Synthesis of an Optically Active Platinum(II) Complex Containing a New Terdentate P–C–P Ligand and Its Catalytic Activity in the Asymmetric Aldol Reaction of Methyl Isocyanoacetate. X-ray Crystal Structure of [2,6-Bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]phenyl](η^1-nitrato)platinum(II)

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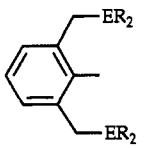
The compound (*E*,*E*)-1,3-bis(3′-hydroxyprop-1′-enyl)benzene, obtained by reduction of (*E*,*E*)-1,3-bis[2′-(methoxycarbonyl)ethenyl]benzene with diisobutylaluminum hydride, was selectively transformed into 1,3-bis[(1′*S*,2′*S*)-1′,2′-epoxy-3′-hydroxypropyl]benzene by a Sharpless oxidation. After protection of the hydroxyl groups as their TBDMS ethers, the epoxide rings were selectively opened by reacting them with $LiPPh_2$ and the resulting diphosphine, after reaction with elemental sulfur, gave 1,3-bis[(1′*S*,2′*S*)-1′-(diphenylthiophosphinyl)-2′,3′-dihydroxypropyl]benzene. After conversion to the corresponding bis(dioxolane), the latter compound was desulfurized using P(*n*-Bu)$_3$. The overall yield of the ligand precursor, 1,3-bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]benzene, based on the commercial isophthalaldehyde starting material used, was ca. 30%. The complex [2,6-bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]phenyl]chloroplatinum(II) (**18**) was obtained by reacting the above ligand precursor with $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(CH_3)CH_2)_2]$. The X-ray crystal structure of [2,6-bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]phenyl[(η^1-nitrato)platinum(II) (**19**) obtained from **18**, by reacting it with $AgNO_3$, was determined. Its structural features are closely related to those of the corresponding compound in which the dioxolane unit has been replaced by a methyl group. Crystals of **19**·toluene are orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 10.160(1)$ Å, $b = 15.721(2)$ Å, and $c = 28.799(2)$ Å. The corresponding triflato complex, obtained by reacting the chloro compound **18** with silver triflate, was used as catalyst precursor (1–2 mol %) in the aldol reaction of aldehydes with methyl isocyanoacetate in the presence of a cocatalytic amount of NEt*i*-Pr$_2$. Enantioselectivities up to 65% were obtained for the major diastereoisomeric *trans*-oxazoline product, whereas the overall catalytic activity was comparable to that of known systems.

Introduction

The coordinating properties of the anionic terdentate ligands of type **1** have been very extensively studied, particularly those where E is either phosphorus or nitrogen.[1,2] The use of these ligands has (1) allowed the preparation of many new types of complexes,[1,2] (2) provided a better understanding of the cyclometalation reaction,[3] (3) revealed a number of unusual reactivity patterns, and (4) provided novel applications in the field of homogeneous catalysis.[4]



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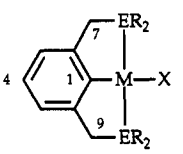

2

2a: M = Pt; E = P; R = Ph; X = CF_3SO_3

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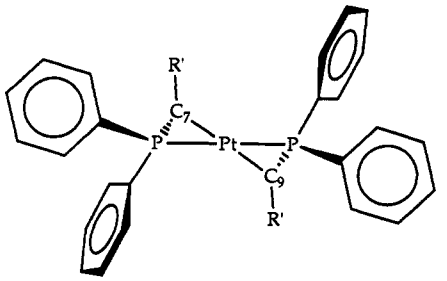
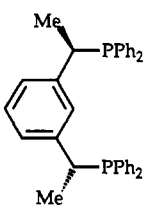


Figure 1. Schematic view of a complex of type 4 seen along the C_2 axis.

In a previous publication[5] from this laboratory it was pointed out that square planar complexes of type **2** containing terdentate P–C–P-ligands are readily formed and that they possess an approximate C_2 symmetry axis going through the anionic ligand X, the metal center M, and the C1 and C4 atoms of the central benzene ring. It was also pointed out that C7 and C9 are, respectively, above and below the coordination plane, giving an arrangement of the terminal phenyl substituents, on each side of the molecule, where one of them is axial and the other equatorial (see Figure 1, R′ = H). Thus, complexes of type **2** are chiral in the solid state. However, when R′ = H, the energy barrier for a change of conformation (λ/δ enantiomers) in solution is quite low.

It was further shown that stereochemical rigidity can be achieved by replacing one of the hydrogen atoms on C7 and C9 by a substituent such as a methyl group (see Figure 1, R′ = CH_3).

However, it also became evident that the preparation of an optically pure P–C–P-ligand precursor, e.g., compounds **3**, from its racemate[5] would be too cumbersome to



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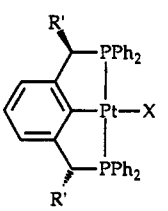

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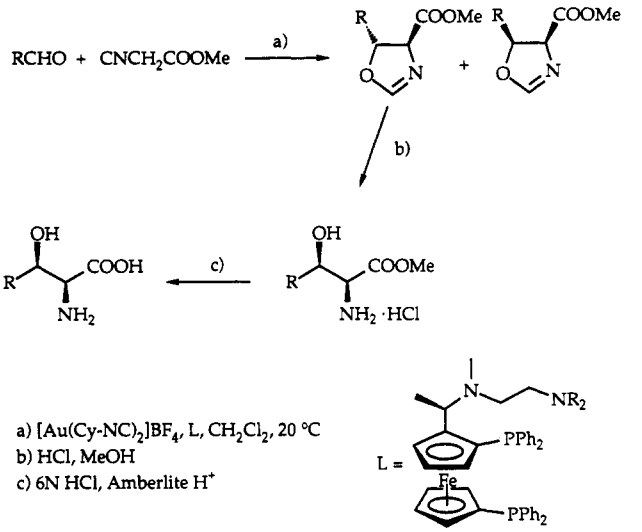
rac-**4a**: R′ = Me, X = Cl
rac-**4b**: R′ = Me, X = CF_3SO_3

be of real value and, therefore, a stereospecific synthetic route for an optically pure complex of type **4** would be desirable.

When one considers the wide range of known optically active bidentate ligands having C_2 symmetry[6] and their successful use in homogeneously catalyzed reactions, it is surprising that optically active terdentate ligands having the same symmetry have received only sporadic attention. A possible explanation for this scarce interest may be due to the results of the early studies which showed that the use of *terdentate* ligands gave enantiomeric discriminations that seldom equaled those obtained using related bidentate ligands. However, Niewahner and Meek[7] reported that the complex [RhCl{PhP($CH_2CH_2CH_2PPh_2$)$_2$}], in the presence of $AlEt_3$, can be used for the catalytic

Scheme 1



hydrogenation of alkenes and claimed that, *under their reaction conditions*, the above system was significantly more active than [RhCl(PPh_3)$_3$].

Furthermore, the preparation of the optically pure terdentate ligands (*S,S*)-PhP(CH_2CH_2PPhAn)$_2$ (**5**) and (*S,S,S*)-PhAnPCH(CH_2CH_2PPhAn)$_2$ (**6**) (An = *o*-anisyl) has been described and their rhodium(I) complexes have been used as catalysts for the asymmetric hydrogenation of some α-(acetylamino)acrylic acids. Thus, for the hydrogenation of α-(acetylamino)-β-phenylacrylic acid, while a maximum of 94% ee was obtained with the bidentate ligand (*S,S*)-PhAnP$CH_2CH_2CH_2$PPhAn, when **5** was used only a 47% ee could be achieved. On the other hand, the use of **6**, although it afforded 87% ee, it required much more vigorous reaction conditions. It is not unlikely that this latter ligand, under catalytic conditions, may have been acting only as bidentate.[8]

Finally, Nishiyama *et al.*[9] have recently described the successful use of a C_2 symmetric terdentate ligand, i.e., a 2,6-bis(oxazolidinyl)pyridine for the enantioselective hydrosilylation reaction.

We report herein the preparation of an enantiomerically pure P–C–P-ligand precursor, its platinum(II) complex of type **4**, and the use of a cationic complex obtained from the latter as a catalyst precursor in the asymmetric aldol reaction.

The synthesis of optically active oxazolines, using a gold(I)-catalyzed aldol addition reaction starting from aldehydes and isocyanoacetates, was first described by Hayashi, Ito, and co-workers.[10] Chiral induction was achieved using ferrocenylphosphine ligands such as that shown in Scheme 1.

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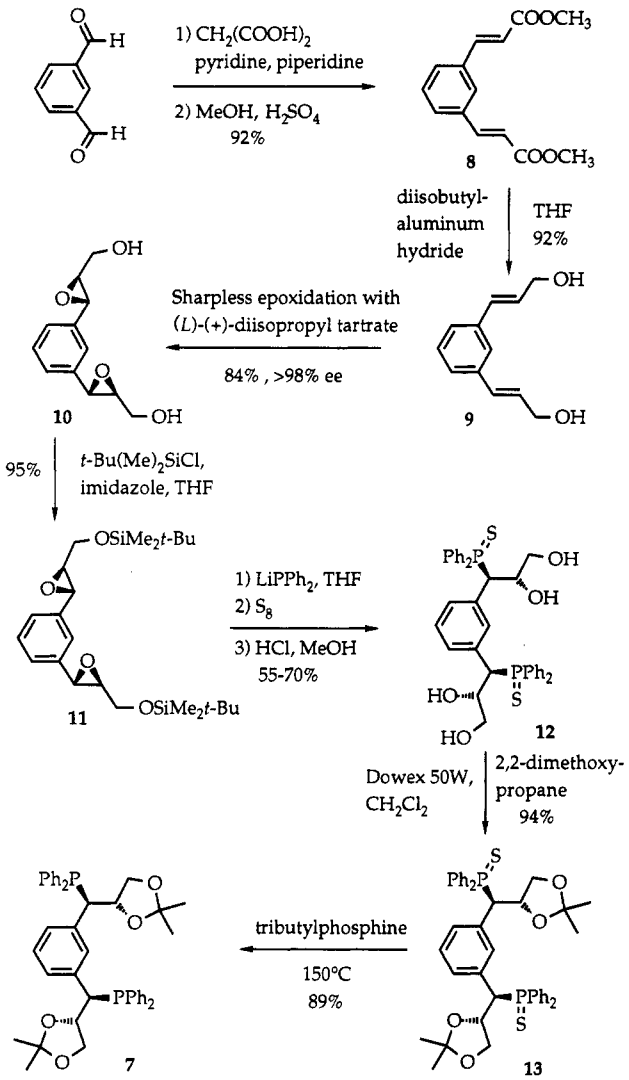
(10) (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Ito, Y.; Sawamura, M.; Hayashi, T. *Tetrahedron Lett.* **1987**, *28*, 6215. (c) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Ibid.* **1988**, *29*, 235. (d) Ito, Y.; Sawamura, M.; Hayashi, T. *Ibid.* **1988**, *29*, 239. (e) Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7. (f) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron* **1988**, *44*, 5253. (g) Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 2247. (h) Sawamura, M.; Hamashima, H.; Ito, Y. *J. Org. Chem.* **1990**, *55*, 5935. (i) Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1990**, *31*, 2723. (j) Sawamura, M.; Ito, Y. Asymmetric Aldol Reactions. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: New York, 1993; pp 367 ff.

Scheme 2



As the use of this catalyst system produced high diastereo- and enantioselectivities, this reaction provided the new route for the preparation of optically active β-hydroxy-α-amino acids as shown in Scheme 1.

These studies were followed by an extensive investigation of this reaction by Togni and Pastor[11] which was mainly concerned with mechanistic aspects of the stereoselection.

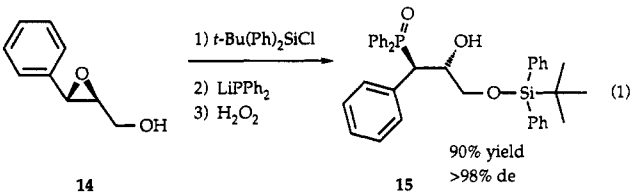
Results and Discussion

Ligand Synthesis. The ligand precursor chosen, **7**, and the synthetic route for its preparation are shown in Scheme 2.

The diester (*E,E*)-1,3-bis[(2′-methoxycarbonyl)ethenyl]-benzene (**8**) obtained as reported in the literature,[12,13] was reduced with diisobutylaluminum hydride[14] to the corresponding dihydroxy compound (*E,E*)-1,3-bis(3′-hydroxyprop-1′-enyl)benzene (**9**) in 92% yield.

The asymmetric diepoxide **10** was smoothly obtained in 84% yield and >98% ee by the Sharpless epoxidation[15] of **9** using (L)-(+)-diisopropyl tartrate and *tert*-butyl hydroperoxide. The absolute configuration of the epoxides formed was assigned as described for (2*S*,3*S*)-3-phenylglycidol (**14**) obtained by epoxidizing (*E*)-cinnamyl alcohol.[15a]

Literature reports[16] indicate that nucleophilic attack at phenyl epoxides, notably optically pure (2*S*,3*S*)-3-phenylglycidol (**14**) occurs at the benzylic position with inversion of configuration.[17] Furthermore, the nucleophilic attack of diphenylphosphide, in the form of its lithium salt, on epoxides is well documented.[19] Thus, the successive step of the ligand synthesis was tested on commercial (2*S*,3*S*)-3-phenylglycidol (**14**). This, after protection with *tert*-butyldiphenylchlorosilane, was successively reacted with lithium diphenylphosphide and hydrogen peroxide (eq 1). Only isomer **15** could be detected by ^{1}H NMR spectroscopy.



An analogous reaction was carried out on intermediate **11**, after protection of the hydroxyl groups of **10** as their TBDMS ethers.[18] However, the bis(phosphine) formed was directly transformed into the corresponding bis(phosphine sulfide) **12**, as this type of compound is less hygroscopic than the corresponding oxide. Removal of the silyl group was carried out using HCl in methanol. Optimization studies showed that this reaction sequence was best carried out in small batches, i.e., millimolar quantities of **11**, or lower.

The bis(dioxolane) **13** was conveniently prepared by a transacetalization reaction using Dowex 50 W as a catalyst.[20] Finally, desulfurization of the bis(phosphine sulfide) **13** was accomplished by reacting it with tri-*n*-butylphosphine at 150 °C.[1d] The overall yield of the final product **7**, based on the commercial isophthalaldehyde, which was used as a starting material, was ca. 30%.

Although the generation of the stereogenic centers by a Sharpless epoxidation reaction took place in one of the early steps of the reaction sequence, a ^{1}H NMR study of the subsequent intermediates and of the final product did not show the presence of isomeric species in any of these compounds.

Attempts were also made to obtain chiral ligand precursors related to **3**, e.g., by removing the two diols on

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(13) Ruggli, P.; Staub, A. *Helv. Chim. Acta* **1934**, *17*, 1523.

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(15) (a) Goa, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765 and references cited therein. (b) Hill, J. G.; Sharpless, K. B.; Exon, C. M.; Regenye, R. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, p 461.

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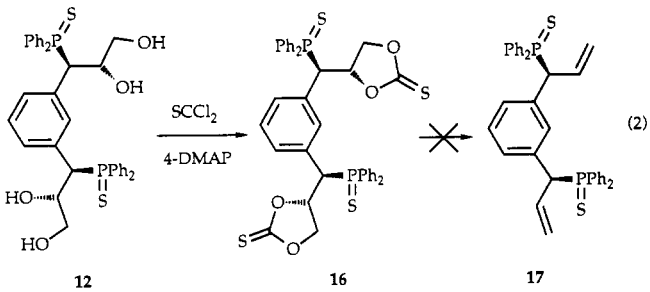
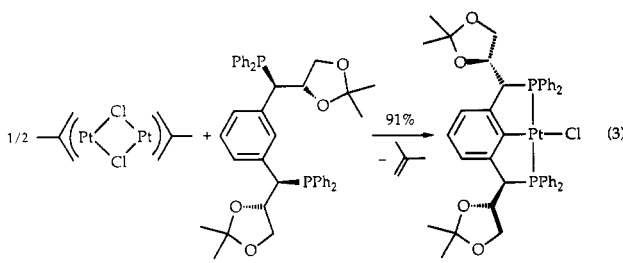
intermediate **12** by the reaction sequence shown below (eq 2). However, while derivative **16** could be easily



12 **16** **17**

obtained by reacting **12** with thiophosgene, attempts to prepare **17** using either a Corey–Winter reaction employing $P(OMe)_3$[21] or $P(n\text{-}Bu)_3$, or the mild reaction with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine,[22] led to the formation of mixtures of several phosphorus-containing compounds. These attempts were, therefore, discontinued.

Preparation of the Platinum Complex [PtCl(PCP*)] 18. As reported previously[5] complexes of type **4** can be readily prepared by reacting the corresponding ligand precursor, e.g., **3**, with $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(CH_3)CH_2)_2]$. Thus complex **18** could be obtained in 91% yield by the reaction shown in eq 3.



7 [PtCl(PCP*)] **18**

It did not prove possible to grow single crystals suitable for X-ray diffraction of compound **18**, and, therefore, the corresponding nitrate **19** was prepared by reacting the former compound with silver nitrate.

X-ray Crystal Structure of [2,6-Bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]phenyl](η^1-nitrato)platinum(II), [Pt(NO$_3$)(PCP*)] (19). The crystals contain discrete molecules of **19** and toluene separated by normal van der Waals distances. An ORTEP view of the complex is depicted in Figure 2 and a selection of bond distances and angles is presented in Table 1.

The structural features of compound **19** are best discussed by comparing them with those of the related compound *rac*-**4a**, whose data are also listed in Table 1. As can be seen there, and by comparing Figure 3, parts a and b, the coordination environment in the two compounds is very similar except for the area near the coordinated nitrate anion and the regions around C7 and C9.

The coordination mode of the nitrate is monodentate as the shortest Pt–O distance is 2.135(6) Å and the next

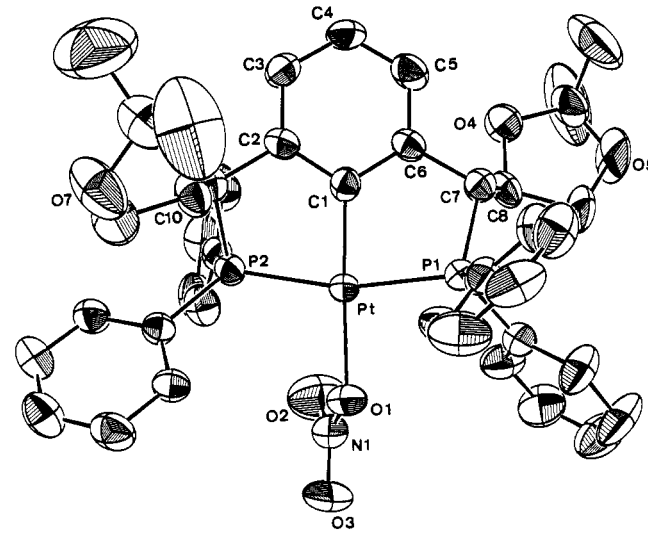


Figure 2. ORTEP view of compound **19**.

is 3.021(8) Å. The Pt–O and N–O distances and the Pt–O–N and N–O–N bond angles fall in the normal range.[23]

However, the P1–Pt–O1 and P2–Pt–O1 angles differ significantly from one another (94.5(2) and 100.8(2)°, respectively) more than P1–Pt–Cl and P2–Pt–Cl in *rac*-**4a** (99.44(9) and 97.14(9)°, respectively). As proposed previously,[5] this could be a way of releasing the strain consequent upon the formation of two adjacent five-membered chelate rings, this strain being larger in the complex with bulkier substituents.

The more interesting part of the molecule is the stereogenic region. Firstly, one notices that the relative positions of the "skeletal" atoms Pt, P1, C7, C6, C1, C2, C9, and P2 in **19** and *rac*-**4a** do not show significant differences, while the two axial carbon atoms C8 and C10 are somewhat bent away from their ideal positions, presumably to accommodate the bulky dioxolane groups, which are also likely to be responsible for the differences in the orientations of the terminal phenyl groups.

Obviously, the presence of the two dioxolane substituents contributes to stabilizing the conformation of the two chelate rings. This accounts in part for the observation of two different sets of resonances in the ^{1}H NMR spectrum for the diastereotopic phenyl groups. In contrast, the enantiotopic Ph groups in the unsubstituted complex **2a** (M = Pt; E = P; R = Ph; X = Cl) appear as equivalent on the NMR time scale, this being indicative of rapid conformational equilibria in solution.

The steric role played by the peripheral dioxolane rings in the catalytic reactions to be discussed below is difficult to discern. In the crystal, these substituents are bent away from the coordination plane (see Figure 2 and Table 1). Although they are not static in solution, molecular models show that only partial rotation around the C7–C8 and C9–C10 axes is possible, because of interference with the terminal phenyl groups. Thus, it does not appear to be possible to place the dioxolane substituents sufficiently close to the active site to directly affect the stereoselectivity of the catalytic reaction. Nevertheless, when the dioxolane moieties are placed as close as possible to the coordination plane they appear to block the positions above and below this plane. Thus, if these axial sites play a significant role

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Table 1. Selection of Bond Lengths (Å) and Angles (deg) for Compounds 19 and *rac*-4a

	19	*rac*-4a
Pt–C1	1.977(7)	2.003(9)
Pt–P1	2.268(2)	2.273(2)
Pt–P2	2.279(2)	2.268(2)
Pt–X	2.135(6)	2.384(2)
N1–O1	1.28(1)	
N1–O2	1.22(1)	
N2–O3	1.24(1)	
P1–Pt–X	94.5(2)	99.44(9)
P2–Pt–X	100.8(2)	97.14(9)
P1–Pt–C1	82.1(2)	82.3(3)
P2–Pt–C1	82.4(2)	81.2(3)
Pt–P1–C7	103.1(2)	103.0(3)
Pt–P2–C9	99.7(2)	101.6(3)
Pt–O1–N1	118.9(6)	
P1–C7–C6	103.4(5)	105.5(6)
P2–C9–C2	104.7(5)	105.3(6)
Pt–C1–C2	121.6(5)	121.0(7)
Pt–C1–C6	122.3(6)	120.8(7)
X–Pt–C1	174.7(3)	177.6(3)
P1–Pt–P2	164.50(7)	163.1(1)
O1–N1–O2	119.4(8)	
O1–N1–O3	117.4(9)	
O2–N1–O3	123.1(9)	
Pt–P1–C7–C6	30.0(4)	30.5(6)
Pt–P2–C9–C2	37.2(5)	34.2(6)
Pt–C1–C2–C9	5.8(9)	2(1)
Pt–C1–C6–C7	0.4(9)	8(1)
C1–C6–C7–C8	99.8(7)	94(1)
C1–C2–C9–C10	88.2(8)	93(1)
Pt–P1–C7–C8	–93.4(5)	–89.4(7)
Pt–P2–C9–C10	–81.3(5)	86.1(6)
Pt–P1–C111–C112	36.5(7)	49.0(9)
Pt–P1–C121–C122	39.4(6)	24.6(9)
Pt–P2–C211–C212	–177.3(5)	–157.1(7)
Pt–P2–C221–C222	94.2(7)	77.3(9)
P1–C7–C8–O4	166.0(4)	
P2–C9–C10–O6	166.8(8)	
Deviations (Å) from the Pt, X, C1, P1, P2 Mean Square Plane (+ = above plane)		
Pt	–0.0433(2)	+0.0153(3)
X	+0.027(6)	+0.0353(3)
C1	+0.032(7)	+0.060(8)
P1	–0.009(2)	–0.055(2)
P2	–0.007(2)	–0.056(2)
C7	–0.705(7)	–0.693(9)
C8	–2.207(7)	–2.24(1)
C9	+0.920(7)	+0.785(9)
C10	+2.456(8)	+2.24(1)
Angle between the above Plane and the Plane of the Central Benzene Ring C1–C6	16.7(5)	14.7(7)
Deviations (Å) from the Pt, N1, O1, O2, O3 Mean square plane (+ = above plane)		
Pt	–0.0295(2)	
N1	+0.008(7)	
O1	+0.044(5)	
O2	+0.014(8)	
O3	–0.036(7)	
Angle between the above Two Planes		

in determining stereoselectivity, a change in bulk of the dioxolane groups could also affect the enantiomer distribution.

Enantioselective Aldol Reaction of Methyl α-Isocyanoacetate with Aldehydes. The catalyst precursor [Pt(CF_3SO_3)(PCP*)] (**20**) was obtained from complex **18** by chloride abstraction with silver triflate. Thus a labile coordination site is now available for the binding of the isocyanoacetate. However, for the aldol condensation to occur, a base is needed in order to generate the intermediate isocyano enolate coordinated to platinum (**21**) depicted below. This enolate can then act as a nucleophile and

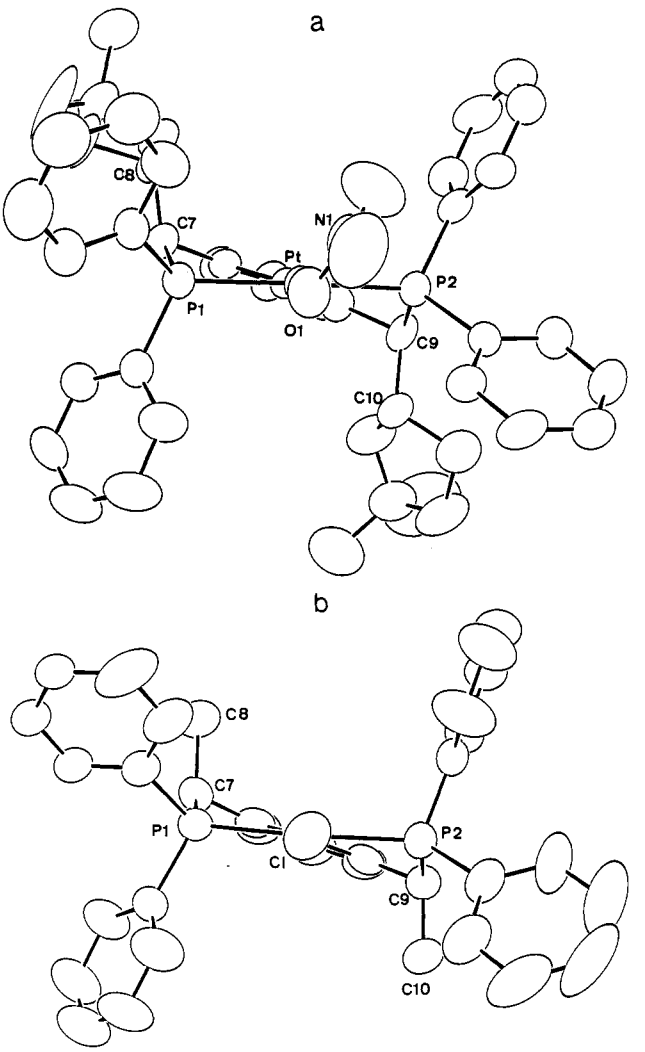
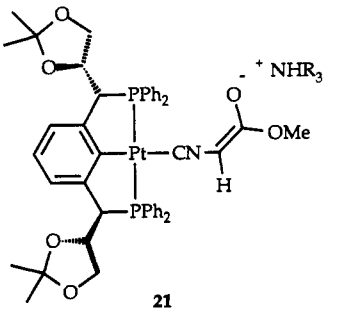


Figure 3. Views (a) of compounds **19** and (b) *rac*-**4a** (R′ = Me; X = Cl), seen along the C_2 axis.

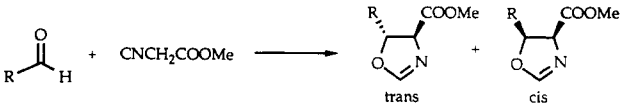
attack the aldehyde, analogously to what is occurring in the gold(I)/ferrocenylphosphine system.[11f]

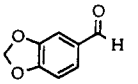
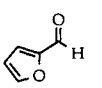
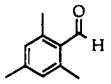
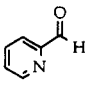
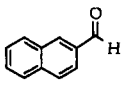
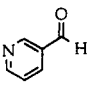
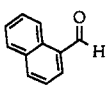
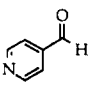
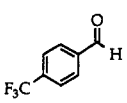
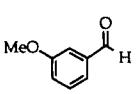
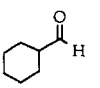
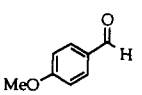


21

The initial experiments were carried out with NE*t*-Pr_2 (10 mol %) as a base, the catalyst (1.5 mol %), and with relatively high substrate concentration (ca. 1 M), in 1,2-dichloroethane, at room temperature. Under these conditions the major diastereomeric product, i.e., the *trans*-oxazoline, was obtained in 45% ee. It was also established that slow addition of the aldehyde during 6 h increased the enantioselectivity to 55%, whereas the slow addition of the isocyanoacetate led to a significantly lower selectivity (30% ee). It was later found that the highest ee's (63–64%) were obtained when the initial concentration of the substrates was kept below 0.2 M. The enantioselectivity for the minor product, the (4*R*,5*R*)-*cis*-oxazoline, decreased

Table 2. Aldol Addition of Methyl α-Isocyanoacetate to Aldehydes[a]



entry	aldehyde	yield[b] [%]	trans/cis[c] [%]	ee trans [%][d]	ee cis [%]	entry	aldehyde	yield[b] [%]	trans/cis[c] [%]	ee trans [%][d]	ee cis [%]
1		96	70/30	65(4*S*,5*R*)	3	10		84	68/32	54	6
2		96	85/15	61	9	11		96	73/27	62	14
3		65[e]	90/10	15	22	12		90	66/34	13	29
4		95	69/31	52	6	13		91	56/44	41	25
5		94	87/13	54	8	14		89	65/31	20	22
6		95	65/35	41	20	15		93	69/31	14	24
						16		92	75/25	18	32
7		97	69/31	58	31	17		94	90/10	29	32
8		97	68/32	49	17	18		95	93/7	39	–
9		89	72/78	64	24	19		91	–	15	

[a] Conditions: benzaldehyde (500 μmol), $CNCH_2COOMe$ (500 μmol), cat. (1.5%), $NEt(i\text{-}Pr)_2$ (12%), 4 mL of CH_2Cl_2, 20 °C. [b] Isolated yield obtained by bulb-to-bulb distillation. [c] Determined by ^1H NMR analysis. [d] Determined by ^1H NMR analysis using $Eu(dcm)_3$ as chiral shift reagent. [e] $ClCH_2CH_2Cl$, 50 °C, 20 h.

with increasing dilution, and, at highest dilution (0.06 M), the opposite enantiomer was preferentially formed, albeit with a very low selectivity (3% ee). A similar erratic behavior for *cis*-oxazolines has been previously reported.[11f] Dichloromethane and toluene could also be used as solvents and, while the former did not show significant differences in selectivity, the latter caused a slight reduction in rate. On the other hand, when diglyme or THF were used, a drastic decrease in catalytic activity resulted, coupled with a slight change in enantioselectivity (61 and 54%, respectively). The reduced reaction rates may be due to the coordinating properties of these solvents.

The relative amount of base used as cocatalyst was also found to be important. Optimum selectivity in the standard reaction of benzaldehyde and methyl isocyanoacetate was obtained when at least 13 mol % of $NEt(i\text{-}Pr)_2$ was present. Lower amounts resulted in both lower activity and selectivity. Thus equimolar amounts of catalyst and base afforded the major product in only 30% ee and the reaction rate was at least 1 order of magnitude slower. The use of dibasic amines, i.e., (−)-sparteine, TMEDA, DBU, instead of $NEt(i\text{-}Pr)_2$, had similar detrimental effects.

The results obtained with several aromatic and aliphatic aldehydes are collected in Table 2. It is interesting to note that for heteroatom-containing aldehydes (e.g., entries 12–14), selectivities depend on the position of the heteroatom. A qualitatively similar trend has been previously reported and discussed for the gold(I)/ferrocenylphosphine system.[11f] These findings possibly indicate very similar mechanistic features for the Pt and Au-catalyzed reactions.

Competition experiments between benzaldehyde and several *para*-substituted benzaldehydes provided evidence that the electrophilic attack of the aldehyde on the coordinated isocyano enolate is the rate-determining step of the catalytic reaction. A linear free energy relationship was found for six different *para*-substituted benzaldehydes, as illustrated in the Hammett plot shown in Figure 4 ($\log k_{rel}$ vs σ_p). A positive slope ($\rho = 1.6$) was obtained, indicative of increased electron density at the carbonyl carbon in the transition state of the C–C bond-forming step. This behavior is very similar to that previously observed for the gold(I)-catalyzed reaction[11f] and it strongly supports the contention that coordination of the aldehyde to the metal center is not involved in the catalytic cycle. Thus, although the enantioselectivities obtained are lower

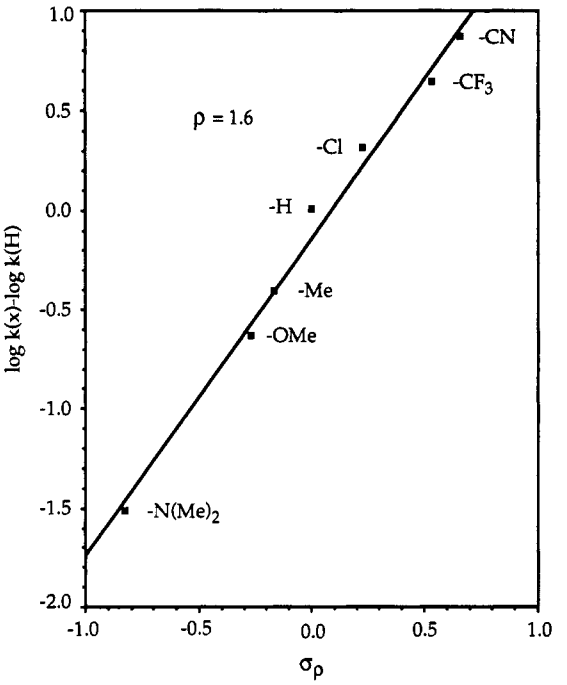


Figure 4. Hammett plot for the platinum-catalyzed aldol reaction using substituted benzaldehydes and methyl isocyanoacetate.

than those previously reported for the higherto unique Au(I)/ferrocenylphosphine system, this study indicates that also a Pt(II) complex, bearing a rather rigid and symmetric ligand, is a suitable catalyst for this still-intriguing reaction. As expected, the achiral catalyst precursor **2a**, as well as the racemic dimethyl-substituted analogs, *rac*-**4b** and the corresponding *meso*-form, *meso*-**4b**, are active catalysts for the aldol reaction of methyl α-isocyanoacetate with aldehydes. Thus the reactivities of these complexes, relative to that of **20**, were tested using PhCHO and $CNCH_2COOMe$ and the conditions given in Table 2. The most notable feature of this reaction, using the former catalyst precursors, was their slowness. Thus, in all three cases, 80% conversion was reached in ca. 24 h while with **20** only 4 h were needed to get 100% conversion. Furthermore, **2a**, *rac*-**4b**, and *meso*-**4b** gave a trans/cis ratio of 84/16 as opposed to the 70/30 obtained with **20**. Although it appears likely that these differences could be connected with the presence of oxygen atoms in **20**, further studies will be necessary to support this hypothesis.

Experimental Section

Isophthalaldehyde,[24] (*E*,*E*)-1,3-bis(2′-carboxyethenyl)benzene,[12] (*E*,*E*)-1,3-bis[(2′-methoxycarbonyl)ethenyl]benzene,[13] $LiPPh_2$,[25] bis(μ-chloro)bis[(η^3-2-methylallyl)platinum],[26] [2,6-bis[(diphenylphosphino)methyl]phenyl][(trifluoromethyl)sulfonyl]platinum(II) (**2a**),[5] [2,6-bis[(*R**,*R**)-1′-(diphenylphosphino)ethyl]phenyl][(trifluoromethyl)sulfonyl]platinum(II) (*rac*-**4b**),[5] and [2,6-bis[(*R**,*S**)-1′-(diphenylphosphino)ethyl]phenyl][(trifluoromethyl)sulfonyl]platinum(II) (*meso*-**4b**)[5] were prepared as described in the appropriate references.

The 1.5 M solution of diisobutylaluminum hydride in toluene and (*R*)-(−)-MTPA chloride were purchased from Aldrich and JPS Chimie, Bevaix (CH), respectively. All other reagents were purchased from Fluka AG and used without further purification. Merck silica gel 60 (230–400 mesh) was used for flash column chromatography. Solvents were dried by standard procedures under argon and stored over molecular sieves.

All glassware were dried in a drying oven at 150 °C and cooled under inert gas. *All manipulations involving free phosphines were carried out under an atmosphere of prepurified dinitrogen or argon*, using conventional Schlenk-tube techniques.

All melting points were determined in open capillary tubes and are uncorrected. The NMR spectra were measured either on a Bruker AC-200 or a Bruker WM-250 NMR spectrometer. The ^1H, ^{13}C, ^{31}P, and ^{195}Pt chemical shifts are reported in ppm, relative to tetramethylsilane, external 85% phosphoric acid, and 0.1 M Na_2PtCl_6, respectively. A positive value denotes a shift downfield of the reference. The following abbreviations have been used to denote the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dt, doublet of triplets; t(virt), apparent triplet (special solution of the spin system AA′XX′). Coupling constants (J) are given in hertz. Elemental analyses were performed by the "Mikroelementaranalytisches Laboratorium der Eidgenössischen Technischen Hochschule Zürich". The >98% ee indicates that the other diastereomer was not detectable by NMR.

(*E*,*E*)-1,3-Bis(3′-hydroxyprop-1′-enyl)benzene (9). To a stirred suspension of (*E*,*E*)-1,3-bis[(2-methoxycarbonyl)ethenyl]-benzene (**8**), (54.1 g, 220 mmol), in THF (500 mL), at 0 °C, was added a 1.5 M solution of diisobutylaluminum hydride in toluene (590 mL, 879 mmol) through a steel syringe. The cooling bath was removed and the colorless solution was stirred for 1 h and then slowly dropped into an ice-cold 40% aqueous solution of sodium potassium tartrate (1 L). (*The evolution of isobutane can be very vigorous if the order of the addition of the reagents is reversed*). Diethyl ether (300 mL) was then added and the emulsion was vigorously stirred for about 30 min until a clean two-phase system formed. The organic phase was separated and the aqueous phase extracted twice with 150-mL quantities of a mixture of THF/Et_2O, 1/1. The combined organic layers were dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The residue was crystallized from ca. 700 mL of $CHCl_3$ to give 38.1 g (92%) of pure product **9**: mp 91–92 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 1.44 (t, ^3J(HH) = 5.9, 2H, OH), 4.34 (ddd, ^3J(HH) = 5.9, ^3J(HH) = 5.7, ^4J(HH) = 1.4, 4H, CH_2), 6.39 (dt, ^3J(HH) = 15.8, ^3J(HH) = 5.7, 2H, $CHCH_2$), 6.62 (dt, ^3J(HH) = 15.8, ^4J(HH) = 1.4, 2H, $CHCHCH_2$), 7.29 (m, 3H, C_6H_4), 7.40 (s, 1H, C_6H_4); $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6) δ 63.3 (s, 2C, CH_2), 125.3 (s, 1C, aromatic CH), 126.1 (s, 2C, aromatic or olefinic CH), 129.7 (s, 1C, aromatic CH), 130.0 (s, 2C, aromatic or olefinic CH), 131.4 (s, 2C, aromatic or olefinic CH), 138.6 (s, 2C, aromatic C). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.94; H, 7.40.

1,3-Bis[(1′*S*,2′*S*)-1′,2′-epoxy-3′-hydroxypropyl]benzene (10). A dried 3-L three-necked flask, equipped with thermometer, magnetic stirrer, and argon inlet, was charged with (L)-(+)-diisopropyl tartrate (3.60 g, 15.4 mmol) and CH_2Cl_2 (2.0 L). The solution was stirred under argon, cooled with a dry ice-2-propanol bath to −20 °C and treated sequentially with activated, powdered 4-Å molecular sieve (11 g), titanium(IV) isopropoxide (3.0 mL, 10.2 mmol), and a 3.5 M solution of *tert*-butyl hydroperoxide in CH_2Cl_2 (115 mL, 402 mmol). The mixture was stirred at −20 °C for 1 h and then the diol **9** (18.8 g, 98.8 mmol) was added over 45 min. After 4 h at −20 °C, the reaction was quenched with a 30% solution of NaOH (18 mL). Diethyl ether (200 mL) was then added, the cold bath was removed, and the stirred mixture allowed to warm to 10 °C. Stirring was maintained for an additional 15 min at 10 °C, and then $MgSO_4$ (18 g) and Celite (11 g) were added. After further stirring for 15 min, the mixture was filtered through a pad of Celite and the pad washed twice with 100 mL of CH_2Cl_2. The solution was evaporated on a rotary evaporator and the remaining *tert*-butyl hydroperoxide was removed by azeotropic distillation with toluene under reduced pressure, affording the crude product which was dried under

(24) Ackermann, J. H.; Surrey, A. R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 668.
(25) Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *95*, 822.
(26) Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 294.

high vacuum. Yield: 20.0 g (91%) (none of the other diastereomer could be detected by ^{1}H NMR). Recrystallization from THF/hexane gave 18.5 g (84%) of pure **10** (>98% ee by analysis of the diester derived from **10** and (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetic acid chloride[27]): mp 128 °C dec; $[\alpha]_D = -86.0$ (ethanol, $c = 1$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.75 (dd, ^3J(HH) = 7.8, ^3J(HH) = 5.0, 2H, OH), 3.21 (ddd, ^3J(HH) = 2.1, ^3J(HH) = 2.2, ^3J(HH) = 3.6, 2H, C*H*CH$_2$), 3.81 (ddd, ^2J(HH) = 12.8, ^3J(HH) = 3.6, ^3J(HH) = 7.8, 2H, CHCH$_2$), 3.93 (d, ^3J(HH) = 2.1, 2H, C*H*OCHCH$_2$), 4.05 (ddd, ^2J(HH) = 12.8, ^3J(HH) = 2.2, ^3J(HH) = 5.0, 2H, CHCH$_2$), 7.19–7.37 (m, 4H, C_6H_4); ^{13}C{^{1}H} NMR (50 MHz, acetone-d_6) δ 55.9 (s, 2C,CHCH$_2$), 62.4 (s, 2C, CH$_2$), 63.5 (s, 2C, CHCHCH$_2$), 123.7 (s, 1C, aromatic CH), 126.1 (s, 2C, aromatic CH), 129.2 (s, 1C, aromatic CH), 139.1 (s, 2C, aromatic C). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.73; H, 6.55.

1,3-Bis[(1′*S*,2′*S*)-1′,2′-epoxy-3′-(*tert*-butyldimethylsiloxy)propyl]benzene (11). A stirred solution of **10** (16.0 g, 72 mmol) and imidazole (19.6 g, 288 mmol), in THF (200 mL), was treated with *tert*-butyldimethylchlorosilane (21.3 g, 144 mmol). After 2 h at room temperature, the reaction was complete (TLC control, EtOAc/hexane, 2:1 volume). The imidazole hydrochloride was filtered off and the solvent was removed by rotary evaporation. The resulting oily residue was extracted with pentane (200 mL) and the extract kept at 4 °C for 12 h. The remaining imidazole, which had quantitatively precipitated, was filtered off and the solvent was removed under reduced pressure to give 30.8 g (95%) of oily **11**. This material was sufficiently pure (>97% purity by GC) for further reactions. A 500-mg sample was bulb-to-bulb distilled for analytical purposes: viscous oil, $bp_{0.1}$ 230 °C; $[\alpha]_D = -43.5$ ($CHCl_3$, $c = 1$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.10 (s, 6H, CH$_3$), 0.11 (s, 6H, CH$_3$), 0.92 (s, 18H, C(CH$_3$)$_3$), 3.12 (m, 2H, C*H*CH$_2$), 3.80 (d, ^3J(HH) = 1.7, 2H, C*H*OCHCH$_2$), 3.82 (dd, ^2J(HH) = 12.1, ^3J(HH) = 4.2, 2H, CHCH$_2$), 3.96 (dd, ^2J(HH) = 12.1, ^3J(HH) = 3.0, 2H, CHCH$_2$), 7.18–7.35 (m, 4H, C_6H_4); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ −5.2 (s, 4C, Si(CH$_3$)$_2$), 18.5 (s, 2C, SiC(CH$_3$)$_3$), 26.0 (s, 6C, SiC(CH$_3$)$_3$), 55.7 (s, 2C, CHCH$_2$), 62.9 (s, 2C, CH$_2$), 62.9 (s, 2C, CHCHCH$_2$), 122.8 (s, 1C, aromatic CH), 125.7 (s, 2C, aromatic CH), 128.7 (s, 1C, aromatic CH), 137.8 (s, 2C, aromatic C). Anal. Calcd for $C_{24}H_{42}O_4Si_2$: C, 63.95; H, 9.39. Found: C, 63.78; H, 9.43.

1,3-Bis[(1′*S*,2′*S*)-1′-(diphenylthiophosphinyl)-2′,3′-dihydroxypropyl]benzene (12). To a stirred solution of **11** (3.83 g, 8.5 mmol), in THF (40 mL), at 0 °C, was quickly added an ice-cold 0.74 M THF solution of $LiPPh_2$ (23 mL, 17 mmol). The mixture was stirred for further 10 min and then treated with acetic acid (1 mL, 17 mmol) and elemental sulfur (561 mg, 17 mmol). After 1 h at room temperature the solvent was removed under reduced pressure and the residue was redissolved in 100 mL of methylene chloride. This solution was extracted with water (3 × 50 mL) to remove the lithium salts formed, and then the organic solvent was evaporated under reduced pressure, leaving an oily residue containing the silyl-protected intermediate. This was hydrolyzed by dissolving the residue in 20 mL of methanol and adding 1 mL of concd HCl. After stirring for 1 h at 40 °C, the resulting mixture was cooled to 5 °C and the product filtered off and washed with methanol. Yield: 3.8 g (68%) of **12**. Mp: 260 °C dec. $[\alpha]_D = -37$ (DMF, $c = 1.0$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.95 (broad s, 2H, CH$_2$O*H*), 3.00 (m, 2H, CHCH$_2$), 3.26 (m, 2H, CHCH$_2$), 4.11 (d, ^2J(PH) = 12.6 2H), 4.35 (m, 2H, C*H*CH$_2$), 4.74 (d, ^3J(HH) = 1.5, 2H, CHO*H*), 6.94 (t, ^3J(HH) = 7.7, 1H, C_6H_4), 7.88 (s, 1H, C_6H_4), 7.14–8.19 (m, 22H, C_6H_4 and C_6H_5). ^{13}C{^{1}H} NMR (50 MHz, DMSO-d_6): δ 45.7 (d, ^1J(PC) = 53.9, 2C, CHPS), 63.3 (s, ^3J(PC) = 10.8, 2C, CH$_2$), 70.9 (s, 2C, CHCH$_2$), 126.0–132.9 (12 different aromatic C atoms). ^{31}P{^{1}H} NMR (81 MHz, DMSO-d_6): δ 46.9. Anal. Calcd for $C_{36}H_{36}O_4P_2S_2$: C, 65.64; H, 5.51. Found: C, 65.55; H, 5.58.

1,3-Bis[(1′*S*,2′*S*)-1′-(diphenylthiophosphinyl)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]benzene (13). A solution of **12** (10.0 g, 15.2 mmol) and acetone dimethyl acetal (22 mL, 180 mmol) in 200 mL of CH_2Cl_2 was treated with 1 g of the acidic ion-exchange resin Dowex 50W. After the mixture was stirred for 12 h at room temperature, the resin was filtered off and the solvent was removed by rotary evaporation. The product was purified by recrystallization from toluene to give 10.5 g (93%) of **13**: mp 250–251 °C; $[\alpha]_D = -212$ ($CHCl_3$, $c = 1$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.20 (s, 3H, CH$_3$), 1.29 (s, 3H, CH$_3$), 3.10 (dd, ^2J(HH) = 8.4, ^3J(HH) = 8.1, 2H, CH$_2$), 3.73 (dd, ^2J(HH) = 8.4, ^3J(HH) = 5.4, 2H, CH$_2$), 3.92 (dd, ^2J(PH) = 9.1, ^3J(HH) = 9.1, 2H, C*H*CHCH$_2$), 5.05 (m, C*H*CH$_2$), 6.69 (t, ^3J(HH) = 7.6, 1H, C_6H_4), 7.94 (s, 1H, C_6H_4), 6.89–8.23 (m, 22H, C_6H_4 and C_6H_5); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 25.9 (s, 2C, CH$_3$), 26.8 (s, 2C, CH$_3$), 50.3 (d, ^1J(PC) = 49.4, 2C, CHPS), 67.8 (s, 2C, CH$_2$), 76.7 (d, ^2J(PC) = 7.8, 2C, CHCH$_2$), 108.3 (s, 2C, C(CH$_3$)$_2$), 127.2–133.9 (12 different aromatic C atoms); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 45.2. Anal. Calcd for $C_{42}H_{44}O_4P_2S_2$: C, 68.27; H, 6.00. Found: C, 68.34; H, 6.23.

1,3-Bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]benzene (7). A stirred suspension of **13** (12.0 g, 16.2 mmol), in tributylphosphine (10 mL, 40.5 mmol), was heated slowly up to 180 °C. The resulting solution was then stirred for 1 h at 150 °C and allowed to cool to room temperature. The addition of 30 mL of hexane gave a white, oily precipitate which was washed under argon with two 50-mL portions of ice-cold hexane. The resulting residue was purified by recrystallization from 70 mL of ethanol (20 h at −20 °C) to give 9.7 g (89%) of **7**: mp 95–96 °C; $[\alpha]_D = -169$ ($CHCl_3$, $c = 1$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.17 (s, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$), 3.09 (dd, ^2J(HH) = 8.0, ^3J(HH) = 8.3, 2H, CH$_2$), 3.52 (dd, ^2J(PH) = 4.4, ^3J(HH) = 4.4, 2H, C*H*CHCH$_2$), 3.62 (dd, ^2J(HH) = 8.0, ^3J(HH) = 5.7, 2H, CH$_2$), 4.07 (m, C*H*CH$_2$), 6.98–7.67 (m, 24H, C_6H_4 and C_6H_5); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 25.7 (s, 2C, CH$_3$), 26.5 (s, 2C, CH$_3$), 46.5 (d, ^1J(PC) = 16.5, 2C, CHPS), 67.2 (d, ^3J(PC) = 4.7, 2C, CH$_2$), 75.6 (d, ^2J(PC) = 14.2, 2C, CHCH$_2$), 108.8 (s, 2C, C(CH$_3$)$_2$), 127.8–137.1 (12 different aromatic C atoms); ^{31}P{^{1}H} NMR (101 MHz, $CDCl_3$) δ −7.4. Anal. Calcd for $C_{42}H_{44}O_4P_2$: C, 74.76; H, 6.57. Found: C, 74.57; H, 6.53.

(1*S*,2*S*)-1-Phenyl-1-(diphenylphosphinyl)-3-(diphenyl-*tert*-butylsiloxy)-2-propanol (15). A stirred solution of (2*S*,3*S*)-phenylglycidol (**14**) (100 mg, 666 μmol) and triethylamine (102 μL, 733 μmol) in CH_2Cl_2 (2 mL) was treated with *tert*-butyldiphenylchlorosilane (179 μL, 699 μmol) and 4-(dimethylamino)pyridine (4 mg, 33 μmol) at 0 °C. The mixture was stirred for 1 h and then left overnight at −25 °C. The resulting solution was then filtered through a pad of silica gel, the pad washed twice with CH_2Cl_2, and the solvent removed under reduced pressure. The oily residue, was redissolved in THF (4 mL) at 0 °C and treated with an ice-cold 0.46 M THF solution of $LiPPh_2$ (1.5 mL, 690 μmol). The mixture was stirred for further 10 min and then treated with acetic acid (37 μL, 650 μmol) and hydrogen peroxide (500 μL). The solvent was then removed under reduced pressure and the residue redissolved in 20 mL of CH_2Cl_2. This solution was extracted with water (3 × 20 mL) to remove the lithium salts formed, and the organic phase, after evaporation of the solvent, afforded a residue containing the silyl-protected, slightly impure product **15**. This was chromatographed on silica gel using CH_2Cl_2/MeOH, 25:1 volume. Yield: 299 mg (76%) of **15**. Mp: 123–126 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.09 (s, 9H, C(CH$_3$)$_3$), 3.28 (dd, ^2J(HH) = 9.6, ^3J(HH) = 9.6, 1H, CHCH$_2$), 3.57 (ddd, ^3J(HH) = 1.5, ^3J(HH) = 4.7, ^3J(HH) = 9.6, 1H, CHCHOH), 4.16 (dd, ^3J(HH) = 1.5, ^2J(PH) = 8.6, 1H, CHCHOH), 4.46 (m, 1H, CHCH$_2$), 4.82 (s, 1H, CHCHO*H*), 7.19–8.06 (m, 25H, C_6H_5). ^{31}P{^{1}H} NMR (101 MHz, $CDCl_3$): δ 37.5.

1,3-Bis[(1′*S*,2′*S*)-1′-(diphenylthiophosphinyl)-2′,3′-*O*-(thiocarbonyl)-2′,3′-dihydroxypropyl]benzene, 16. To a stirred solution of **12** (1.00 g, 1.52 mmol) and 4-DMAP (890 mg, 7.28 mmol) in 20 mL of CH_2Cl_2, at 0 °C, was added thiophosgene (280 μl, 3.64 mmol), and the mixture was stirred for 1 h at 0 °C. After the reaction was complete (TLC control, 2% EtOAc in CH_2Cl_2), the solvent was evaporated under reduced pressure and the

(27) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. Preparation of the ester see ref 15a, p 5773.

Table 3. Experimental Data for the X-ray Diffraction Study of 19·toluene

formula	$C_{49}H_{51}NO_7P_2Pt$
mol wt	1022.99
cryst dimen, mm	0.30 × 0.45 × 0.25
data collect. T, °C	23
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	10.160(1)
b, Å	15.721(2)
c, Å	28.799(2)
V, Å^3	4600(1)
Z	4
ρ(calcd), g, cm^{-3}	1.477
μ, cm^{-1}	31.978
radiation	Mo Kα (graphite monochromated, λ = 0.710 69 Å)
no. of measd reflns	$+h,+k,+l$
θ range, deg	$2.5 < \theta < 25.0$
scan type	$\omega/2\theta$
scan width, deg	1.10 + 0.35 tan θ
max counting time, s	100
bkgd time, s	0.5 × scan time
max scan speed, deg min^{-1}	10.5
prescan rejection limit	0.55 (1.8σ)
prescan acceptance limit	0.025 (40.0σ)
no. data collect. (ind)	4400
no. obsd ref (n_o)	3766 ($\|F_o\|^2 > 3.0\sigma(\|F\|^2)$)
transm coeff	0.79387–0.99829
no. of param refined (n_v)	506
R^a	0.025
R_w^b	0.036
GOF^c	1.124

^{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 $w = [\sigma^2(F_o)]^{-1}$; $\sigma(F_o) = [\sigma^2(F_o^2) + f^4(F_o^2)]^{1/2}/2F_o$ with $f = 0.055$. ^{c} GOF = $[\sum w(|F_o| - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

residue was loaded onto a short column of silica gel and eluted with 2% EtOAc in CH_2Cl_2. The solvent was evaporated on a rotary evaporator and the remaining colorless product **16** (1.06 g, 94%) was dried under high vacuum: mp 170 °C dec; $[\alpha]_D$ = −227 (DMF, c = 1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.90 (dd, ^2J(HH) = 9.0, ^3J(HH) = 9.0, 2H, CH_2), 4.10 (dd, ^2J(HH) = 9.8, ^3J(HH) = 9.8, 2H, CH_2), 4.64 (dd, ^2J(PH) = 9.0, ^3J(HH) = 7.7, 2H, C*H*CHCH$_2$), 5.88 (m, C*H*CH$_2$), 6.75–8.22 (m, 24H, C_6H_4 and C_6H_5); ^{13}C{^{1}H} NMR (500 MHz, DMSO-d_6) δ 46.8 (d, ^1J(PC) = 50.1, 2C, *C*HPS), 71.7 (s, 2C, CH_2), 82.2 (s, 2C, *C*HCH$_2$), 127.4–132.3 (12 different aromatic C atoms), 190.9 (s, 2C, CS); ^{31}P{^{1}H} NMR (81 MHz, DMSO-d_6) δ 45.5. Anal. Calcd for $C_{38}H_{32}O_4P_2S_4$: C, 61.44; H, 4.34. Found: C, 61.53; H, 4.37.

[2,6-Bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]phenyl]chloroplatinum(II) (18). A solution of **7** (1.89 g, 2.80 mmol) and $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(CH_3)CH_2)_2]$ (0.80 g, 1.40 mmol) in $CHCl_3$ (50 mL) was stirred for 20 min at room temperature. After removal of the solvent by rotary evaporation, the residue was recrystallized from toluene and gave 2.31 g (91%) of **18**: mp 235–238 °C; $[\alpha]_D$ = +388 ($CHCl_3$, c = 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.69 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 3.08 (dd, ^2J(HH) = 8.6, ^3J(HH) = 5.6, 2H, CH_2), 3.43 (dd, ^2J(HH) = 8.6, ^3J(HH) = 6.8, 2H, CH_2), 4.00 (m, 2H, C*H*CH$_2$), 4.13 (m, ^2J(PtH) = 57, C*H*CHCH$_2$), 7.05–8.03 (m, 23H, C_6H_3 and C_6H_5); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 25.1 (s, 2C, CH_3), 25.6 (s, 2C, CH_3), 55.3 (t(virt), ^1J(PC) + ^3J(PC) = 34.7, ^2J(PtC) = 79.6, 2C, *C*HP), 67.1 (s, 2C, CH_2), 76.5 (s, 2C, *C*HCH$_2$), 108.5 (s, 2C, *C*(CH$_3$)$_2$), 124.2–146.1 (12 different aromatic C atoms); ^{31}P{^{1}H} NMR (101 MHz, $CDCl_3$) δ 40.7 (s, ^1J(PtP) = 3046); ^{195}Pt{^{1}H} NMR (54 MHz, $CDCl_3$) δ −4159.6 (t, ^1J(PtP) = 3046). Anal. Calcd for $C_{42}H_{44}O_4P_2ClPt$: C, 55.72; H, 4.90; Cl, 3.92. Found: C, 55.61; H, 5.02; Cl, 4.36.

[2,6-Bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]phenyl](η^1-nitrato)platinum(II) (19). A solution of **18** (40 mg, 44 μmol) and silver nitrate (7.5 mg, 44 μmol), in $CHCl_3$ (10 mL), was stirred at room temperature for 2 h. The silver chloride precipitate was filtered off over Celite and the solvent was evaporated under reduced pressure to ca. 0.5 mL, transferred to an NMR tube, and layered with toluene. Suitable crystals for X-ray diffraction formed slowly.

Table 4. Final Positional and Isotropic Equivalent Displacement Parameters for 19·toluene (esd's Given in Parentheses)

atom	x	y	z	B^a (Å^2)
Pt	0.95968(2)	0.89268(2)	0.82267(1)	2.866(4)
P1	1.0600(2)	0.9514(1)	0.76006(6)	3.10(3)
P2	0.8130(2)	0.8563(1)	0.87915(6)	3.09(3)
O1	1.1339(5)	0.8325(4)	0.8480(2)	4.6(1)
O2	1.0365(8)	0.7106(4)	0.8425(3)	8.2(2)
O3	1.2331(7)	0.7194(5)	0.8716(3)	8.1(2)
O4	0.7727(6)	0.9107(4)	0.6641(2)	4.7(1)
O5	0.9226(8)	0.9114(8)	0.6063(2)	11.6(3)
O6	0.7001(8)	1.1020(4)	0.8962(2)	6.6(2)
O7	0.7603(9)	1.1088(4)	0.9719(2)	8.3(2)
N1	1.1334(7)	0.7520(5)	0.8540(2)	4.9(2)
C1	0.8080(6)	0.9582(4)	0.7988(2)	3.0(1)
C2	0.6979(7)	0.9768(4)	0.8272(3)	3.5(1)
C3	0.5895(7)	1.0201(5)	0.8103(3)	4.1(2)
C4	0.5883(7)	1.0488(5)	0.7652(3)	4.3(2)
C5	0.6972(8)	1.0354(5)	0.7367(3)	4.1(2)
C6	0.8037(7)	0.9900(4)	0.7532(2)	3.0(1)
C7	0.9205(6)	0.9733(5)	0.7200(2)	3.3(1)
C8	0.8980(8)	0.9006(5)	0.6860(2)	4.0(2)
C9	0.7062(7)	0.9520(5)	0.8783(2)	3.6(1)
C10	0.7698(9)	1.0257(5)	0.9069(3)	4.4(2)
C11	0.792(1)	0.9137(6)	0.6145(3)	5.2(2)
C12	0.9936(9)	0.9002(7)	0.6467(3)	6.3(2)
C13	0.739(2)	0.9929(9)	0.5946(4)	11.8(4)
C14	0.730(2)	0.8383(8)	0.5924(4)	12.0(5)
C15	0.712(1)	1.1567(6)	0.9345(3)	6.7(3)
C16	0.759(1)	1.0224(5)	0.9583(3)	6.2(2)
C17	0.573(2)	1.189(1)	0.9454(6)	14.7(5)
C18	0.812(2)	1.2278(9)	0.9255(5)	13.9(6)
C111	1.1852(7)	0.8855(5)	0.7323(3)	3.6(1)
C112	1.1647(8)	0.7981(5)	0.7301(3)	5.1(2)
C113	1.252(1)	0.7463(5)	0.7097(4)	6.3(2)
C114	1.369(1)	0.7786(6)	0.6919(4)	7.1(3)
C115	1.395(1)	0.8652(7)	0.6955(4)	7.6(3)
C116	1.3019(9)	0.9183(5)	0.7154(3)	5.6(2)
C121	1.1409(7)	1.0530(4)	0.7724(3)	3.6(1)
C122	1.1376(9)	1.1206(5)	0.7411(3)	4.7(2)
C123	1.2027(9)	1.1957(5)	0.7516(3)	5.4(2)
C124	1.2679(8)	1.2025(5)	0.7934(4)	5.5(2)
C125	1.2729(9)	1.1354(6)	0.8241(4)	6.1(2)
C126	1.2074(8)	1.0615(5)	0.8130(3)	4.9(2)
C211	0.8622(7)	0.8393(4)	0.9394(2)	3.1(1)
C212	0.7702(7)	0.8138(5)	0.9720(3)	4.1(2)
C213	0.8053(9)	0.8096(6)	1.1083(3)	5.2(2)
C214	0.9304(9)	0.8288(6)	1.0319(3)	5.2(2)
C215	1.0258(9)	0.8510(5)	0.9994(3)	4.9(2)
C216	0.9897(7)	0.8576(5)	0.9526(3)	3.7(1)
C221	0.7068(7)	0.7668(5)	0.8659(2)	3.6(1)
C222	0.5886(8)	0.7742(6)	0.8417(3)	4.9(2)
C223	0.5159(9)	0.7019(7)	0.8311(3)	6.1(2)
C224	0.5570(9)	0.6239(6)	0.8450(3)	5.6(2)
C225	0.672(1)	0.6149(6)	0.8694(3)	5.6(2)
C226	0.7456(8)	0.6871(5)	0.8802(3)	4.6(2)
C1s^b	0.880(2)	0.5953(9)	0.0459(5)	10.6(4)*
C2s	0.800(1)	0.5347(9)	0.0620(5)	9.1(3)*
C3s	0.756(2)	0.473(1)	0.0335(6)	11.4(4)*
C4s	0.810(2)	0.467(1)	−0.0150(6)	11.7(5)*
C5s	0.899(2)	0.535(1)	−0.0274(5)	11.1(4)*
C6s	0.930(2)	0.595(1)	0.0041(6)	11.6(5)*
C7s	0.675(4)	0.409(2)	0.041(1)	30(2)*

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Starred atoms were refined isotropically. ^{b} Atoms labeled C1s–C7s are those of the clathrated toluene molecule.

[2,6-Bis[(1′*S*,2′*S*)-1′-(diphenylphosphino)-2′,3′-*O*-isopropylidene-2′,3′-dihydroxypropyl]phenyl]trifluoromethanesulfonoplatinum(II) (20). A solution of **18** (350 mg, 387 μmol) and $AgCF_3SO_3$ (99.7 mg, 388 μmol), in 30 mL of CH_2Cl_2, was stirred at room temperature for 2 h. The silver chloride

precipitate was filtered off over Celite and the solvent was evaporated under reduced pressure. The solid residue, recrystallized from toluene, gave 363 mg (92%) of **20**: mp 186–187 °C; $[\alpha]_D$ = +235 ($CHCl_3$, c = 1); ^1H NMR (250 MHz, $CDCl_3$) δ 0.66 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 3.26 (dd, ^2J(HH) = 8.5, ^3J(HH) = 5.8, 2H, CH_2), 3.36 (dd, ^2J(HH) = 8.5, ^3J(HH) = 6.7, 2H, CH_2), 4.00 (m, ^2J(PtH) = 56, 2H, $CHCHCH_2$), 4.03 (m, 2H, $CHCH_2$), 7.02–7.85 (m, 23H, C_6H_3 and C_6H_5); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 25.1 (s, 2C, CH_3), 25.5 (s, 2C, CH_3), 53.6 (t(virt), ^1J(PC) + ^3J(PC) = 34.6, 2C, CHP), 67.1 (s, 2C, CH_2), 75.6 (s, 2C, $CHCH_2$), 108.9 (s, 2C, $C(CH_3)_2$), 125.1–146.2 (12 different aromatic C atoms); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 45.5 (s, ^1J(PtP) = 3143); $^{195}Pt\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ −3989.8 (t, ^1J(PtP) = 3143). Anal. Calcd for $C_{43}H_{44}O_7F_3P_2SPt\cdot H_2O$: C, 49.81; H, 4.47. Found: C, 49.57; H, 4.24.

Standard Procedure of the Pt(II)-Catalyzed Aldol Reaction. A stirred solution of 7 mg (7.5 μmol, 1.5 mol %) of **20**, in 4 to 5 mL of CH_2Cl_2, was treated sequentially with methyl α-isocyanoacetate (46 μL, 500 μmol), the aldehyde (500 μmol), and diisopropylethylamine (11 μL, 65 μmol). The colorless reaction mixture was stirred at room temperature for 4–18 h (TLC control: EtOAc/hexane, 1:1 volume, monitored with $KMnO_4$/0.1 M NaOH). After the solvent had been removed by rotary evaporation, the remaining residue was bulb-to-bulb distilled ($bp_{0.1\ torr}$: 100–200 °C), to give the pure *cis/trans* mixture of the 4,5-oxazolines. The *cis/trans* ratio was determined by integrating the methyl singlet of the ester in the ^1H NMR spectrum. The enantiomeric excesses were determined by ^1H NMR spectroscopy using Eu(dcm)$_3$ as the chiral shift reagent.[28]

Procedure for the Relative Rate Determination of the Aldol Reaction of *Para*-Substituted Benzaldehydes. A stirred solution of **20** (7 mg, 7.5 μmol, 1.5%), in CH_2Cl_2 (4 to 5 mL), was sequentially treated with methyl α-isocyanoacetate (46 μL, 500 μmol), benzaldehyde 51 μL (500 μmol), the *para*-substituted benzaldehyde (500 μmol), and diisopropylethylamine (11 μL, 65 μmol, 13%). The reaction mixture was stirred at room temperature for 3–8 h until TLC showed that all the isocyanide had reacted. The remaining amount of benzaldehyde was determined by GLC (Carlo Erba Strumentazione 6000; SE 54, 50 m; 100 kPa helium; 80–250 °C, 20°/min) with naphthalene as an internal standard.

Crystallography. Suitable crystals of compound **19** were obtained by crystallization from $CHCl_3$/EtOH, in the presence of toluene, and are air-stable.

A prismatic crystal was chosen for the data collection and mounted on a glass fiber at a random orientation. An Enraf-Nonius CAD4 diffractometer was used for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by a least squares fit of the 2θ values of 25 high-order reflections (9.6 < θ < 15.4°) using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table 3.

Data were recorded with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every hour; no significant variation was detected.

The 4440 measured reflections were corrected for Lorentz and polarization factors and for absorption by using the azimuthal (Ψ) scans of three reflections at high "χ" angles (χ > 87°, 10.1 < θ < 18.4°). The standard deviations on intensities were calculated in term of statistics alone, while those on F_o were calculated as reported in Table 3.

The structure was solved by Patterson and Fourier methods and refined by full matrix least squares.[29] The function minimized was $[\sum w(|F_o| - 1/k|F_c|)^2])$ with $w = [\sigma^2(F_o)]^{-1}$. No extinction correction was deemed to be necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[30]

Toward the end of the refinement, a Fourier difference map revealed a clathrated toluene molecule which was included in the refinement. Anisotropic displacement parameters were used for all atoms except those of toluene, while the contributions of the hydrogens, in their idealized positions (C–H = 0.95 Å, B = $1.3B_{(C\ bonded)}$ Å^2), were taken into account but not refined. Upon convergence (no parameter shift > 0.2σ(p)) the final Fourier difference map showed no significant residual peaks.

All calculations were carried out by using the Enraf-Nonius MOLEN crystallographic programs.[31]

The handedness of the crystal was tested by refining the two enantiomorphs. The positional parameters of the enantiomer giving the lower R_w factor are listed in Table 4.

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Supplementary Material Available: Tables giving (a) anisotropic displacement parameters (Table S1), (b) calculated positional parameters for the hydrogen atoms (Table S2), and (c) extended list of bond distances, bond angles, and torsion angles (Table S3) and a figure giving full numbering scheme (Figure S1) for **19** (16 pages). Ordering information is given on any current masthead page.

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