Synthesis of (1*R*,1′*S*)- and (1*S*,1′*S*),(1*R*,1′*R*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene Derivatives and Their Cyclometalation Reactions with Platinum(II) Compounds. X-ray Crystal Structures of [2,6-Bis[(diphenylphosphino)methyl]phenyl]chloropalladium(II), [(1*R*,1′*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]chloroplatinum(II), and [(1*R*,1′*R*),(1*S*,1′*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]chloroplatinum(II)

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Equimolecular amounts of the ligands (1*S*,1′*S*),(1*R*,1′*R*)-1,3-bis[1-(diphenylphosphino)ethyl]-benzene, *rac*-form, and of the corresponding *meso*-form, were obtained by two methods. The first involved the reaction of 1,3-bis[(diphenylthiophosphino)methyl]benzene (1) with *n*-butyllithium followed then with methyl iodide, (2) separation of the *rac*- and *meso*-forms of the products by fractional crystallization, and (3) their desulfurization with tri-*n*-butylphosphine. In the second method the methylation reaction was carried out on 1,3-bis[(diphenylphosphino)-methyl]benzene–bisborane and the borane removed from the products by reaction with diethylamine. The complexes *rac*-[(1*S*,1′*S*),(1*R*,1′*R*)-1,3-bis[1-(diphenylphosphino)ethyl]-phenyl]chloroplatinum(II), **9a,b**, and the corresponding *meso*-form, **9c**, were obtained by reacting the respective phosphines either with *cis*-$[PtCl_2(PPh_3)_2]$, followed by elemental sulfur, or with $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$. Reaction of the above complexes with $AgCF_3SO_3$ gave the corresponding trifluoromethanesulfonates while the action of $AgPF_6$ and (*R*)-methyl-4-tolyl sulfoxide gave the corresponding sulfoxide complexes as their PF_6 salts, **24a,b** and **24c**, respectively. The pure isomeric forms **24a** and **24b** could not be obtained by fractional crystallization. The complex [2,6-bis[(diphenylphosphino)methyl]phenyl]methylplatinum, when reacted with methyllithium, followed by methyl iodide, gave a mixture of *rac*-[(1*S*,1′*S*),-(1*R*,1′*R*)-2,6-bis[1-(diphenylphosphino)ethyl]phenyl]methylplatinum **21a,b**, and the corresponding *meso*-form, **21c**, in ratios varying between 14 and 37% of the former and the remainder of the latter, depending on the reaction temperature. Similar results were obtained when LDA was used as a base. Deprotonation of either pure **21a,b** and **21c** with methyllithium, followed by hydrolysis, gave isomeric mixtures with ratios corresponding to those quoted above. However, when LDA was used for this reaction, **21a,b** was obtained in 45% yield. The X-ray crystal structures of [2,6-bis[(diphenylphosphino)methyl]phenyl]chloropalladium, **7a**, and of **9a,b** and **9c** are reported. Their structural features are very similar to those of several related compounds, the only significant difference between **9a,b** and **9c** being the steric repulsion between a terminal phenyl group and the equatorial methyl substituent in the latter compound.

Introduction

Molecules of the type 1,3-$(LCH_2)_2C_6H_4$ (L = $-PR_2$,[1-4] NR_2,[5] and $-SR$[6]), **1**, or their derivatives, easily react with suitable transition metal complexes, giving species which contain terdentate ligands bonded to the metal center through the central carbon atom of the benzene ring and the two donor atoms of the groups L, **2**.

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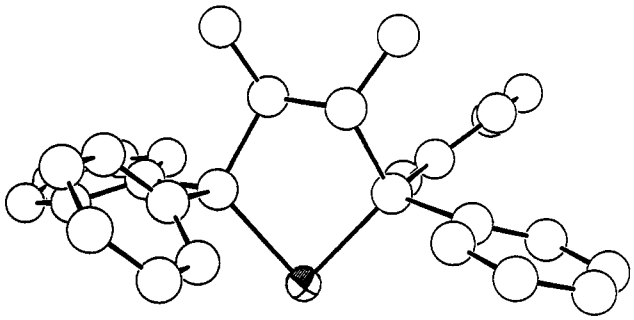
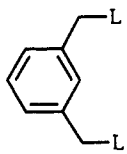
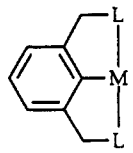


Figure 1. ORTEP view of the "Chiraphos Rh" moiety.

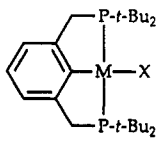


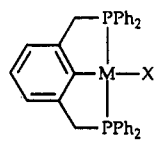
1a: L = P-*t*-Bu$_2$
1b: L = PPh$_2$
1c: L = PMe$_2$
1d: L = PEt$_2$



2

The first complexes containing a moiety of type **2** reported in the literature were obtained by treating 1,3-bis[(di-*tert*-butylphosphino)methyl]benzene, **1a**, with appropriate nickel(II), palladium(II), and platinum(II) chloro compounds, giving the complexes **3a–5a**, respectively.[1] Some rhodium and iridium complexes containing the same terdentate ligand were also reported.[1,4]





3a:	M = Ni,	X = Cl	6a:	M = Ni,	X = Cl
3b:	M = Ni,	X = H	6b:	M = Ni,	X = Br
4a:	M = Pd,	X = Cl	7a:	M = Pd,	X = Cl
4b:	M = Pd,	X = H	7b:	M = Pd,	X = Br
5a:	M = Pt,	X = Cl	8a:	M = Pt,	X = Cl
5b:	M = Pt,	X = H	8b:	M = Pt,	X = Br
			8c:	M = Pt,	X = Me
			8d:	M = Pt,	X = CO_2H
			8e:	M = Pt,	X = CF_3SO_3

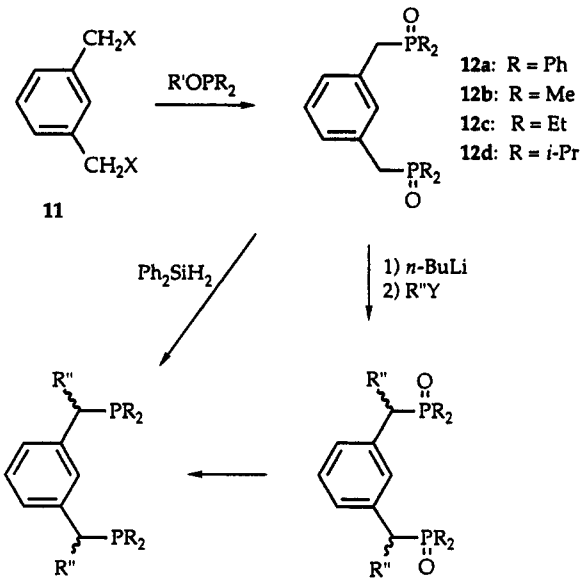
The most striking features of these early studies are the ease with which compound **1a** undergoes cyclometalation reactions and the extent to which the presence of a moiety such as **2**, when L = P-*t*-Bu$_2$, stabilizes complexes of unusual type, e.g, hydrido complexes **3b**, **4b**, and **5b**, or the formation of five-coordinate complexes of d^6-metal centers such as rhodium(III) and iridium(III).[1,4]

It was shown later that careful choice of the metal compounds used as starting materials induced easy cyclometalation of ligands of type **1** even when the terminal substituents on the donor groups L were much less bulky than *t*-Bu, i.e., Ph,[2,3] e.g., **6a–8e**, Et and even Me.[7]

In an earlier publication[2c] it was also pointed out that it should be relatively easy to prepare optically active complexes containing a moiety derived from **2**, e.g., by

(7) Chaloupka, S.; Lu, Q.; Rimml, H.; Venanzi, L. M. Unpublished observations.

Scheme 1



11

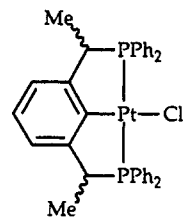
12a: R = Ph
12b: R = Me
12c: R = Et
12d: R = *i*-Pr

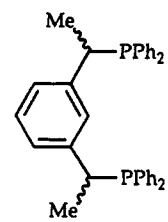
1) *n*-BuLi
2) R"Y

1b: R = Ph, R" = H
1c: R = Me, R" = H
1d: R = Et, R" = H

13a,b and c: R = Ph, R" = Me
14a,b and c: R = Ph, R" = Et
15a,b and c: R = Ph, R" = *i*-Pr

replacing one of the hydrogen atoms on each methylene group by a substituent such as a methyl group. Furthermore, the shape of the chiral pocket in the resulting optically active complexes when the substituent R on phosphorus is a phenyl group, e.g., in the racemic **9a,b**,





9a,b *rac*-form
9c *meso*-form

10a,b *rac*-form
10c *meso*-form

appears to be similar to that in the "Rh((*S*,*S*)-chiraphos)" moiety, as can be seen by comparing the X-ray crystal structures of **7a** (see later) and of the chiral pocket in (1,5-cyclooctadiene)-(2*S*,3*S*)-[2,3-bis(diphenylphosphino)-butane]rhodium(I) perchlorate[8] shown in Figure 1. Thus, complexes having the basic structure present in **9a,b** might be interesting catalysts for enantioselective reactions.

Complexes of type **9a,b** should be obtainable from ligands **10a,b** by following the usual cyclometalation route. The latter compounds should be readily accessible by the route outlined in Scheme 1.

Indeed, the isomeric mixtures of phosphine oxides **13–15** were obtained as indicated in this scheme.[3] However, no attempts were made to reduce them to the corresponding phosphines, although several phosphine oxides, e.g., **12a–d** were successfully reduced to the corresponding phosphines **1b–d**, respectively, using diphenylsilane.[3]

A problem inherent in this route is caused by the chemical nature of phosphine oxides. Although, as mentioned above, their reduction to the corresponding phosphines can be carried out using silanes, this reaction requires conditions which often induce the cleavage of

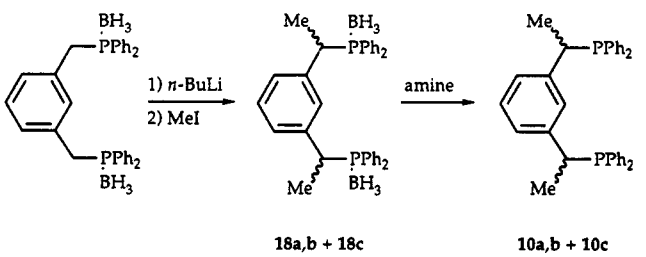
(8) Ball, R. G.; Payne, N. C. *Inorg. Chem.* **1977**, *16*, 1187.

P–C bonds. Furthermore, one can encounter practical problems with the deprotonation of the CH_2 groups adjacent to the phosphine oxides, as the latter often are quite hygroscopic and, therefore, difficult to obtain in the required anhydrous state.

Problems of the above type have been overcome[3] by using the corresponding phosphine sulfides, which are not hygroscopic and can be relatively easily desulfurized, as shown in Scheme 2.

This reaction sequence provides a convenient route for the preparation of the bis(phosphines) **1c** and **1d**.[3]

Mention should be made here that the recent use of phosphine boranes[9] has revolutionized phosphine synthesis. These compounds, of the type $PR_3{\cdot}BH_3$, are stable in air, and even in acid solution, but the protecting group can be easily transferred to an aliphatic amine, e.g., morpholine. Furthermore, CH_2 groups on phosphine boranes are acidic and can be deprotonated by alkyllithium reagents.[9,10] Thus it is expected that one can carry out the following reactions:



Regrettably, these synthetic approaches do not solve a major problem, i.e., the lack of stereoselectivity of the alkylation reaction, as it produces a *meso*-form, as well as a *rac*-form, in statistical amounts.

However, as it was pointed out earlier that complexes such as **7a** possess some potentially interesting structural characteristics: the orientation of the terminal phenyl substituents is such that one of them, on one side of the complex, projects above the square planar moiety, while one on the other side of the complex projects below the same plane on the opposite side of the coordination plane (see Figure 4). Furthermore, X-ray diffraction studies show that the same arrangement of the organic ligand is present in the analogous complex **7a** (see later), as well as in **6b**, **7b**, and **8b**, which are isostructural.[11] Thus, it seemed likely that deprotonation of the methylene groups in a complex such as **8c**, followed by alkylation, e.g., with a methyl halide, should lead to the selective formation of the corresponding enantiomeric pair of complexes **9a,b**. Furthermore, either the (+)- or (−)-form of **9**, i.e., **9a** or **9b**, could be preferentially produced if the alkylation reaction were carried out on a complex in which the chloride anion had been replaced by an optically active ligand. This would constitute a template synthesis of an optically active complex from a nonchiral precursor using an optically active auxiliary ligand.

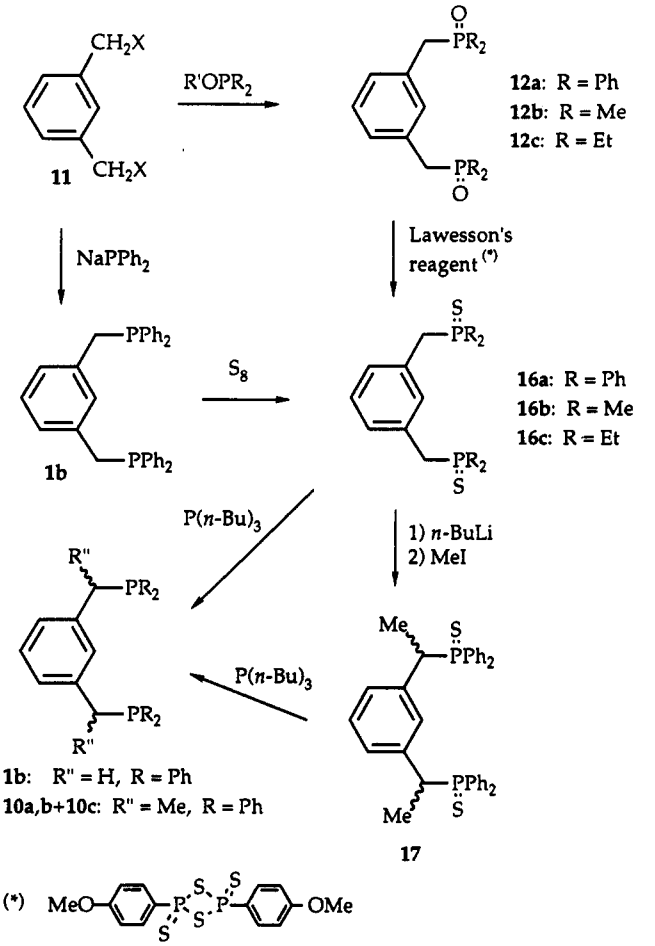
This paper reports a series of experiments designed to test the ideas outlined above.

(9) (a) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301 and reference cited therein. (b) Oshiki, T.; Imamoto, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3719. (c) Imamoto, T.; Oshiki, T.; Onazawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244 and reference cited therein.

(10) Ward, T. R.; Venanzi, L. M.; Albinati, A.; Lianza, F.; Gerfin, T.; Gramlich, V.; Ramos Tombo, G. M. *Helv. Chim. Acta* **1991**, *74*, 983.

(11) Bachechi, F. Unpublished observations, quoted in ref 3.

Scheme 2

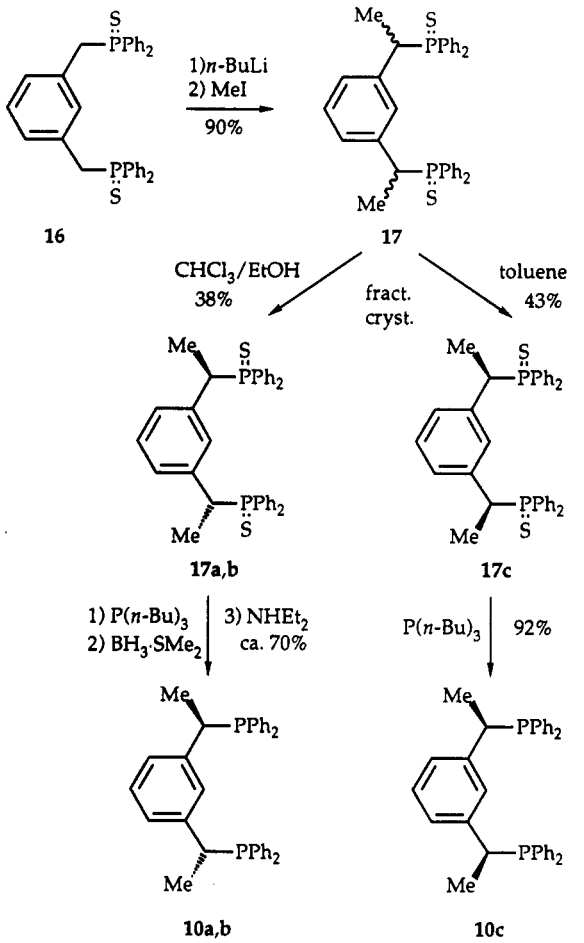


Results and Discussion

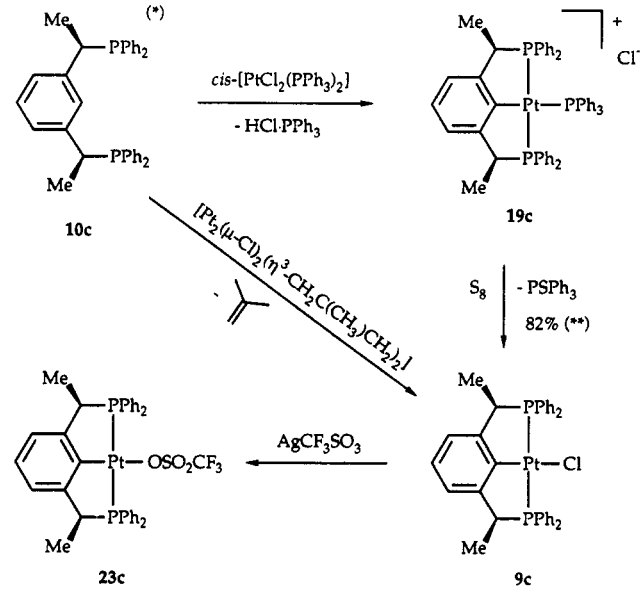
Ligand Synthesis. The reactions carried out are summarized in Scheme 3. The phosphine sulfide **16**, prepared by reacting the phosphine **1b** with elemental sulfur, was deprotonated by adding 2 equiv of *n*-butyllithium and the resulting dianion alkylated with methyl iodide. This gave a 1:1 mixture of the stereomeric sulfides (1*R*,1′*S*)-, (1*S*,1′*S*)-, and (1*R*,1′*R*)-1,3-bis[1-diphenylthiophosphino)ethyl]benzene, **17a–c**, respectively. Fractional crystallization from toluene of the crude mixture gave pure (1*R*,1′*S*)-1,3-bis[1-(diphenylthiophosphino)ethyl]benzene, **17c**, in 43% yield, based on **16**. The pure enantiomeric mixture (1*S*,1′*S*)- and (1*R*,1′*R*)-1,3-bis[1-(diphenylthiophosphino)ethyl]benzene, **17a,b**, was obtained in 38% yield (also based on **16**) from the mother liquor of the above crystallization by evaporation of the solvent and recrystallization of the residue from chloroform/ethanol. Attempts to separate the enantiomers **17a** and **17b** by HPLC using several chiral columns (see Experimental Section) did not result in useful separations.

The diphosphines **10a,b** and **10c** were obtained by refluxing the corresponding sulfides, **17a,b** and **17c**, respectively, with tri-*n*-butylphosphine at 180 °C. While the *meso*-form of the diphosphine, **10c**, could be easily purified by standard procedures, this did not prove possible for the racemic mixture **10a,b**. Therefore, the latter was transformed into its BH_3 adduct, **18a,b**, which, after purification, was converted back to the free phosphine by treatment with diethylamine. Attempts were made to separate the (+)- and (−)-enantiomers of **18a,b** by HPLC, using several chiral columns (see Experimental Section), but also in this case, no significant separation was achieved.

Scheme 3



Scheme 4



(*) Similar reactions were carried out using racemic **10a,b**, to obtain **9a,b**, and **23a,b**.

(**) Based on **10c**.

As expected, also the adduct **1b**·2BH_3 could be deprotonated with *n*-butyllithium and the resulting dianion alkylated with methyl iodide. The resulting isomeric mixture, **18a,b** and **18c**, was separated by fractional crystallization from CH_2Cl_2/hexane; however, the above separation was not as effective as that of the corresponding sulfides. The corresponding phosphines, **10a,b** and **10c**, could be obtained by deprotection of the boranes by treating the boranes with $NHEt_2$.

Cyclometalation Reaction. The reactions used to prepare cyclometalated platinum(II) complexes containing ligand **10c** are shown in Scheme 4. A similar reaction sequence was carried out using the racemic ligand **10a,b**. As found previously for the corresponding cyclometalation reaction of the unsubstituted ligand **1b**,[2,3] the reaction of **10c** with $\{PtCl_2\}_x$, $[PtCl_2(MeCN)_2]$, or $K_2[PtCl_4]$ gave mixtures consisting largely of insoluble, presumably, polymeric materials. The ^{31}P NMR spectra of the soluble fractions showed the presence of several complexes containing ligand **10c**, i.e., no cyclometalation had occurred. While the formation of Pt–C bonds in the above mixtures of complexes could not be induced by either thermal treatment or irradiation, cyclometalation occurred when a suspension of this solid was refluxed in the presence of triphenylphosphine. The product thus formed, **19c**, contained one molecule of coordinated triphenylphosphine, which, however, was labile and was in equilibrium with the desired product **9c**. The PPh_3-containing intermediate **19c** was best obtained by reacting *cis*-$[PtCl_2(PPh_3)_2]$ with **10c**, as the coordinated PPh_3 could be conveniently removed by adding elemental sulfur to the solution. Finally, the chloro complex **9c** was most easily prepared by reacting the ligand **10c** with $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(CH_3)CH_2)_2]$ using the method described Anklin *et al.*[12]

"Methylation" of a Cyclometalated Complex. As mentioned in an earlier section, when the "methylation reaction" is carried out on the phosphine sulfide **16a** one obtained a 1:1 mixture of the substituted products **17a,b** and **17c**. However, in the Introduction it was pointed out that the geometrical features of a static moiety of type **2** in a complex such as **8a** indicate that the *rac*-form of the corresponding complex, in which one of the hydrogen atoms of each CH_2 group had been replaced by a methyl group, i.e., **9a,b**, should be preferred over the corresponding *meso*-form, **9c**. Thus the direct methylation of a complex such as **8a** should give a larger proportion of **9a,b** relative to **9c**.

Furthermore, the methylene groups in complexes **6–8** should be sufficiently acidic to be deprotonated by bases such as *n*-BuLi, as coordination of the P donors to a metal center should have an effect on the CH_2 groups analogous to that of bonding an oxygen or a sulfur atom to the neighboring P atom.[13]

However, the direct addition of an *n*-alkyllithium compound to a complex **6–8** would result in the replacement of the ligand X by the alkyl group. Thus, the deprotonation reaction is best carried out on a complex in which X has been previously replaced by an alkyl group. Finally, in order to obtain stable products for easy characterization by NMR spectroscopy, platinum was chosen as the central metal atom and methyl was chosen as the alkyl group.

The reactions carried out are summarized in Scheme 5.

Careful addition of 1 equiv of methyllithium to a THF or 2-MeTHF solution of **8a**, at 10 °C, gave the methyl complex **8c**.[3] Furthermore, its dianion, **20**, could be

(12) Anklin, C. G.; Pregosin, P. S.; Wombacher, F. J.; Rüegg, H. J. *Organometallics* **1990**, *9*, 1953.

(13) (a) Laurenco, C.; Villien, L.; Kaufmann, G. *Tetrahedron* **1984**, *40*, 2731. (b) Laurenco, C.; Villien, L.; Kaufmann, G. *J. Chem. Res.* **1982**, 12 (*Synop.*); 232–252 (*Miniprint*). (c) Abicht, H.-P.; Issleib, K. *Z. Anorg. Allg. Chem.* **1978**, *447*, 53. (d) Abicht, H.-P.; Issleib, K. *Z. Anorg. Allg. Chem.* **1982**, *494*, 55.

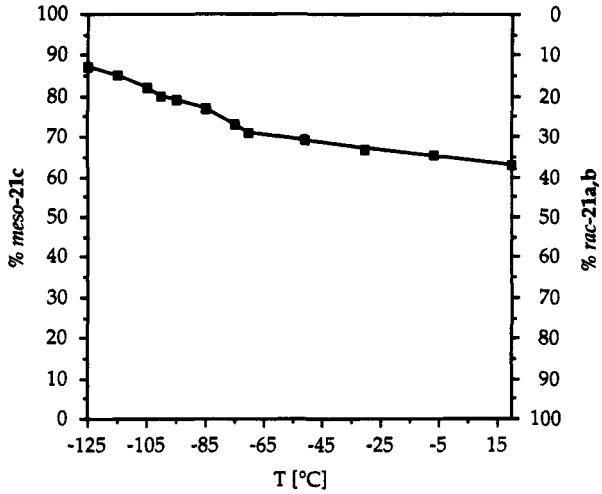
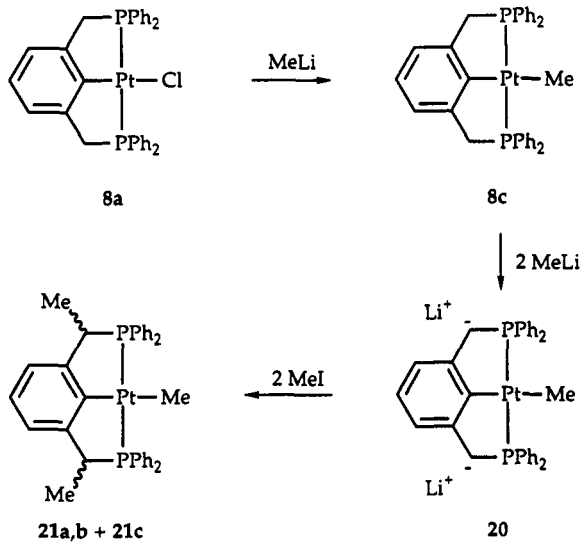


Figure 2. Temperature dependence of the **21a,b:21c** ratio for the "methylation" reaction of **8c**.

Scheme 5



conveniently prepared *in situ* by addition of 3 equiv of methyllithium to the chloro complex **8a**. Reaction of **20** with 2 equiv of methyl iodide gave the isomeric mixtures of the methyl-substituted complex, **21a,b** and **21c**. The ratio of these two forms depended on the temperature at which the reaction was carried out, as shown in Figure 2.

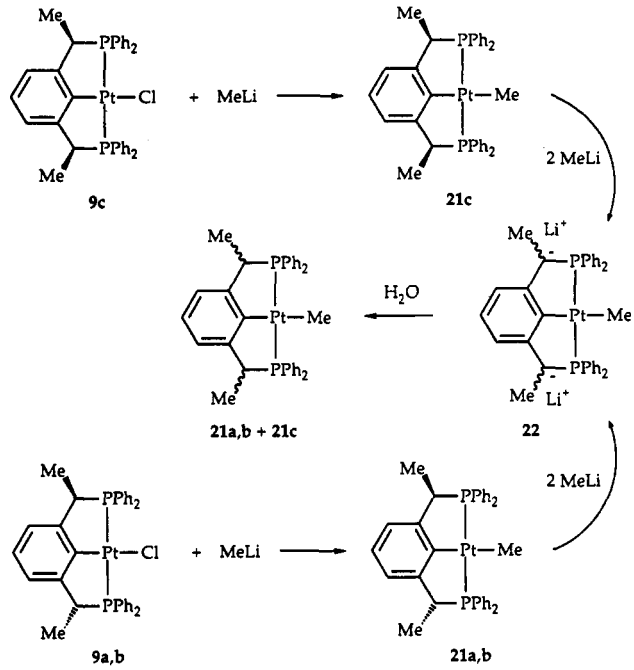
When the "methylation" reaction was carried out above −30 °C also small amounts (ca. 10%) of two byproducts (^{31}P NMR ($CDCl_3$): δ 54.1 and 48.5) were produced. They may be the platinum(IV) complexes *meso-* and *rac-*[PtIMe(21)]. As the corresponding J(PtP) couplings could not be observed because of the poor signal-to-noise ratio, this assignment must remain tentative. As can be seen in Figure 2, the kinetically controlled product is the *meso-*form **21c** (ca. 86% at −125 °C).

As it is well-established that product distribution in alkylations of the above type is strongly influenced by the nature of the lithium reagent used,[14] complex **8c** was deprotonated using an excess of lithium diisopropylamide (LDA) in THF. However, even in this case, at parity of temperature, the ratio of **21a,b:21c** obtained did not differ from that produced using MeLi.

In order to obtain additional information about the relative stabilities of **21a,b** vs **21c**, the isomerization experiments shown in Scheme 6 were carried out.

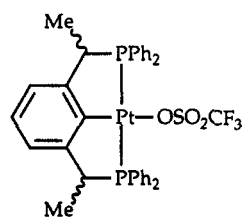
(14) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624 and references quoted therein.

Scheme 6



The pure *meso*-compound **9c** was reacted first with 1 equiv of methyllithium to get the methyl complex **21c** which was, subsequently, deprotonated with 2 equiv of methyllithium and then the dianion hydrolyzed with water. The same reaction sequence was carried out starting from the pure racemate **9a,b**. Isomerization occurred in both sets of experiments and the resulting isomer ratios were identical to those obtained in the preparative experiments; i.e., they depended only on the temperature at which the reaction was carried out and not on the starting complex (see Scheme 5 and Figure 2). Also this reaction was tested using LDA as the base. In this case a somewhat higher amount of the racemate **21a,b** was produced as the ratio of **21a,b:21c** was 46%:54% when hydrolysis was carried out at 0 °C. Thus, in all cases, the apparently more sterically crowded complex was predominantly formed. In order to test whether this crowding was indeed greater in **9c** than in **9a,b** the X-ray crystal structures of the complexes **9a,b** and **9c** were carried out (see later).

Many catalytic reactions, e.g., acetalization,[15] allylic alkylation,[16] and aldol reactions,[17] can be carried out using cationic complexes or their precursors in the form of compounds containing weakly held oxygen donors, e.g., triflate.[18] Thus the complexes **8e** and **23a–c** were prepared by reacting the corresponding chlorides, **8a**, **9a,b**, and **9c**, respectively, with silver trifluoromethanesulfonate.



23a,b (*rac*-form)
23c (*meso*-form)

Preliminary experiments show that at least compound **8e** is an active catalyst for the acetalization reaction. The

(15) Gorla, F.; Venanzi, L. M. *Helv. Chim. Acta* **1990**, *73*, 690.
(16) Bovens, M.; Togni, A.; Venanzi, L. M. *J. Organomet. Chem.* **1993**, *451*, C28.
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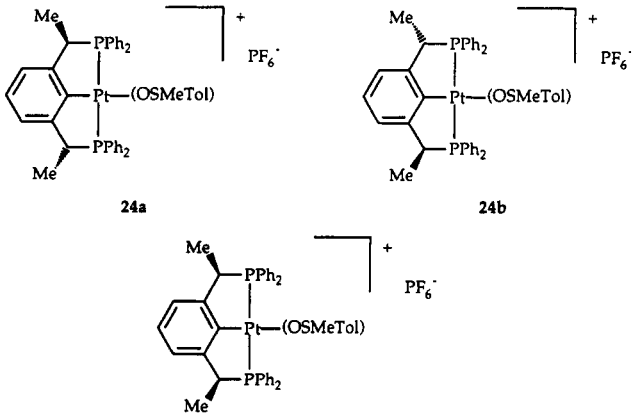
(18) (a) Hartley, F. R.; Murray, S. G.; Wilkinson, A. *Inorg. Chem.* **1989**, *28*, 549. (b) Diver, C.; Lawrance, A. *J. Chem. Soc., Dalton Trans.* **1988**, 931.

use of these triflate complexes for the above catalytic reactions will be described in a later publication.

Before attempting the separation of the racemic mixture of the complexes **9a,b**, an analytical method for the identification of the single enantiomers had to be developed. The technique eventually used was ^{31}P NMR of the complexes **24a–c**, obtained by reacting the corresponding chlorides **9a–c** with silver hexafluorophosphate in the presence of (*R*)(+)-methyl 4-tolyl sulfoxide, OSMeTol.



The sulfoxides are likely to be O-bonded in these complexes, as their ^1H NMR spectra show δ values for the sulfoxide methyl group of 2.40, 2.43, and 2.53 ppm, respectively, i.e., in the range of those found for other O-bonded sulfoxides.[19] The spectrum of the diastereomeric pair **24a** and **24b** consists of two singlets, each with the corresponding ^{195}Pt satellites, the two phosphorus donors of these isomers being equivalent because of the free rotation of optically active sulfoxide. The spectrum of the *meso*-form **24c** is more complex, its appearance being that of an AB system (arising from the inequivalence of the two P donors), flanked by the corresponding ^{195}Pt satellites.

Preliminary experiments showed that it was not possible to differentiate between the enantiomeric forms of the complexes, analogous to **24a,b**, but containing either (–)-mandelate or (*R*)(+)-*N*,*N*-dimethyl-1-phenylethylamine, instead of the chiral sulfoxide, as the ^{31}P NMR chemical shifts of the corresponding diastereomeric forms showed only small differences.

Finally, attempts were made to separate the diastereomeric mixture **24a,b** by fractional crystallization from a variety of solvent mixtures. However, no enrichment of one of the forms was observed. These attempts were not pursued, as an optically pure ligand related to **10** could be obtained using conventional organic synthesis. This and its complexes will be described in a later publication. For the same reason no attempts were made to "methylate" the CH_2 groups of complexes containing the moiety **2** and an optically active ligand in a *trans* position to the C donor.

Crystal Structures. The X-ray crystal structures of several compounds containing the moiety **2** have been determined, e.g., **6b**,[11] **7b**,[11] **8b**,[11] and **8d**.[20] Their structural features are very similar. However, as details of those of **6b**, **7b**, and **8b** are not easily available, the geometries of the complexes **9a,b** and **9c** will be compared with those of **7a**, reported here, and with **8d**.

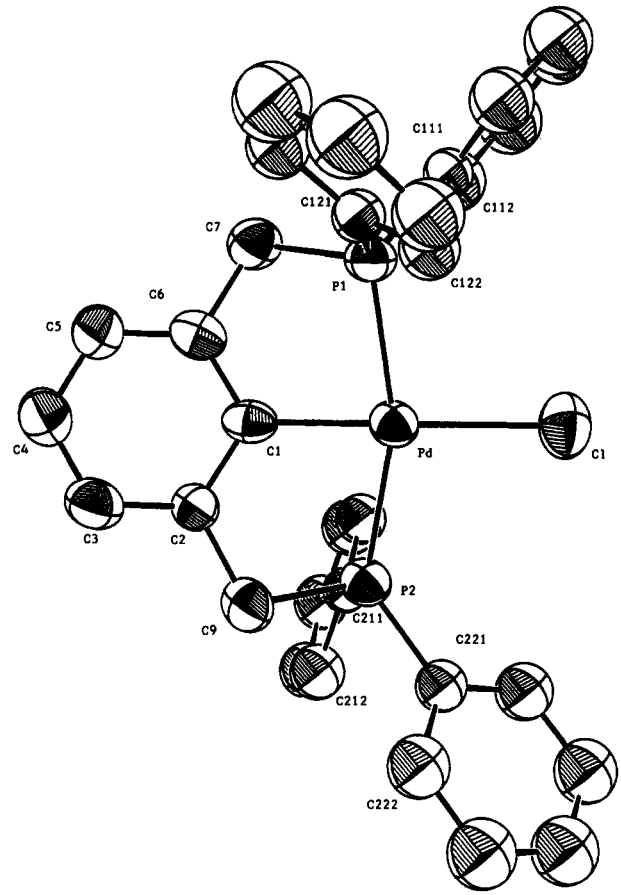
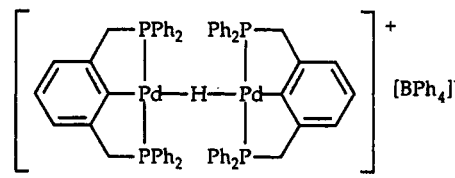


Figure 3. ORTEP view of **7a**. (Ellipsoids have been drawn at 50% probability.)

Crystals of **7a** were obtained in an attempt to grow single crystals of the hydrido-bridged compound **25**[3] from a solvent mixture containing CH_2Cl_2.



25

The crystals contain discrete molecules of **7a** separated by normal van der Waals interactions. An ORTEP view of the molecule is shown in Figure 3, and a selection of bond lengths and angles are given in Table 1.

The main features of this structure, relevant for the discussion of those of **9a,b** and **9c**, are (1) the square planar geometry shows a slight tetrahedral distortion, the angles P1–Pd–P2 and C1–Pd–Cl being 162.0(3) and 178.7(3)°, respectively, (2) the angle between the mean square coordination plane, defined by Pd, Cl, C1, P1, and P2, and that of the cyclometalated benzene ring is 19.8(5)° (see Figure 4), and (3) the two chelating rings are quite strained because of the constraints imposed by the atoms forming the two adjacent five-membered chelate rings. This strain is partly relieved by the formation of unequal Cl–Pd–P1 and Cl–Pd–P2 bond angles, 98.1(1) and 99.9(1)°, respectively. Furthermore, the puckering differs in the two rings, C7 being on one side of the plane defined by Pd, Cl, C1, P1, and P2 while C9 is on the opposite side of the same

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Table 1. Selection of Bond Lengths (Å) and Angles (deg) for Compounds 7a, 8d, 9a,b, and 9c

	7a[a]	9a,b[b]	9c[b]	8d[c]
	Bond Lengths and Angles			
M–C1	1.998(8)	2.003(9)	2.00(2)	2.066(3)
M–P1	2.288(3)	2.273(2)	2.269(6)	2.269(1)
M–P2	2.294(3)	2.268(2)	2.253(6)	2.261(1)
M–X	2.367(3)	2.384(2)	2.368(6)	2.058(3)
P1–M–X	98.1(1)	99.44(9)	99.0(2)	100.0(1)
P2–M–X	99.9(1)	97.14(9)	97.5(2)	96.9(1)
P1–M–C1	81.3(3)	82.3(3)	82.2(6)	82.2(1)
P2–M–C1	80.8(3)	81.2(3)	81.2(6)	81.1(1)
M–P1–C7	101.0(4)	103.0(3)	101.4(8)	104.6(2)
M–P2–C9	101.3(3)	101.6(3)	100.4(7)	102.8(2)
P1–C7–C6	105.7(6)	105.5(6)	105(1)	109.3(3)
P2–C9–C2	105.4(6)	105.3(6)	105(2)	105.5(3)
M–C1–C2	121.3(6)	121.0(7)	121(1)	120.8(3)
M–C1–C6	122.0(7)	120.8(7)	120(1)	122.2(3)
X–M–C1	178.7(3)	177.6(3)	178.5(6)	176.8(2)
P1–M–P2	162.0(1)	163.1(1)	163.4(2)	161.87(4)
M–P1–C7–C6	34.5(6)	30.5(6)	33(2)	17.2(3)
M–P2–C9–C2	33.6(6)	34.2(6)	35(1)	34.0(3)
M–C1–C2–C9	–3(1)	2(1)	–1(3)	5.5(8)
M–C1–C6–C7	2(1)	8(1)	7(3)	0.0(7)
C1–C6–C7–C8		94(1)	89(2)	
C1–C2–C9–C10		93(1)	27(2)	
M–P1–C7–C8		–89.4(7)	–86(2)	
M–P2–C9–C10		86.1(6)	17(2)	
M–P1–C111–C112	57.6(9)	49.0(9)	–160(2)	–160.6(3)
M–P1–C121–C122	47.5(9)	24.6(9)	6(2)	3.1(4)
M–P2–C211–C212	–172.0(7)	–157.1(7)	–2(3)	19.6(4)
M–P2–C221–C222	111.4(8)	77.3(9)	173(2)	130.2(4)
	Deviations (Å) from the M, X, C1, P1, P2 Mean Square Plane (+ = above Plane)			
M	+0.007(1)	+0.0153(3)	+0.0017(7)	+0.0351(1)
X	+0.019(3)	+0.035(3)	+0.019(5)	+0.064(3)
C1	+0.033(9)	+0.060(8)	+0.03(2)	+0.094(3)
P1	–0.030(3)	–0.055(2)	–0.025(5)	–0.095(1)
P2	–0.030(2)	–0.056(2)	–0.025(6)	–0.098(1)
C7	–0.82(1)	–0.693(9)	–0.76(2)	–0.469(5)
C8		–2.24(1)	–2.35(2)	
C9	+0.83(1)	+0.785(9)	+0.84(2)	+0.688(4)
C10		+2.24(1)	+0.67(2)	
	Angle (deg) between the Above Plane and the Plane of the Central Benzene Ring C1–C6			
	19.8(5)	14.7(7)	17(1)	11.4(5)

[a] M = Pd; X = Cl. [b] M = Pt; X = Cl. [c] M = Pt; X = CO_2H.

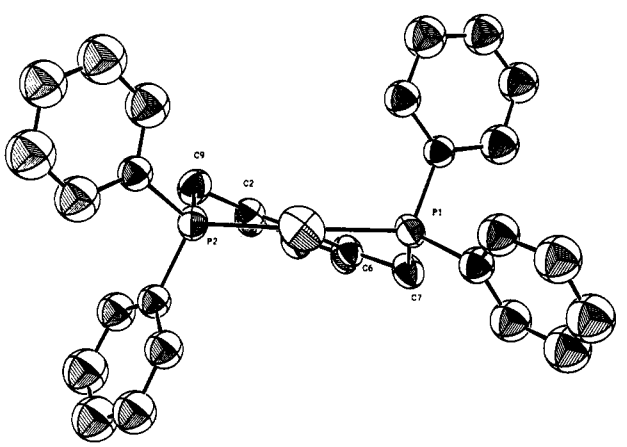

Figure 4. ORTEP view of **7a** projected along the Cl–Pd–Cl axis. (Ellipsoids have been drawn at 50% probability.)

plane. As a consequence, on each side of the molecule one of the terminal phenyl groups is pseudoequatorial while the other is pseudoaxial. Furthermore, while the pseudoaxial substituent on one side of the molecule is above the coordination plane, the corresponding substituent on the other side is below the coordination plane.

As mentioned in the Introduction, the positions of the terminal phenyl groups are almost C_2-symmetric, on each side of the molecule one of them being axial and the other equatorial. This arrangement is a consequence of the

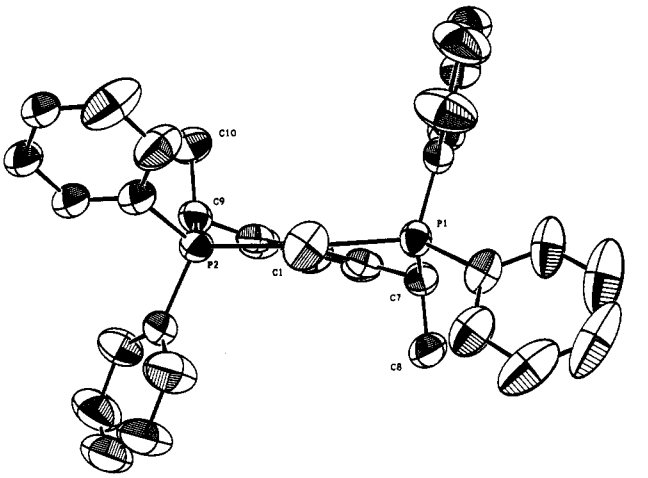

Figure 5. ORTEP view of **9a,b** projected along the Cl–Pt–C1 axis. (Ellipsoids have been drawn at 50% probability.)

doubly chelating structure which places C7 below the Pd, Cl, C1, P1, and P2 plane (–0.469(5) Å) and C9 above that plane (+0.688(4) Å).

There are no significant structural differences between the chloro complex **7a** and its bromo analog **7b**.[11]

A comparison of the palladium chloro complex **7a** with the platinum carboxyl complex **8d** shows (1) a lengthening of the Pt–C1 bond in the latter compound (2.066(3) Å) relative to the former (1.998(8) Å), likely to be caused by the high *trans* influence of the carbon donor of the carboxyl ligand, and (2) changes in the orientations of the terminal phenyl groups consequent upon the above bond lengthening which influences the bond angles of the two chelate rings. However, complex **8d** has a dimeric hydrogen-bonded structure in the solid state and, therefore, it is possible that the relative positions of the latter end groups could be influenced by van der Waals interactions between the two monometallic units. Furthermore, as the data available for **8b**[11] have high standard deviations, it will be more appropriate to compare the structural features of **9a,b** and **9c** with those of **7a**.

The structure of the racemic complex **9a,b** will be discussed first, as its geometry is more regular. An ORTEP view of the molecule is shown in Figure 5, and a selection of bond lengths and angles is given in Table 1. As can be best seen by comparing Figures 4 and 5, its structure and that of the palladium complex **7a** are very similar, including the puckering of the chelate rings which are not significantly altered by the presence of the two axial methyl substituents.

The orientations of the phenyl end groups are basically the same as those found in the palladium complex except for slight rotation around the P–C bonds, e.g., M–P2–C211–C212 in **7a** is –172.0(7)° and in **9a,b** is –157.1(7)° and M–P1–C111–C112 in **7a** is 57.6(9)° and in **9a,b** is 49.0(9)°.

Particularly interesting is the comparison of the molecular geometries of **9a,b** and **9c** (an ORTEP view of the latter molecule is shown in Figure 6, and a selection of bond lenghts and angles is given in Table 1). One observes that the bond distances and angles of the two chelating rings are strictly comparable in both structures. Furthermore, in the ring containing P1, C6, and C7, the conformation of the chelate ring and that of its substituents remain practically unchanged relative to those in isomer **9a,b**. However, while in **9a,b** and **9c** the bond distances and angles in the other ring are almost the same as in the

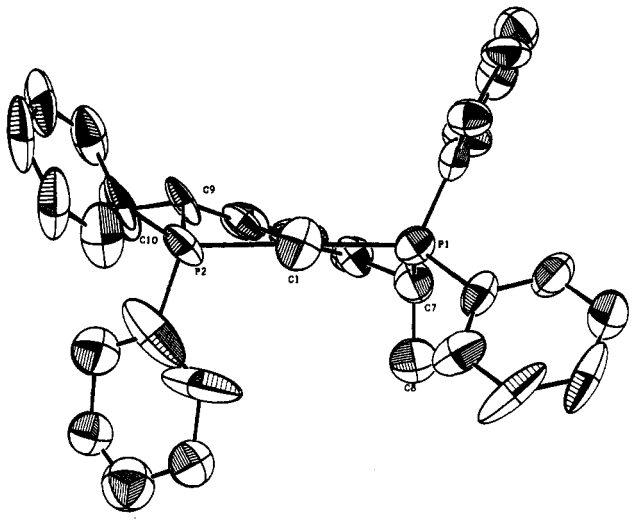

Figure 6. ORTEP view of **9c** projected along the Cl–Pt–Cl axis. (Ellipsoids have been drawn at 50% probability.)

first, the methyl substituent on C10 is displaced from its expected axial position and has become practically equatorial. Associated with this movement is a change in relative orientation of the neighboring terminal phenyl groups, as can be seen from the data of Table 1, particularly from the positions in **9c** of C8 (−2.35(2) Å) and C10 (+0.67(2) Å) relative to the above-mentioned coordination plane. This appears to be due to steric crowding which cannot be decreased by rotating the terminal phenyl groups, as their positions tend to be fixed by the presence of the two chelate rings which requires, even in the unsubstituted compound **7a** (see Figure 4), that of the two atoms C7 and C9 one should be above and one below the coordination plane. Thus, as expected from a static model, the structure of **9c** is more strained than that of **9a,b**. This result renders the ratio **9a,b**:**9c** obtained during the "methylation" and in isomerization reactions even more surprising.

Experimental Section

The compounds *cis*-$[PtCl_2(PPh_3)_2]$,[21] $LiPPh_2$,[22] bis(μ-chloro)-bis[(η³-2-methylallyl)platinum],[23] [2,6-bis[(diphenylphosphino)-methyl]phenyl]chloroplatinum(II), **8a**,[3] and [2,6-bis[(diphenylphosphino)methyl]phenyl]methylplatinum(II), **8c**,[3] were prepared as described in the appropriate references. All other reagents were purchased from Fluka AG and used without further purification. Solvents were dried by standard procedures under argon and stored over molecular sieves. All manipulations with free phosphines were carried out using conventional Schlenk-tube techniques under an atmosphere of prepurified dinitrogen or argon. All melting points were determined in open capillary tubes and are uncorrected. The NMR spectra were measured on a Bruker AC-200 or a Bruker WM-250 NMR spectrometer. The ^1H, ^{13}C, ^{31}P, and ^{195}Pt chemical shifts, in ppm, are given relative to tetramethylsilane, external 85% phosphoric acid and 0.1 M $Na_2[PtCl_6]$, respectively, a positive value denoting a shift downfield of the reference. The following abbreviations have been used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dq, doublet of quartets; t(virt), apparent triplet (special solution of the spin system AA'XX'); q(virt), apparent quartet (special solution of the spin system $A_3A'_3BB'XX'$). Elemental analyses were performed by the "Mikroelementaranalytisches Laboratorium der Eidgenössischen Technischen Hochschule Zürich". Merck silica gel 60 (230–400 mesh) was used for flash column chromatography. The following columns were used for the attempted separations of racemic mixtures: Chira Spher (Merck), Chiracel OD and OD-H (Daicel Chemical Ind.), and Pirkle Covalent Phenylglycine (Pirkle).

1,3-Bis[(diphenylthiophosphino)methyl]benzene, 16. To a solution of 1,3-bis[(diphenylphosphino)methyl]benzene, **1b** (26.1 g, 55 mmol), in 200 mL of chloroform, was added sulfur (3.53 g, 110 mmol). The suspension was then refluxed for 1 h, and the clear yellow solution was concentrated to a third of the volume under reduced pressure. Ethanol was added to this boiling solution until the first crystals appeared. After several hours at 4 °C the white crystalline product was filtered off, washed with ethanol, and dried. Yield: 28.1 g (95%). The analytical data were identical to those reported in the literature.[3]

(1*R*,1'*S*)-, 17c, and (1*R*,1'*R*),(1*S*,1'*S*)-1,3-Bis[1-(diphenylthiophosphino)ethyl]benzene, 17a,b. To a solution of 1,3-bis[(diphenylthiophosphino)methyl]benzene, **16** (38.8 g, 72 mmol), in 1200 mL of tetrahydrofuran, was added a 1.6 M solution of *n*-butyllithium in hexane (92 mL, 147 mmol) at −70 °C. The dark red solution was stirred for 1 h, and then a solution of methyl iodide (9.2 mL, 147 mmol), in 100 mL of tetrahydrofuran, was added over 15 min. The cooling bath was then removed, and the mixture was stirred for 2 h at room temperature. The solvent was removed by rotary evaporation, and the resulting residue was redissolved in 400 mL of dichloromethane and 200 mL of water. The organic phase was washed with three portions of 200 mL of water and dried with $MgSO_4$, and the solvent was removed by rotary evaporation. The oily crude product was purified by crystallization from chloroform/ethanol and gave a mixture of about 1:1 of *rac*-**17a,b** and *meso*-**17c**. Yield: 37.0 g (90%). Three crystallizations from toluene gave 16.9 g (yield, relative to **16**, 43%) of **17c** of >97% purity. The collected mother liquors were concentrated to dryness, and the residue was recrystallized three times from chloroform/ethanol. This gave 15.2 g (yield, relative to **16**, 38%) of **17a,b** of >98% purity.

***meso*-17c**: mp 224–225 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.30 (dd, ^3J(HH) 7.1 Hz, ^3J(PH) 18.9 Hz, 6H, CH_3), 3.95 (qd, ^3J(HH) 7.1 Hz, ^2J(PH) 9.3 Hz, 2H, CH), 6.92–8.13 (m, 24H, C_6H_4 and C_6H_5); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 15.3 (s, 2C, CH_3), 40.9 (d, ^1J(PC) 49.7 Hz, 2C, CH), 127.1–136.3 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 51.8. Anal. Calcd for $C_{34}H_{32}P_2S_2$: C, 72.06; H, 5.69. Found: C, 71.96; H, 5.65.

***rac*-17a,b**: mp 196–198 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.52 (dd, ^3J(HH) 7.1 Hz, ^3J(PH) 18.7 Hz, 6H, CH_3), 3.89 (qd, ^3J(HH) 7.1 Hz, ^2J(PH) 9.2 Hz, 2H, CH), 6.83–8.13 (m, 24H, C_6H_4 and C_6H_5); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 16.6 (s, 2C, CH_3), 41.0 (d, ^1J(PC) 50.6 Hz, 2C, CH), 127.5–137.5 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 51.0. Anal. Calcd for $C_{34}H_{32}P_2S_2$: C, 72.06; H, 5.69. Found: C, 72.29; H, 5.77.

(1*R*,1'*S*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene, 10c. A suspension of **17c** (15.3 g, 27 mmol) in tri-*n*-butylphosphine (15 g, 74 mmol) was gradually heated to 180 °C. The resulting solution was stirred 2 h at this temperature and then cooled to room temperature. Addition of 50 mL of hexane gave a white precipitate which was washed twice with 50 mL of hexane under argon. After filtration, the residue was purified by recrystallization from ethanol and gave 12.5 g (92%) of **10c** as white plates: mp 96–98 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 1.31 (dd, ^3J(HH) 7.1 Hz, ^3J(PH) 14.8 Hz, 6H, CH_3), 3.50 (qd, ^3J(HH) 7.1 Hz, ^2J(PH), 7.1 Hz, 2H, CH), 6.85–7.66 (m, 24H, C_6H_4 and C_6H_5); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ 19.9 (d, ^2J(PC) 20.0 Hz, 2C, CH_3), 39.4 (d, ^1J(PC) 12.4 Hz, 2C, CH), 126.7–143.7 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 1.9. Anal. Calcd for $C_{34}H_{32}P_2$: C, 81.26; H, 6.42; P, 12.33. Found: C, 80.98; H, 6.42; P, 12.34.

(1*R*,1'*S*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene–Bisborane, 18c. To a stirred solution of **10c** (1.20 g, 2.39 mmol), in 30 mL of toluene, was added borane dimethyl sulfide (476 μL, 5.0 mmol). After 1 h at room temperature the solution was evaporated to dryness. The residue was purified by recrystallization from benzene/hexane to give 1.18 g (93%) of **18c**: mp 165–167 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.5–1.5 (6H, BH_3), 1.31 (dd, ^3J(HH) 7.3 Hz, ^3J(PH) 16.5 Hz, 6H, CH_3), 3.74 (qd, ^3J(HH) 7.3 Hz, ^2J(PH) 15.7 Hz, 2H, CH), 6.79–7.92 (m, 24H,

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C_6H_4 and C_6H_5); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ 15.8 (s, 2C, CH_3), 36.7 (d, ^1J(PC) 31.1 Hz, 2C, CH), 127.1–137.0 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 24.6. Anal. Calcd for $C_{34}H_{38}B_2P_2$: C, 77.02; H, 7.22. Found: C, 76.95; H, 7.39.

(1*R*,1′*R*),(1*S*,1′*S*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene, 10a,b. It was prepared as described for **10c**. As problems were encountered with its purification, the reaction mixture **10a,b**/tributylphosphine sulfide/tributylphosphine, in the ratio 1:2:0.74, was used directly for the cyclometalation reaction. Alternatively, the product could be purified by preparing the corresponding borane adducts as described below: $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 1.2.

(1*R*,1′*R*),(1*S*,1′*S*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene–Bisborane, 18a,b. To a stirred solution of the mixture of **10a,b**/tributylphosphine sulfide/tributylphosphine described above (15.5 g), in 60 mL of toluene, was added borane dimethyl sulfide (3.0 mL, 31.6 mmol). After 2 h at room temperature the solvent was evaporated, leaving the crude product as an oily residue. This was first purified by column chromatography (SiO_2, hexane/ethyl acetate, 3:1) and then by crystallization from benzene/hexane. Yield: 4.1 g (ca. 94%) of **18a,b**. Mp: 157–160 °C. ^1H NMR (250 MHz, $CDCl_3$): δ 0.5–1.5 (6H, BH_3), 1.49 (dd, ^3J(HH) 7.3 Hz, ^3J(PH) 16.2 Hz, 6H, CH_3), 3.68 (qd, ^3J(HH) 7.3 Hz, ^2J(PH) 15.1 Hz, 2H, CH), 6.90–8.11 (m, 24H, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 16.9 (d, ^2J(PC) 3.2 Hz, 2C, CH_3), 37.5 (d, ^1J(PC) 31.1 Hz, 2C, CH), 127.6–138.1 (12 different aromatic C atoms). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 24.6. Anal. Calcd for $C_{34}H_{38}B_2P_2$: C, 77.02; H, 7.22. Found: C, 76.97; H, 7.50.

Alkylation Reaction of the Borane Adduct of Phosphine 1b. To a stirred solution of **1b** (2.8 g, 6.0 mmol), in 40 mL of toluene, was added the borane dimethyl sulfide (1.25 ml, 13 mmol). After 1 h at room temperature the solution was evaporated to dryness. The residue was redissolved in 50 mL of THF and a 1.6 M solution of *n*-butyllithium in hexane (7.8 mL, 12.5 mmol) was added at −70 °C. The dark red solution was stirred for ca. 30 min and then a solution of methyl iodide (782 μL, 12.5 mmol), in 10 mL of THF, was added. The cooling bath was removed, and the mixture was stirred for 1 h at room temperature. The solvent was removed by rotary evaporation, and the resulting residue was redissolved in 50 mL of CH_2Cl_2 and 25 mL of water. The organic phase was washed with three 20-mL portions of water and dried with $MgSO_4$, and the solvent was removed by rotary evaporation. The crude product, after purification by crystallization from CH_2Cl_2/hexane, gave a mixture of about 1:1 of *meso*-**18c** and *rac*-**18a,b**. Yield: 2.8 g (88%). The separation of the two diastereomers, by crystallization from benzene/hexane, was not as effective as the separation of the corresponding phosphine sulfides. Thus the pure **18a,b** and **18c** were prepared by reaction of the corresponding pure phosphines **10a,b** and **10c** with $BH_3{\cdot}S(Me)_2$. Their NMR parameters were given earlier.

(1*R*,1′*R*),(1*S*,1′*S*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene, 10a,b. A suspension of **18a,b** (5.3 g, 10 mmol) in 40 mL of diethyl amine was heated to 40 °C. The resulting solution was stirred for 3 h at this temperature and then cooled to room temperature. After evaporation of the amine the resulting oily residue was purified by recrystallization from ethanol at −10 °C to give 3.8 g (75%) of **10a,b** as a viscous oil: mp 0–10 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 1.39 (dd, ^3J(HH) 7.1 Hz, ^3J(PH), 14.6 Hz, 6H, CH_3), 3.49 (qd, ^3J(HH) 7.1 Hz, ^2J(PH), 7.1 Hz, 2H, CH), 6.98–7.69 (m, 24H, C_6H_4 and C_6H_5); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ 19.8 (d, ^2J(PC) 20.5 Hz, 2C, CH_3), 38.9 (d, ^1J(PC) 12.3 Hz, 2C, CH), 125.8–143.3 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 1.2. Anal. Calcd for $C_{34}H_{32}P_2$: C, 81.26; H, 6.42. Found: C, 80.98; H, 6.67.

[(1*R*,1′*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]chloroplatinum(II), 9c. A suspension of **10c** (1.96 g, 3.90 mmol) and *cis*-$[PtCl_2(PPh_3)_2]$ (3.0 g, 3.80 mmol), in 200 mL of chloroform, was refluxed for 20 h. The resulting solution, containing the quantitatively formed intermediate **19c** $^{31}P\{^1H\}$ NMR (81 MHz, acetone-d_6) δ 20.4 (t, ^2J(PP) 20.1 Hz, ^1J(PPt) 2079 Hz, PPh_3), 55.2 (d, ^2J(PP) 20.1 Hz, ^1J(PPt) 2764 Hz, PPh_2)}, was reduced to 20 mL, and elemental sulfur (245 mg, 7.60 mmol), potassium chloride (567 mg, 7.60 mmol), and acetone (170 mL) were successively added. The suspension was stirred at 50 °C for 3–5 h until the product **9c** had quantitatively formed (checked by ^{31}P NMR). The crude product was first purified by column chromatography (SiO_2, CH_2Cl_2/ethyl acetate, 20:1) and then recrystallized from tetrahydrofuran/hexane. Yield: 2.3 g (82%).

Alternatively, a solution of **10c** (1.41 g, 2.80 mmol) and bis(μ-chloro)bis[(η^3-2-methylallyl)platinum] (0.80 g, 1.40 mmol), in 50 mL of chloroform, was refluxed for 10 min. The solvent was removed by rotary evaporation and the residue, recrystallized from THF/hexane, gave 1.85 g (90%) **9c**: mp 257–258 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 1.31 (q(virt), $A_3A'_3BB'XX'$, ^3J(HH) 7.7 Hz, ^3J(PH) + ^5J(PH) 15.1 Hz, 6H, CH_3), 4.09 (m, 2H, CH), 7.02–7.17 (m, 3H, C_6H_3), 7.34–7.81 (m, 20H, C_6H_5); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 19.3 (s, 2C, CH_3), 45.4 (t(virt), $AA'XX'$, ^1J(PC) + ^3J(PC) 35.2 Hz, 2C, CH), 122.7–151.9 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 50.1 (s, ^1J(PtP) 2966 Hz); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ −4210.6 (t, ^1J(PtP) 2966 Hz). Anal. Calcd for $C_{34}H_{31}P_2ClPt$: C, 55.78; H, 4.27; Cl, 4.84. Found: C, 55.52; H, 4.28; Cl, 4.90.

[(1*R*,1′*R*),(1*S*,1′*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]chloroplatinum(II), 9a,b. It was prepared as described for **9c**, using the mixture containing **10a,b**/tributylphosphine sulfide/tributylphosphine (in the approximate ratio 1:2:0.74), prepared as described earlier, and an amount of sulfur (334 mg, 10.41 mmol) corresponding to the quantity of tributylphosphine present, which gave, after column chromatography (SiO_2, CH_2Cl_2/ethyl acetate, 20:1) and crystallization with THF/hexane, 2.1 g (75%) of **9a,b**: mp 244–246 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.14 (q(virt), $A_3A'_3BB'XX'$, ^3J(HH) = 8.1 Hz, ^3J(PH) + ^5J(PH) 16.0 Hz, 6H, CH_3), 4.07 (m, 2H, CH), 7.09 (m, 3H, C_6H_3), 7.36–7.95 (m, 20H, C_6H_5); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 21.2 (s, 2C, CH_3), 46.2 (t(virt), $AA'XX'$, ^1J(PC) + ^3J(PC) 36.2 Hz, 2C, CH), 122.4–153.3 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 47.5 (s, ^1J(PtP) 2973 Hz); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ −4172.9 (t, ^1J(PtP) 2973 Hz). Anal. Calcd for $C_{34}H_{31}P_2ClPt$: C, 55.78; H, 4.27; Cl, 4.84. Found: C, 55.48; H, 4.25; Cl, 4.86.

This complex was also prepared starting from $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2]$ as described for **9c**. Yield: 1.83 g (89%).

[(1*R*,1′*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]methylplatinum(II), 21c. To a solution of **9c** (200 mg, 273 μmol), in 40 mL of tetrahydrofuran, was slowly added a 1.6 M solution of methyllithium in diethyl ether (172 μL, 274 μmol) at room temperature. After stirring for 10 min, the solvent was removed by rotary evaporation and the resulting residue redissolved in 80 mL of CH_2Cl_2. The organic phase was washed with three portions of 100 mL of water and dried with $MgSO_4$, and the solvent was removed by rotary evaporation. The resulting residue was purified by crystallization from benzene/hexane and gave 165 mg (85%) **21c**: mp 200–202 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.40 (t, ^3J(PH) 4.7 Hz, ^2J(PtH) 56.2 Hz, 3H, CH_3) 1.29 (q(virt), $A_3A'_3BB'XX'$, ^3J(HH) 7.4 Hz, ^3J(PH) + ^5J(PH) 15.1 Hz, 6H, CH_3), 4.24 (m, 2H, CH), 7.13 (m, 3H, C_6H_3), 7.31–7.71 (m, 20H, C_6H_5); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ −13.0 (s, 1C, Pt–CH_3), 18.9 (s, 2C, CH_3), 49.9 (t(virt), $AA'XX'$, ^1J(PC) + ^3J(PC) 36.7 Hz, ^2J(PtC) 77.5 Hz, 2C, CH), 121.3–152.5 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 51.2 (s, ^1J(PtP) 3031 Hz); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ −4300.9 (t, ^1J(PtP) 3031 Hz). Anal. Calcd for $C_{35}H_{34}P_2Pt$: C, 59.07; H, 4.82. Found: C, 59.16; H, 4.84.

[(1*R*,1′*R*),(1*S*,1′*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]methylplatinum(II), 21a,b. It was prepared as described for **21c** starting from **9a,b**. Yield: 169 mg (87%): mp 218–220 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.49 (t, ^3J(PH) 4.8 Hz, ^2J(PtH) 55.9 Hz, 3H, CH_3), 1.16 (q(virt), $A_3A'_3BB'XX'$, ^3J(HH) 7.5 Hz, ^3J(PH) + ^5J(PH) 15.5 Hz, 6H, CH_3), 4.27 (m, 2H, CH), 7.14 (m, 3H, C_6H_3), 7.30–7.80 (m, 20H, C_6H_5); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ −13.6 (s, 1C, Pt–CH_3), 20.2 (s, 2C, CH_3), 50.6 (t(virt), $AA'XX'$, ^1J(PC) + ^3J(PC) 37.0 Hz, 2C, CH), 121.1–153.3 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 49.4 (s, ^1J(PtP) 3041 Hz); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ

−4275.5 (t, ^1J(PtP) 3041 Hz). Anal. Calcd for $C_{35}H_{34}P_2Pt$: C, 59.07; H, 4.82. Found: C, 59.13; H, 4.81.

[2,6-Bis[(diphenylphosphino)methyl]phenyl][(trifluoromethyl)sulfonyl]platinum(II), 8e. A solution of **8a** (480 mg, 682 μmol) in 50 mL of CH_2Cl_2 and $AgCF_3SO_3$ (175.5 mg, 683 μmol) was stirred at room temperature for 2 h. The precipitated silver chloride was filtered off over Celite, and the solvent was evaporated under reduced pressure. The solid was recrystallized from toluene and gave 541 mg (97%) of **8e**: mp 234–235 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.82 (t(virt), $A_2A'_2$-XX', ^3J(PH) + ^4J(PH) 9.1 Hz, ^3J(PtH) 29.1 Hz, 4H, CH_2), 7.01 (m, 3H, C_6H_3), 7.46–7.83 (m, 20H, C_6H_5); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 41.6 (t(virt), AA'XX', ^1J(PC) + ^3J(PC) 36.5 Hz, 2C, CH_2), 123.1–147.0 (8 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 39.9 (s, ^1J(PtP) 3036 Hz); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ −4008.1 (t, ^1J(PtP) 3036 Hz). Anal. Calcd for $C_{38}H_{27}O_3F_3P_2SPt$: C, 48.47; H, 3.33. Found: C, 48.55; H, 3.33.

[(1*R*,1'*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl][(trifluoromethyl)sulfonyl]platinum(II), 23c. A solution of **9c** (500 mg, 682 μmol) in 50 mL of CH_2Cl_2 and $AgCF_3SO_3$ (175.5 mg, 683 μmol) were stirred at room temperature for 2 h. The precipitated silver chloride was filtered off over Celite and the solvent evaporated under reduced pressure. The solid was recrystallized from toluene/hexane and gave 542 mg (94%) of **23c**: mp 250–251 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.32 (q(virt), $A_3A'_3BB'XX'$, ^3J(HH) 7.6 Hz, ^3J(PH) + ^5J(PH) 15.3 Hz, 6H, CH_3), 4.01 (m, 2H, CH), 6.95–7.19 (m, 3H, C_6H_3), 7.38–7.79 (m, 20H, C_6H_5); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ 18.6 (s, 2C, CH_3), 44.3 (t(virt), AA'XX', ^1J(PC) + ^3J(PC) 35.0 Hz, 2C, CH), 122.9–151.6 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 55.1 (s, ^1J(PtP) 3037 Hz); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ − 4048.9 (t, ^1J(PtP) 3038 Hz). Anal. Calcd for $C_{38}H_{31}O_3F_3P_2SPt$: C, 49.71; H, 3.69. Found: C, 49.63; H, 3.75.

[(1*R*,1'*R*),(1*S*,1'*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl][(trifluoromethyl)sulfonyl]platinum(II), 23a,b. It was prepared as described for **23c**. Yield: 531 mg (92%). Mp: 251–252 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.20 (q(virt), $A_3A'_3$-$BB'XX'$, ^3J(HH) 8.0 Hz, ^3J(PH) + ^5J(PH) 15.7 Hz, 6H, CH_3), 3.98 (m, 2H, CH), 7.04 (m, 3H, C_6H_3), 7.39–7.84 (m, 20H, C_6H_5). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 20.8 (s, 2C, CH_3), 44.8 (t(virt), AA'XX', ^1J(PC) + ^3J(PC) 36.1 Hz, 2C, CH), 122.6–152.9 (12 different aromatic C atoms). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 51.5 (s, ^1J(PtP) 3035 Hz). $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$): δ −4022.7 (t, ^1J(PtP) 3035 Hz). Anal. Calcd for $C_{38}H_{31}O_3F_3P_2$-SPt: C, 49.71; H, 3.69. Found: C, 50.00; H, 3.88.

[(1*R*,1'*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]((*R*)-methyl 4-tolyl sulfoxide)platinum(II) Hexafluorophosphate, 24c. A solution of **9c** (130 mg, 178 μmol), (*R*)-methyl 4-tolyl sulfoxide (28.1 mg, 182 μmol) and silver hexafluorophosphate (46.0 mg, 182 μmol) in 50 ml of acetone were stirred at room temperature for 2 h. The silver chloride precipitate was filtered off over Celite and the solvent was reduced to 2mL. The addition of 50 mL of water gave 168 mg (95%) of white product **24c**: mp 140–150 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.46 (m, 6H, CH_3), 2.31 (s, 3H, tolyl CH_3), 2.53 (s, ^4J(PtH) 10.2 Hz, 3H, $SOCH_3$), 4.36 (m, 2H, CH), 6.95–7.77 (m, 27H, C_6H_3, C_6H_4, C_6H_5); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 18.2 (s, 1C, CH_3), 19.3 (s, 1C, CH_3), 21.4 (s, 1C, $C_6H_4CH_3$), 47.2 (m, 1C, CH), 47.4 (m, 1C, CH), 48.6 (s, 1C, $SOCH_3$), 123.6–150.9 (26 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ −143.6 (hept, ^1J(PF) 712 Hz, PF_6), 53.9/55.5 (dd, AB, ^2J(PP') 332 Hz, ^1J(PtP) 2808 Hz, ^1J(PtP') 2814 Hz); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ −4585.7 (t, ^1J(PtP) 2814 Hz). Anal. Calcd for $C_{42}H_{41}OF_6P_3SPt$: C, 50.66; H, 4.15. Found: C, 50.57; H, 4.27.

[(1*R*,1'*R*),(1*S*,1'*S*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]((*R*)-methyl 4-tolyl sulfoxide)platinum(II) Hexafluorophosphate, 24a,b. It was prepared from **9a,b** as described for **24c**. Yield of the diastereomeric mixture **24a,b**: 150 mg (85%). Mp: 150–160 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.49 (m, 12H, CH_3), 2.25 (s, 3H, tolyl CH_3), 2.30 (s, 3H, tolyl CH_3), 2.40 (s, 3H, $SOCH_3$), 2.43 (s, 3H, $SOCH_3$), 4.43 (m, 2H, CH), 4.59 (m, 2H, CH), 6.88–7.72 (m, 54H, C_6H_3, C_6H_4, C_6H_5). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ −144.7 (hept, ^1J(PF) 712 Hz, PF_6), 56.9 (s, ^1J(PtP) 2806 Hz), 58.5 (s, ^1J(PtP) 2839 Hz). Anal. Calcd for $C_{42}H_{41}OF_6P_3SPt$: C, 50.66; H, 4.15. Found: C, 50.37; H, 4.29.

"Methylation" Reaction. (a) To a solution of **8a** (40 mg, 56.8 μmol), in 8 mL of 2-MeTHF, was slowly added a 1.6 M solution of methyllithium in diethyl ether (107 μL, 171 μmol) at −10 °C. After stirring for 10 min, the red solution was cooled to the desired temperature and stirred for another 10 min, and methyl iodide (7.2 μL, 114 μmol) was added. After 30 min the mixture was quenched with a drop of a saturated NH_4Cl solution and the solvent was removed by rotary evaporation. The resulting residue was extracted with $CDCl_3$ and the product ratio was determined by ^{31}P NMR.

(b) To a solution of **8a** (40 mg, 56.8 μmol), in 7 mL of THF, was slowly added a 1.6 M solution of methyllithium in diethyl ether (36 μL, 57 μmol) at 0 °C. After stirring for 10 min, a 0.5 M solution of LDA in THF (1.0 mL, 500 μmol) was added at −10 °C. After stirring for 1.5 h, the red solution was cooled to the desired temperature and stirred for another 10 min, and methyl iodide (7.2 μL, 114 μmol) was added. After 15 min the mixture was quenched with a saturated NH_4Cl solution. After addition of CH_2Cl_2 the organic phase was separated and dried with $MgSO_4$, the solvent was removed by rotary evaporation, and the resulting residue was extracted with $CDCl_3$. The product ratio was determined by ^{31}P NMR.

Isomerization Reaction. (a) To a solution of **9c** (40 mg, 54.6 μmol), in 8 mL of 2-MeTHF, was slowly added a 1.6 M solution of methyllithium in diethyl ether (103 μL, 164 μmol) at −10 °C. After stirring for 10 min, the red solution was cooled to the desired temperature, stirred for another 10 min, and quenched with a drop of a saturated NH_4Cl solution. The solvent was removed by rotary evaporation, the resulting residue was extracted with $CDCl_3$, and the product ratio was determined by ^{31}P NMR.

The isomerization reaction on **9a,b** was similarly carried out.

(b) To a solution of **21c** (40 mg, 56.2 μmol), in 5 mL of 2-MeTHF, was slowly added a 0.5 M solution of LDA in THF (1.0 mL, 500 μmol) at −10 °C. After stirring for 3 h, the red solution was cooled to the desired temperature, stirred for another 10 min, and quenched with a saturated NH_4Cl solution. After addition of CH_2Cl_2 the organic phase was separated and dried with $MgSO_4$, the solvent was removed by rotary evaporation, and the resulting residue was extracted with $CDCl_3$. The product ratio was determined by ^{31}P NMR.

Crystallography. Colorless crystals suitable for X-ray diffraction of **7a** were obtained by attempting to grow single crystals of {[2,6-bis[(diphenylphosphino)methyl]phenyl]palladium−(μ-hydrido)−[2,6-bis[(diphenylphosphino)methyl]phenyl]-palladium} tetraphenylborate from CH_2Cl_2/ethanol,[3] while those of **9a,b** were grown from $CHCl_3$/hexane and those of **9c** from $CHCl_3$/methanol.

All crystals were mounted on glass fibers, at a random orientation, on an Enraf-Nonius CAD4 diffractometer, for the unit cell and space group determinations and for the data collections. Unit cell dimensions were obtained by a least squares fit of the 2θ values of 25 high order reflections ($9.11 < \theta < 11.20°$ for **7a**, $9.67 < \theta < 17.36°$ for **9a,b**, $9.41 < \theta < 13.91°$ for **9c**) using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table 2.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystals and of the experimental conditions and measured every hour. The collected intensities were corrected for Lorentz and polarization factors;[24] an empirical absorption correction was applied to the data for **9a,b** and **9c** by using azimuthal (Ψ) scans of "high-χ" angle reflection (for **9a,b** three reflections having $\chi > 85°$; two reflections with $\chi > 87.3°$ for **9c**). Given the negligible absorption, no correction was applied to **7a**.

The standard deviations on intensities were calculated in terms of statistics alone, while those on F_0 were calculated as shown in Table 2.

(24) MOIEN: Molecular Structure Solution Procedure. Enraf-Nonius, Delft, The Netherlands, 1990.

Table 2. Experimental Data for the X-ray Diffraction Study of Compounds 7a, 9a,b, and 9c

compd	7a	9a,b·$CHCl_3$	9c
formula	$C_{32}H_{27}ClP_2Pd$	$C_{33}H_{32}Cl_4P_2Pt$	$C_{34}H_{31}ClP_2Pt$
mol wt	615.37	851.50	732.12
cryst dim, mm	0.20 × 0.20 × 0.15	0.20 × 0.30 × 0.35	0.20 × 0.15 × 0.30
data coll T, °C	23	23	23
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/c$	$Pbca$
a, Å	10.257(3)	11.850(2)	21.807(3)
b, Å	16.051(5)	15.150(3)	17.020(5)
c, Å	17.329(6)	19.873(2)	16.519(2)
α, deg	90.0	90	90
β, deg	73.32(3)	98.69(1)	90
γ, deg	90.0	90	90
V, Å^3	2732.9(9)	3524.2(9)	6131(2)
Z	4	4	8
ρ(calcd), g cm^{-3}	1.496	1.604	1.586
μ, cm^{-1}	9.027	44.374	48.354
radiation	Mo Kα (graphite monochromated, λ = 0.710 69 Å)		
no. of measd reflns	$\pm h,+k,+l$	$\pm h,+k,+l$	$+h,+k,+l$
θ range, deg	$2.5 < \theta < 21.0$	$2.5 < \theta < 25.0$	$2.5 < \theta < 25.0$
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	1.10 + 0.35 tan θ	1.20 + 0.35 tan θ	1.10 + 0.35 tan θ
max counting time, s	60	70	70
bkgd time, s	0.5 × scan time	0.5 × scan time	0.5 × scan time
max scan speed, deg min^{-1}	10.2	6.8	6.8
prescan rejection limit	0.50 (2.0σ)	0.55 (1.82σ)	0.55 (1.82σ)
prescan acceptance limit	0.03 (33.3σ)	0.025 (40.0σ)	0.025 (40.0σ)
horiz receiving slit, mm	1.80 + tan θ	1.60 + tan θ	1.70 + tan θ
vert receiving slit, mm	4.0	4.0	4.0
no. data coll (ind)	2640	4447	5377
no. obs reflns (n_o)	1710 ($\|F_o\|^2 > 3.0\sigma(\|F\|^2)$)	4261 ($\|F_o\|^2 > 3.0\sigma(\|F\|^2)$)	1990 ($\|F_o\|^2 > 3.0\sigma(\|F\|^2)$)
transm coeff	0.9652–0.9998	0.8482–0.9952	0.6742–0.9997
no. of params refined (n_p)	206	379	343
f	0.055	0.050	0.060
$\Delta p/\sigma(p)$ (at conv)	<0.06	<0.18	<0.18
R^a	0.044	0.044	0.049
$R_w{}^b$	0.058	0.058	0.059
GOF^c	1.713	1.780	1.443

^{a} $R = \sum(\|F_o\| - (1/k)\|F_c\|)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - (1/k)|F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$; $\sigma(F_o) = [\sigma^2(F_o^2) + f^4(F_o^2)]^{1/2}/2F_o$. ^{c} GOF = $[\sum w(|F_o| - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

Table 3. Final Positional and Isotropic Equivalent Displacement Parameters for 7a (Esd's Given in Parentheses)

atom	x	y	z	B^a (Å^2)	atom	x	y	z	B^a (Å^2)
Pd	0.00890(7)	0.20422(4)	0.46544(4)	3.42(2)	C121	0.1839(9)	0.1933(5)	0.6074(5)	3.7(2)*
C1	0.1634(3)	0.2927(2)	0.3738(2)	5.46(7)	C122	0.301(1)	0.1798(6)	0.5508(6)	4.7(2)*
P1	0.0499(3)	0.2499(2)	0.5814(1)	3.72(6)	C123	0.409(1)	0.1373(7)	0.5670(7)	6.1(3)*
P2	–0.0837(2)	0.1350(2)	0.3780(1)	3.63(6)	C124	0.395(1)	0.1124(8)	0.6433(7)	7.2(3)*
C1	–0.1181(8)	0.1286(6)	0.5435(5)	3.6(2)	C125	0.279(1)	0.1246(8)	0.7022(7)	7.4(3)*
C2	–0.1669(9)	0.0554(5)	0.5180(5)	3.5(2)	C126	0.166(1)	0.1649(7)	0.6852(6)	5.3(2)*
C3	–0.247(1)	0.0010(6)	0.5734(6)	5.0(3)	C211	–0.2453(8)	0.1802(5)	0.3778(5)	3.4(2)*
C4	–0.283(1)	0.0172(6)	0.6540(6)	5.3(3)	C212	–0.328(1)	0.1405(7)	0.3358(6)	5.4(2)*
C5	–0.241(1)	0.0896(6)	0.6817(6)	4.8(3)	C213	–0.452(1)	0.1801(7)	0.3370(7)	5.8(3)*
C6	–0.1605(8)	0.1449(6)	0.6266(5)	3.8(2)	C214	–0.487(1)	0.2494(7)	0.3744(7)	5.8(3)*
C7	–0.111(1)	0.2247(6)	0.6557(6)	4.6(3)	C215	–0.409(1)	0.2916(7)	0.4132(7)	6.1(3)*
C9	–0.1272(9)	0.0356(6)	0.4288(6)	4.3(2)	C216	–0.286(1)	0.2539(7)	0.4155(6)	4.5(2)*
C111	0.0817(9)	0.3580(6)	0.5975(5)	3.9(2)*	C221	–0.0043(9)	0.1150(6)	0.2733(5)	4.1(2)*
C112	–0.015(1)	0.4159(7)	0.5934(7)	6.2(3)*	C222	0.034(1)	0.0368(7)	0.2418(7)	5.7(3)*
C113	0.004(1)	0.5011(9)	0.6056(7)	7.3(3)*	C223	0.094(1)	0.0230(8)	0.1587(7)	7.0(3)*
C114	0.118(1)	0.5263(7)	0.6216(7)	6.4(3)*	C224	0.114(1)	0.0896(8)	0.1095(7)	6.9(3)*
C115	0.216(1)	0.4709(8)	0.6234(7)	7.3(3)*	C225	0.077(1)	0.1677(8)	0.1373(7)	6.4(3)*
C116	0.199(1)	0.3863(7)	0.6123(7)	6.3(3)*	C226	0.020(1)	0.1790(7)	0.2199(6)	5.3(2)*

^{a} Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

The structures were solved by a combination of Patterson and Fourier methods and refined by full matrix least squares[24] (the function minimized being $\sum[w(F_o - 1/kF_c)^2]$). No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion,[25] were taken from the literature.[25]

The contribution of the hydrogen atoms in calculated positions (C–H = 0.95 Å, B(H) = 1.3B(C_{bonded}) Å^2) was taken into account but not refined.

Upon convergence (see Table 2) no significant features were found in the Fourier difference maps of the compounds.

All calculations were carried out using the Enraf-Nonius MOLEN package.[24]

Structural Study of 7a. A set of 2640 data were collected of which 1710 were considered as observed and used for the refinement.

Full matrix least-squares refinement was carried out using anisotropic displacement parameters for the palladium, the chlorine, and the atoms of the chelating ligand, while all the others were treated isotropically. Final agreement factors and other relevant data are given in Table 2.

Final atomic coordinates and isotropic equivalent displacement parameters are given in Table 3.

(25) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table 4. Final Positional and Isotropic Equivalent Displacement Parameters for 9a,b·$CHCl_3$ (Esd's Given in Parentheses)

atom	x	y	z	B^a (Å²)	atom	x	y	z	B^a (Å²)
Pt	0.18918(3)	0.07021(2)	0.28920(2)	3.432(6)	C114	0.124(1)	0.299(1)	0.0504(6)	8.5(4)
Cl1[a]	0.1313(2)	−0.0573(2)	0.2226(1)	5.39(6)	C115	0.090(1)	0.3487(9)	0.0980(6)	8.0(3)
Cl2[b]	0.3037(6)	−0.1703(4)	0.0790(4)	17.7(2)	C116	0.062(1)	0.3119(7)	0.1575(5)	5.9(3)
Cl3[b]	0.3647(6)	0.0104(5)	0.0778(3)	18.0(2)	C121	−0.0966(8)	0.1269(7)	0.2220(5)	5.1(2)
Cl4[b]	0.1567(6)	−0.0431(5)	0.0039(3)	17.0(2)	C122	−0.178(1)	0.181(1)	0.1914(8)	11.8(4)
P1	0.0491(2)	0.1652(2)	0.2445(1)	3.90(5)	C123	−0.290(1)	0.150(1)	0.177(1)	15.7(6)
P2	0.3390(2)	0.0075(2)	0.3570(1)	3.80(5)	C124	−0.322(1)	0.070(1)	0.1945(8)	8.7(4)
Cc1[b]	0.253(1)	−0.065(1)	0.074(1)	10.4(5)	C125	−0.240(1)	0.0177(9)	0.2283(7)	8.0(3)
C1	0.2446(7)	0.1764(5)	0.3445(4)	3.7(2)	C126	−0.1297(9)	0.0466(8)	0.2424(7)	6.7(3)
C2	0.3561(7)	0.1791(6)	0.3821(4)	4.0(2)	C211	0.4273(8)	−0.0815(6)	0.3341(5)	4.6(2)
C3	0.3942(8)	0.2546(7)	0.4187(5)	5.0(2)	C212	0.489(1)	−0.1357(7)	0.3811(7)	6.8(3)
C4	0.3260(9)	0.3274(7)	0.4198(5)	5.6(2)	C213	0.565(1)	−0.1947(8)	0.3654(9)	9.8(4)
C5	0.2156(9)	0.3273(6)	0.3818(5)	5.3(2)	C214	0.584(1)	−0.2002(9)	0.2985(9)	9.9(4)
C6	0.1744(8)	0.2528(6)	0.3450(4)	4.1(2)	C215	0.523(1)	−0.1494(9)	0.2485(7)	8.4(3)
C7	0.0524(8)	0.2491(6)	0.3107(5)	4.5(2)	C216	0.4430(9)	−0.0901(8)	0.2664(6)	6.3(3)
C8	−0.0278(9)	0.2242(9)	0.3627(5)	6.6(3)	C221	0.2949(7)	−0.0295(6)	0.4353(5)	4.5(2)
C9	0.4335(7)	0.1031(6)	0.3782(5)	4.1(2)	C222	0.232(1)	−0.1078(9)	0.4340(7)	8.4(3)
C10	0.5081(8)	0.1166(7)	0.3235(5)	5.4(2)	C223	0.195(1)	−0.1345(9)	0.4951(7)	10.0(4)
C111	0.0788(7)	0.2213(6)	0.1681(4)	4.4(2)	C224	0.220(1)	−0.0861(9)	0.5536(7)	8.0(3)
C112	0.112(1)	0.1732(8)	0.1181(6)	7.3(3)	C225	0.2777(9)	−0.0117(9)	0.5529(5)	6.2(3)
C113	0.137(1)	0.209(1)	0.0594(6)	8.4(4)	C226	0.3157(9)	0.0166(7)	0.4952(5)	5.0(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. [b] Atoms Cc1, Cl2, Cl3, and Cl4 are those of the solvent.

Table 5. Final Positional and Isotropic Equivalent Displacement Parameters for 9c (Esd's Given in Parentheses)

atom	x	y	z	B^a (Å²)	atom	x	y	z	B^a (Å²)
Pt	0.92095(4)	0.87254(5)	0.78033(5)	3.88(1)	C116	0.943(1)	0.827(2)	0.554(1)	5.7(6)
Cl	0.8736(3)	0.7542(4)	0.7383(4)	5.6(2)	C121	1.071(1)	0.823(1)	0.740(1)	4.9(6)
P1	1.0037(3)	0.8707(4)	0.6971(3)	4.4(1)	C122	1.120(1)	0.863(1)	0.769(2)	6.2(6)
P2	0.8504(3)	0.9082(4)	0.8730(4)	4.9(2)	C123	1.169(1)	0.823(2)	0.798(1)	5.9(6)
C1	0.960(1)	0.972(1)	0.819(1)	4.3(5)	C124	1.173(1)	0.743(2)	0.800(1)	6.8(7)
C2	0.9452(9)	1.004(1)	0.894(1)	4.2(5)	C125	1.123(1)	0.702(1)	0.768(1)	5.4(6)
C3	0.974(1)	1.072(1)	0.920(2)	6.0(7)	C126	1.0701(9)	0.741(1)	0.742(1)	4.5(5)
C4	1.020(1)	1.105(1)	0.873(2)	7.4(8)	C211	0.794(1)	0.974(2)	0.827(2)	10(1)
C5	1.036(1)	1.073(1)	0.798(1)	6.0(7)	C212	0.802(2)	0.993(2)	0.747(2)	12(1)
C6	1.0077(9)	1.007(1)	0.774(1)	4.0(5)	C213	0.761(1)	1.040(2)	0.691(2)	6.4(7)
C7	1.024(1)	0.976(1)	0.693(2)	6.0(7)	C214	0.711(1)	1.070(2)	0.725(2)	8.5(9)
C8	0.983(1)	1.017(2)	0.623(2)	6.5(7)	C215	0.714(1)	1.068(2)	0.802(1)	5.9(7)
C9	0.8991(9)	0.964(1)	0.944(2)	5.3(6)	C216	0.751(1)	1.009(2)	0.862(2)	7.2(7)
C10	0.864(1)	1.019(2)	1.004(2)	7.6(8)	C221	0.8075(9)	0.837(1)	0.929(1)	5.1(6)
C111	0.999(1)	0.831(1)	0.595(1)	4.8(6)	C222	0.762(1)	0.794(2)	0.888(1)	7.1(7)
C112	1.054(1)	0.809(2)	0.555(1)	6.1(7)	C223	0.731(1)	0.739(2)	0.924(2)	7.7(8)
C113	1.050(1)	0.779(2)	0.477(1)	7.1(7)	C224	0.741(1)	0.716(2)	1.001(2)	7.8(8)
C114	0.992(1)	0.777(1)	0.438(1)	7.3(7)	C225	0.786(1)	0.756(2)	1.044(2)	8.0(8)
C115	0.941(2)	0.798(2)	0.478(1)	8.9(9)	C226	0.820(1)	0.814(2)	1.009(1)	6.5(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacent parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Structural Study of 9a,b·$CHCl_3$. A total of 4447 independent data were collected of which 4261 were considered as observed.

The structure was refined as described above, using anisotropic displacement parameters for all atoms and taking into account the contributions of the hydrogen atoms. The relevant parameters for the refinement are given in Table 2.

Toward the end of the refinement a Fourier difference map revealed a clathrathed $CHCl_3$ molecule which was included in the refinement.

Final atomic coordinates and isotropic equivalent displacement parameters are given in Table 4.

Structural Study of 9c. A total of 5377 independent reflections were collected, and after data reduction 1990 were considered as observed.

One of the phenyl rings of the chelating phosphine (atoms labeled C221–C226) is highly disordered, as shown by the high values of the temperature factors (see Table 5), resulting in high esd's on bond distances and angles and a significant spread of their values.

The structure was refined as described above, using anisotropic temperature factors for all atoms. The parameters used in the refinement and agreement factors are listed in Table 2.

Final coordinates and equivalent isotropic displacement parameters are listed in Table 5.

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Supplementary Material Available: Tables giving (a) calculated positional parameters for the hydrogen atoms for **7a** (Table S1), **9a,b** (Table S2), and **9c** (Table S3), (b) anisotropic displacement parameters for **7a** (Table S4), **9a,b** (Table S5), and **9c** (Table S6), and (c) an extended list of bond lengths, bond angles, and torsion angles for **7a** (Table S7), **9a,b** (Table S8), and **9c** (Table S9) and figures giving the full numbering scheme for **7a** (Figure S1), **9a,b** (Figure S2), and **9c** (Figure S3) (32 pages). Ordering information is given on any current masthead page.

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