5-C_8H_{12})$PdCl_2$[16]. The orange solution was stirred at room temperature for 10 min and then treated with sodium iodide (2.07 g, 13.81 mmol) to give a brown mixture, which

was stirred for additional 10 h. After filtration and evaporation of the filtrate to dryness, excess (1,5-C_8H_{15})$PdCl_2$ was removed by flash chromatography on a silica gel column with dichloromethane/ethyl acetate (19:1) as the eluent. Evaporation of solvent from the eluate left complex **8** as yellowish red powder; yield 2.95 g (85%). − $C_{23}H_{44}I_2P_2Pd$ (742.72): calcd. C 37.20, H 5.97; found C 37.53, H 6.14. − MS (EI, 70 eV, 180°C): *m/z* (%) = 742 (19%) [M^+], 615 (100%) [M^+ − I]. − ^{31}P NMR ($CDCl_3$): 40.97 [AB-d, $J(P_A,P_B)$ = 20.7 Hz; P_B of $R_P,S_{P'}$ diastereomer **8c**], 42.83 (s; $R_P,R_{P'}$ diastereomer **8a**), 43.93 (s; $S_P,S_{P'}$ diastereomer **8b**), 47.66 (AB-d; P_A of $R_P,S_{P'}$ diastereomer **8c**); diastereomeric distribution: **8a**, 70%; **8b**, 3%; **8c**, 27%.

For isolation of diastereomerically pure **8a**, the isomeric mixture **8a−c** (2.95 g) was chromatographed on a silica gel column, eluting first with with 5% ethyl acetate in acetone and then with dichloromethane as described above for nickel complex **7**. The residue remaining after removal of solvent from the CH_2Cl_2 eluate was thoroughly washed with acetone to give 0.32 g (15%) of **8a** as yellow-red microcrystals. − ^{1}H NMR ($CDCl_3$): 1.3−1.9 (m, 30 H, CH_2), 1.71 ["d", J(P,H) + J(P′,H) = 10.2 Hz; 6 H, CH_3], 2.25−2.55 (m, 6 H, CH and CH_2), 3.15−3.35 (m, 2 H, CH). − ^{13}C{^{31}P,^{1}H} NMR ($CDCl_3$): 6.05 (CH_3), 23.06, 25.31, 25.55, 26.83, 27.48, 28.30, 30.58, 31.86 (all CH_2), 37.32 (C_8H_{15}-CH), 45.47 (C_5H_8-CH); apparently simple AAX' patterns were observed for the CH_3 and CH resonances in the ^{31}P-coupled spectrum: J(P,C) + J(P′,C) = 24.3 Hz (CH_3), 30.6 Hz (C_8H_{15}-CH), and 45.8 Hz (C_5H_8-CH), respectively.

(1S,2S)-C_5H_8[P(CH_3)C_8H_{15}-cyclo]$_2PtI_2$ (**9**): Solid (COD)PtI_2[17] (0.49 g, 0.88 mmol) was added to a stirred solution of 0.33 g (0.86 mmol) of **6** in 40 ml of dichloromethane. After stirring for 10 h the solvent was removed in vacuo to leave a virtually quantitative yield of 0.72 g of the product as a dark yellow solid. − $C_{23}H_{44}I_2P_2Pt$ (831.41): calcd. C 33.23, H 5.33; found C 32.78, H 5.37. − MS (EI, 70 eV, 180°C): *m/z* (%) = 831 (17%) [M^+], 704 (100%) [M^+ − I]. − ^{31}P NMR ($CDCl_3$): 21.90 [AB-d with ^{195}Pt satellites, $J(P_A,P_B)$ = 2.3, ^1J(Pt,P) = 3320 Hz; P_B of $R_P,S_{P'}$ diastereomer **9c**], 24.94 [s with ^{195}Pt satellites, ^1J(Pt,P) = 3333 Hz; $R_P,R_{P'}$ diastereomer **9a**], 26.39 [s with ^{195}Pt-satellites, ^1J(Pt,P) = 3362 Hz; $S_P,S_{P'}$ diastereomer **9b**], 29.04 [AB-d with ^{195}Pt satellites, ^1J(Pt,P) = 3336 Hz; P_A of $R_P,S_{P'}$ diastereomer **9c**]; diastereomeric distribution: **9a**, 76%; **9b**, 6%; **9c**, 18%. − Crystallization of the diastereomeric mixture from chloroform resulted in preferential precipitation of **9a**.

Cyanolysis of Palladium Complex **8a**: A vigorously stirred suspension of 370 mg (0.5 mmol) of **8a** in 10 ml of water and 15 ml of toluene was treated with a ten-fold excess of solid potassium cyanide at room temperature. Stirring was continued for 8 h to produce a colorless two-phase system. The organic layer was separated and the organic phase was extracted twice with 10 ml of water to remove any residual KCN. Evaporation of the combined organic phases left the free ligand **6** as a 52:27:21 mixture of diastereomers **6a**, **6b**, and **6c**.

X-ray Structure Determinations: Single-crystals of (1*S*,2*S*)-C_5H_8{P(CH_3)C_8H_{15}-*cyclo*-(*R*)}$_2NiCl_2$·(1*S*,2*S*)-C_5H_8{P(CH_3)-C_8H_{15}-*cyclo*-(*S*)}$_2NiCl_2$ (**7a·7b**) (size 0.03 × 0.3 × 0.55 mm), (1*S*,2*S*)-C_5H_8{P(CH_3)C_8H_{15}-*cyclo*-(*R*)}$_2PdI_2$ (**8a**) (size = 0.20 × 0.25 × 0.50 mm), and (1*S*,2*S*)-C_5H_8{P(CH_3)C_8H_{15}-*cyclo*-(*R*)}$_2PtI_2$ (**9a**) (size 0.26 × 0.26 × 0.28 mm) were grown from acetone (**7a·7b**), CH_2Cl_2/hexane (**8a**), and $CHCl_3$ (**9a**), respectively. The measurements were made at −95 ± 2°C (**7a·7b**) and at 20 ± 2°C (**8a**, **9a**) on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å): orientation matrices and unit cell parameters from the setting anlges of 25 centered medium-angle reflections (**7a·7b**: 12 < 2θ < 16°; **8a**: 15 < 2θ < 34°; **9a**: 17 < 2θ < 26°); collection of the diffraction intensities of Ni complex **7a·7b** by ω scans (data uncorrected for absorption); intensity measurements of Pd and Pt compounds **8a** and **9a** by the ω/2θ scan technique (data corrected for absorption by ψ-scans; **8a**: T_{min} = 0.41, T_{max} = 0.99; **9a**: T_{min} = 0.86, T_{max} = 0.99). The structures were solved by direct methods employing the SIR-92[18] program system and subsequently refined by full-matrix least-squares procedures on F^2 (SHELXL-93[19]) with allowance for anisotropic thermal motion of all non-hydrogen atoms. According to the U_{ij} values of three of the cyclooctyl carbon atoms of **7a·7b**, twofold conformational disorder was suggested for these atoms, which was accounted for by assigning the particular carbon positions split occupancies of 0.45 [C(4a), C(7a)] and 0.55 [C(4b), C(7b)] and of 0.40 [C(31a)] and 0.60 [C(31b)], respectively. H atoms were included in the final structural models assuming ideal geometry and using appropriate riding models. − **7a·7b**: $C_{23}H_{44}Cl_2NiP_2$ (512.13); monoclinic, $P2_1$, a = 12.016(3), b = 16.538(4), c = 12.986(7) Å, β = 103.44(3)°, V = 2510(2) Å^3, Z = 4, $d_{calcd.}$ = 1.355 g cm^{-3}, μ(Mo-K_α) = 1.122 mm^{-1}; 5 ≤ 2θ ≤ 45°, 6843 reflections collected (−12 ≤ h ≤ 12, 0 ≤ k ≤ 17, 0 ≤ l ≤ 13, together with Friedel pairs), 6514 reflections independent ($R_{int.}$ = 0.0359); R_{w2} = 0.1115 for all data and 535 parameters, $w = \{\sigma^2(F_o^2) + [0.0433(F_o^2 + 2F_c^2)/3]^2 + 3.2250(F_o^2 + 2F_c^2)/3\}^{-1}$, R = 0.0463 for 4823 data with $I > 2\sigma(I)$, absolute structure parameter[20]: 0.03(3). − **8a**: $C_{23}H_{44}I_2P_2Pd$ (742.72); tetragonal, $P4_1$, a = 11.205(2), c = 21.650(9) Å, V = 2718(1) Å^3, Z = 4, $d_{calcd.}$ = 1.815 g cm^{-3}, μ(Mo-K_α) = 3.080 mm^{-1}; 5 ≤ 2θ ≤ 54°, 12730 reflections collected (−14 ≤ h ≤ 14, 0 ≤ k ≤ 14, 0 ≤ l ≤ 27, together with Friedel pairs), 5917 reflections independent ($R_{int.}$ = 0.0460); R_{w2} = 0.0906 for all data and 257 parameters, $w = \{\sigma^2(F_o^2) + [0.0386(F_o^2 + 2F_c^2)/3]^2 + 0.5985(F_o^2 + 2F_c^2)/3\}^{-1}$, R = 0.0379 for 4732 data with $I > 2\sigma(I)$, absolute structure parameter[20]: −0.01(3). − **9a**: $C_{23}H_{44}I_2P_2Pt$ (831.41); tetragonal, $P4_1$, a = 11.198(1), c = 21.685(5) Å, V = 2719.2(7) Å^3, Z = 4, $d_{calcd.}$ = 2.031 g cm^{-3}, μ(Mo-K_α) = 7.557 mm^{-1}; 5 ≤ 2θ ≤ 52°, 11460 reflections collected (−13 ≤ h ≤ 13, 0 ≤ k ≤ 13, 0 ≤ l ≤ 26), 5313 reflections independent ($R_{int.}$ = 0.0483); R_w2 = 0.0756 for all data and 254 parameters, $w = \{\sigma^2(F_o^2) + [0.0287(F_o^2 + 2F_c^2)/3]^2 + 0.6041(F_o^2 + 2F_c^2)/3\}^{-1}$, R = 0.0381 for 4102 data with $I > 2\sigma(I)$, absolute structure parameter[20]: −0.005(9). − Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-408020 (**7a·7b**), CSD-408024 (**8a**), or CSD-408023 (**9a**).

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