112. Sterically Congested Molecules: 2,2′-[(Biaryldiyl)bis(oxy)]bis[1,3,2-oxazaphospholidines]

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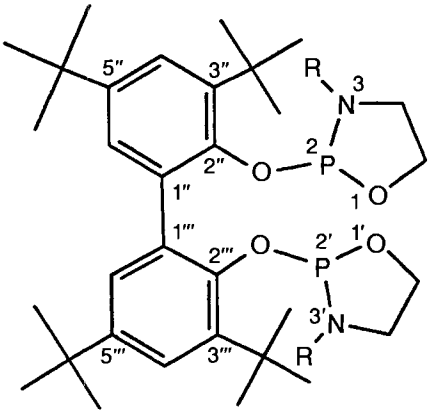
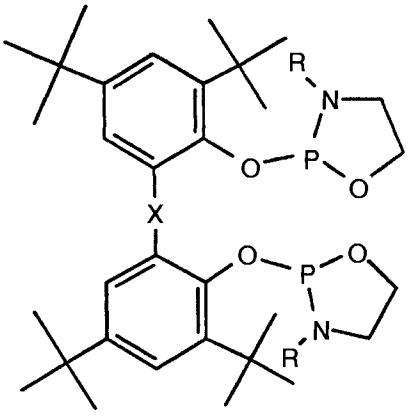
The original suggestion that a through-space mechanism was operative in the seven-bond J(P,P) coupling constant of 30.3 Hz observed for 3,3′-bis(1,1-dimethylethyl)-2,2′-{[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diyl]bis(oxy)}bis[1,3,2-oxazaphospholidine] (**1a**) was investigated. In the solid-state CP-MAS ^{31}P-NMR spectrum of **1a**, two nonequivalent P-atoms were observed; sufficient resolution could not be obtained to determine whether P,P coupling was present. The preparation and spectral data of the *N*-methyl analogue **1b** and of the acyclic *N*-isopropyl analogue **6** (*Scheme 1*) provided evidence that *a*) the essentially exclusive formation (*R**,*R**,*S**)-**1a** in the reaction of the disodium biphenyldiolate **3a** with the phosphorochloridite **4a** is the result of significant differences in the free energy of activation (ΔG^*) for the formation of the various diastereoisomers due to the steric congestion within the molecule and that *b*) the magnitude of the observed P,P coupling is dependent upon the degree of conformational freedom within the molecule. In the ^{31}P-NMR spectrum of the *P*-sulfide **7**, which was prepared by the reaction of **1a** with sulfur, 2*s* resonances were observed that strongly suggested that the lone electrons pair on P are involved in the mechanism for the transmission of coupling data. The chiral analogues (4*S*,5*R*)-**12** and (4*R*,5*S*)-**12** of **1a** were prepared in a three-step reaction sequence starting from the corresponding enantiomerically pure norephredine **8** (*Scheme 2*). Both (4*S*,5*R*)- and (4*R*,5*S*)-**12** were obtained as a diastereoisomer mixture that differ by the configuration of the axis of chirality, *i.e.*, (*R**,*R**,*R**)- and (*R**,*S**,*R**)-**12** were obtained. The major diastereoisomer was obtained upon recrystallization, and the atropisomers were observed to equilibrate in solution by monitoring the H–C(5) resonance in the ^{1}H-NMR with time ($\Delta G^\circ = 0.4$ kcal/mol; *Fig. 2*). The process observed corresponds to the restricted rotation about the central single bond of the biphenyl system. The isolation of an atropisomer *with only a single* ortho *substituent on each aryl ring* is quite rare. In the ^{13}C-NMR spectrum of both (*R**,*R**,*R**)- and (*R**,*S**,*R**)-**12**, C(5) is two-bond-coupled to the oxazaphospholidine P-atom (^2J(C(5),P((2)) = 8.5 Hz) that is further virtually coupled to the P-atom of the other oxazaphospholidine ring ($7J$(P(2),P(2′)) = 30 Hz; ^9J(C(5),P(2′)) = 0 Hz; δ(P(2)) = δ(P(2′)) = 136 ppm). In the ^{31}P-NMR spectrum of (*R**,*R**,*S**)-**12**, which was prepared from the racemic chloridite (mixture of three diastereoisomers was obtained), a ^7J(P(2),P(2′)) of 36 Hz was observed. These observations provide strong evidence that seven-bond P,P coupling occurs in all three diastereoisomers of **12**. *The observed P,P coupling is both independent of the configuration of the chiral axis and the configuration of the asymmetric P-centers.* This independence of P,P coupling upon the configuration on P implies also the independence of the observed coupling upon the orientation of the lone-pair of electrons on P *provided that the conformations of the diastereoisomers are similar in solution.* The X-ray crystal structure of the complex formed from **1a** and dichloro(cycloocta-1,5-diene)platinum(II) was obtained and the solid-state structure discussed. The major diastereoisomer of (4*S*,5*R*)-**12** was used as a chiral ligand in asymmetric hydrosilylation and hydrogenation reactions (*Scheme 3*).

Introduction. – Research efforts in phosphorus chemistry have expanded dramatically in recent times [1]. Not only does phosphorus play a decisive role in both biological systems and the environment, but trivalent organophosphorus ligands have also played a dominant role in the development of synthetic organometallic methodology [2].

Recently, we reported the synthesis of a class of sterically congested oxazaphospholidine molecules and their unique spectral characteristics [3]. In particular, in the ^{31}P-NMR spectrum of oxazaphospholidine **1a**, the P-atoms were observed to be nonequivalent with an unprecedented seven-bond P,P coupling with ^{7}J(P,P) = 30.3 Hz. In the X-ray crystal structure of **1a**, the relative configuration of the two stereogenic P-atoms and of the chiral axis was $P(2)R^*,R^*_{ax},P(2')S^*$ (short form, (R^*,R^*,S^*)[1]). Of course, provided that rotation about the C(aryl)–C(aryl) single bond is not fast on the NMR time scale, the P-atoms are diastereotopic and expected to be nonequivalent barring accidental equivalence. This must be the case because rapid rotation about the single bond connecting the two aryl rings (the chiral axis) would render the P-atoms enantiotopic and indistinguishable in a achiral environment [5]. Quite interestingly, in the X-ray crystal structure of **1a**, the two oxazaphospholidine rings have different ring conformations. In principle, if these conformational differences are maintained in solution (distinct envelope and twist-boat structures with either *R* or *S* absolute configuration at P), two diastereoisomers with relative configuration $P(2)R^*,R^*_{ax},P(2')S^*$ are possible that differ due to the conformation of the ring, *e.g.*, $P(2;$ envelope$)R^*,R^*_{ax},P(2';$ twist-boat$)S^*$ and $P(2;$ twist-boat$)R^*,R^*_{ax},P(2';$ envelope$)S^*$.



1a R = *t*-Bu
b R = Me



2a X = CH_3CH
b X = CH_2
c X = S

In our original paper, we suggested that a through-space mechanism of coupling was operative. Particularly supportive of this suggestion was the fact that a large eight-bond P,P coupling (^{8}J(P,P) = 30 Hz) was observed in **2a** in which a through-bond coupling mechanism involving the aryl π system is interrupted by a bridging ethane-1,1-diyl group. Nevertheless, questions remain as to whether a specific relative configuration of the

[1]) Throughout this paper, (R^*,R^*,S^*) refers to the relative configurations at P(2), chiral axis, and P(2'), respectively. The configuration at P(2) is assigned R^* following the customary convention when the absolute configuration is unknown [4].

P-atoms in **1a** (orientation of the lone pair of electrons on P) is necessary for the observed coupling, and if the lone electron pair on P plays a role in the transmission of the observed coupling as might be expected for a through-space coupling mechanism (*Fermi* contact term). Questions regarding the effect of steric congestion within the molecule upon the magnitude of through-space coupling and the existance of P,P coupling in the solid state remained. In this paper, we report both our efforts in further elucidating the mechanism of long-range P,P coupling, which includes solid-state CP-MAS ^{31}P-NMR spectroscopy, variation of the steric congestion within the molecule, and the synthesis of optically active 2,2′-[(biaryldiyl)bis(oxy)]bis[1,3,2-oxazaphospholidines] along with their use as ligands in transition-metal-mediated asymmetric synthesis [6].

Results and Discussion. – *Solid-State CP-MAS ^{31}P-NMR Spectrum.* The original suggestion that a through-space coupling mechanism was at least partially responsible for the observed seven-bond J(P,P) observed in the ^{31}P-NMR of (R^*,R^*,S^*)-**1a**[1]) was based partly on the consideration of the solid-state X-ray crystal structure. Caution must clearly be exercised because lattice energy and the resultant crystal-packing effects can render the solid state and solution structures different. It was clearly of interest to determine whether the ^7J(P,P) could be observed in the solid state. *Fig. 1* shows the full cross-polarization magic-angle-spinning (CP-MAS) solide-state ^{31}P-NMR spectrum of (R^*,R^*,S^*)-**1a** with MAS sidebands [7]. Two center-band broad *s* resonances were observed at δ 131.5 and 132.4 (*Fig. 1*, insert) compared to δ 133.5 and 135.7 observed in solution. Unfortunately, sufficient resolution of the broadened resonances could not be obtained to resolve whether J(P,P) = 30.3 Hz is present in the solid state.

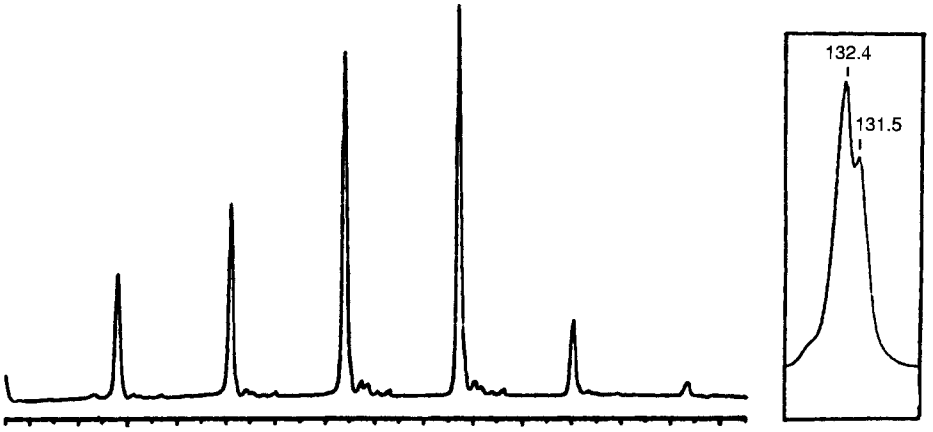


Fig. 1. *Solid-state CP-MAS ^{31}P-NMR spectrum of* **1a**. The center-band resonances are shown within the boxed insert.

Variation of the Steric Congestion. The essentially exclusive formation of (R^*,R^*,S^*)-**1a** in the reaction of the disodium biphenyldiolate **3a** with the phosphorochloridite **4a** was suggested to be the result of significant differences in the free energy of activation (ΔG^*) for the formation of the various diastereoisomers due to the steric congestion within the molecule [3]. This is supported by the fact that in the homologue **5** without the

t-Bu substitution in the aryl rings, two diastereoisomers were observed. The present work (*vide infra*) strongly suggests that in **5** rotation about the bond connecting the two aryl rings is fast on the NMR time scale and renders the P-atoms of the two diastereoisomers either homo- or enantiotopic. Similar considerations apply to the previously prepared methylenebis[(phenylene)oxy]- and thiobis[(phenylene)oxy]bis[1,3,2-oxazaphospholidines], **2b** and **2c**, respectively. Although these examples strongly support the argument that the formation of (*R**,*R**,*S**)-**1a** is due to difference in ΔG^* because of steric congestion within the molecule, the expected equivalence of the P-atoms in the ^{31}P-NMR spectra of these compounds preclude the determination of whether the P-atoms are coupled[2])[3]).

If the explanation that a single diastereoisomer of **1a** is formed as the result of significant differences in the ΔG^* for the formation of the various diastereoisomers due to the steric congestion within the molecule, then the reduction of intramolecular congestion by a smaller *N*-alkyl substituent might be expected to result in the formation of additional diastereoisomers. This was indeed the case. The reaction of lithium phenolate **3b** with the *N*-methyl-substituted chloridite **4b** gave a mixture **1b** of three diastereoisomeric [(biaryldiyl)bis(oxy)]bis[oxazaphospholidines]. Although separation of the isomer mixture was not possible, the ^{1}H- and ^{31}P-NMR of the recrystallized mixture was consistent with a 4.1:1.3:1 ratio of the three expected diastereoisomers. In the ^{31}P-NMR spectrum, two *s* at δ 132.9 (minor diastereoisomer) and 134.0 and one *AB 'q'* at δ 133.2 (major diastereoisomer) were observed, which were assigned to two diastereoisomers with equivalent P-atoms and one diastereoisomer, (*R**,*R**,*S**)-**1b**, with nonequivalent P-atoms. Noteworthy is the fact that the observation of (*R**,*R**,*S**)-**1b** requires that rotation about the single bond connecting the two aryl groups, which constitutes the (chiral axis), must be slow on the NMR time scale because rapid rotation on the NMR time scale would render the P-atoms enantiotopic. Furthermore, rotation about the C–C bond connecting the two aryl groups in the other two diastereoisomer, *i.e.* (*R**,*R**,*R**)- and (*R**,*S**,*R**)-**1b**, must also be slow on the NMR time scale. This must be the case because rapid (on the NMR time scale) rotation would interconvert these two diastereoisomers resulting in a single resonance in the ^{31}P-NMR spectrum. The two P-atoms within both the (*R**,*R**,*R**)- and (*R**,*S**,*R**)-diastereoisomers of **1b** are expected to be equivalent (homotopic due to a C_2 axis within each molecule).

In the ^{31}P-NMR spectrum of (*R**,*R**,*S**)-**1b**, a ^7J(P,P) of 20 Hz was observed. The reduction in of the value of ^7J(P,P) observed for (*R**,*R**,*S**)-**1b** over that observed for (*R**,*R**,*S**)-**1a** is consistent with a reduction in through-space coupling due to increased conformational freedom. This would be the case because the increased conformational freedom resulting from changing from a *N*-(*tert*-butyl) to a *N*-methyl substituent would

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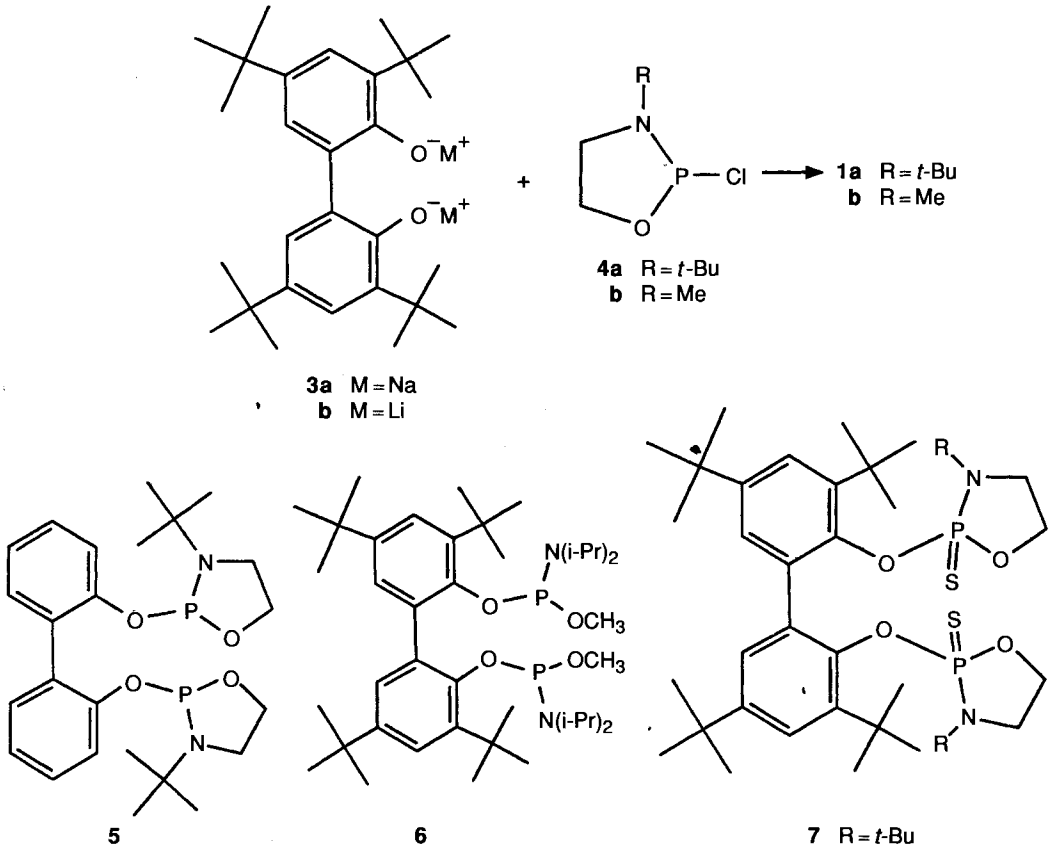
[2]) In principle, the presence of P,P coupling in these molecules with equivalent P-atoms can be determined from the ^{13}C-NMR spectrum because the observed coupling of P to a particular C-atom will be different with respect to whether the P-atoms are coupled or not. In the ^{13}C-NMR spectra of both **2b** and **5**, C(5) appeared as *d*, which suggests that the P-atoms are not coupled. However, poor resolution of the resonances (diastereoisomer mixture) makes this conclusion somewhat tenuous. The apparent lack of coupling supports the conclusion that increased molecular mobility in these molecules is the cause of the loss in coupling.

[3]) The results of this study support the previous contention [3] that increased rotational freedom in **2b** and **2c** leads to formation of two diastereoisomers. The present results strongly suggest both that the lack of observed coupling may only be due to the fact that the P-atoms are either homo- or enantiotopic and, therefore, equivalent in the ^{31}P-NMR spectra of these molecules and that P,P coupling may indeed occur in these molecules.

Scheme 1



allow for an increased time-averaged distance between the two P-atoms. However, one must remain cognizant of the fact that a reduction in the size of the *N*-substituent could lead to a concurrent change in hybridization at the P-atom with a resultant change in the magnitude of the observed coupling.

An acyclic analog of **1a,b** was prepared. The reaction of **3a** with *O*-methyl *N,N*-diisopropylphosphorochloramidite gave **6** (*Scheme 1*) as a mixture of three diastereoisomers. As in the case of **1b**, in the ^{31}P-NMR spectrum of **6**, two *s* (δ 147.0 and 145.9) and one *AB'q'* (δ 147.5) were oberserved in a 1:3:3 ratio, respectively[4]). A ^{7}J(P,P) of 12.3 Hz was observed, which is consistent with a reduced coupling due to increased conformation freedom in the acyclic molecule. As in the case of (*R*,R*,S**)-**1a,b**, rotation about the C–C bond connecting the two aryl groups of (*R*,R*,S**)-**6** must be slow on the NMR time scale (*vide supra*).

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[4]) A forth minor *s* was observed at δ 132.7 in the ^{31}P-NMR spectrum, which is tentatively assigned to the formation of a seven-membered dioxaphosphepine. It is not unreasonable that this assignment and that of one of the upfield *s* could be reversed, however, this does not affect the general conclusions regarding coupling for the diastereoisomer observed as an *AB'q'*. For expected ^{31}P-NMR chemical shifts of dioxaphosphepines, see [8].

Role of the Lone Electron Pair on the P-Atom. The suggestion that the mechanism of the observed ^{7}J(P,P) coupling in (*R**,*R**,*S**)-**1a** is at least in part due to a through-space component leads to the speculation that the lone electron pair on the P-atom plays a role in the transmission of coupling information [3] [9]. The lone electron pair on the adjacent O- and N-atom may well play a role in the transmission of coupling information by interaction (orbital overlap) with the lone electron pair on the P-atom. A recent example was reported by *Goddard et al.* for the through-space coupling of a P- to a H-atom involving the lone electron pair on an O-atom adjacent to the P-atom in a 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin [10].

The P-sulfide **7** (*Scheme 1*) was easily prepared by the reaction of **1a** with elemental sulfur at 80° using chlorobenzene as a solvent. Although a confirming crystal strucutre was not obtained, retention of configuration at the P-atom is expected during the formation of the P-sulfide, *i.e.* **7** is obtained [11]. A comparison of the ^{13}C-NMR chemical shifts of **1a** and **7** (*Table 1*) supports the structure illustrated.

Table 1. *Comparison of the ^{13}C-NMR Spectrum of* **7** *with that of* **1a**

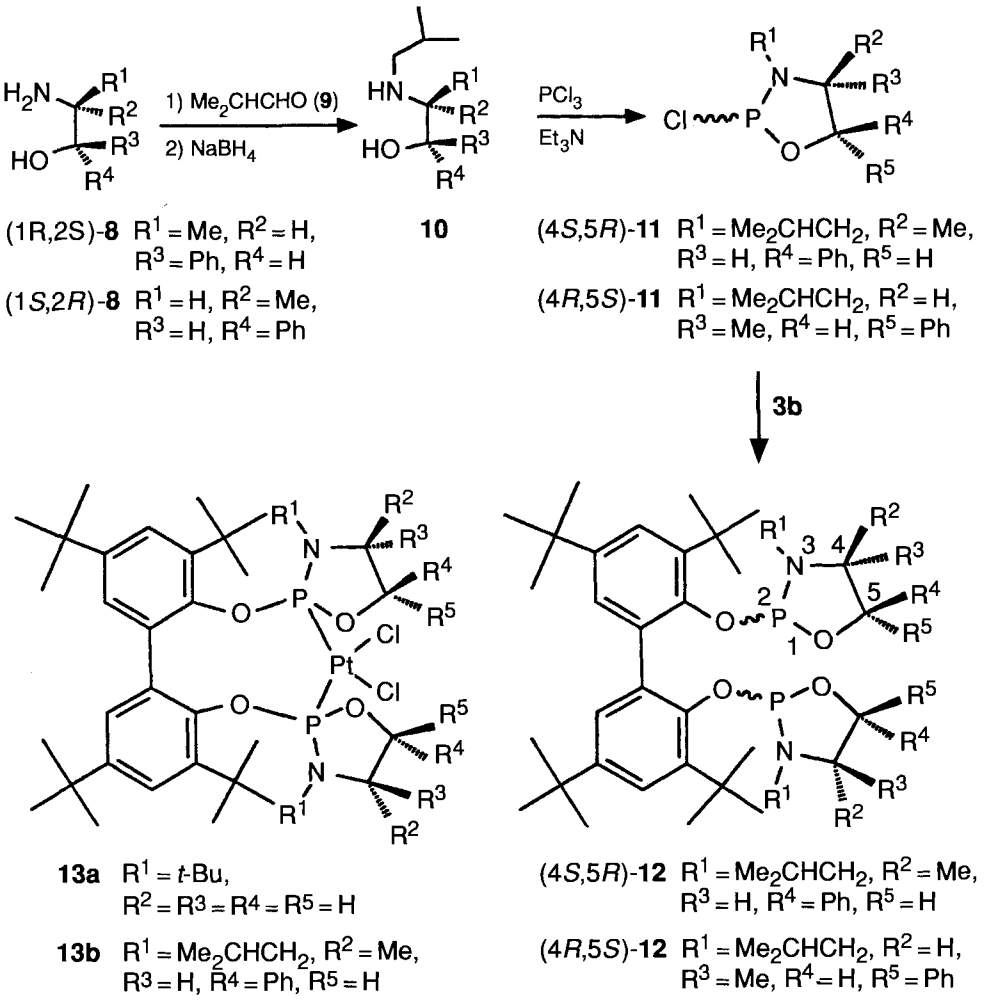
δ [ppm] (^{n}J(C,P) [Hz])		Assignment
1a	**7**	
29.7 (*d*, *J* = 10.5), 29.9 (*dd*, *J* = 10.6, 0.7)	27.6 (*d*, *J* = 3.2), 28.6 (*d*, *J* = 3.3)	$(CH_3)_3C$–N(3,3′)
30.6, 30.7	30.87, 30.93	$(CH_3)_3C$–C(5″,5‴)
31.4, 31.5	31.3, 31.6	$(CH_3)_3C$–C(3″,3‴)
34.1, 34.2	35.11, 35.13	$(CH_3)_3C$–C(5″,5‴)
35.2, 35.4	35.30, 35.32	$(CH_3)_3C$–C(3″,3‴)
42.0 (*d*, *J* = 6.0), 42.2 (*d*, *J* = 6.6)	43.7 (*d*, *J* = 5.9), 43.9 (*d*, *J* = 3.7)	C(4,4′)
51.6 (*d*, *J* = 13.5), 51.7 (*d*, *J* = 13.2)	53.5 (*d*, *J* = 5.9), 54.9 (*d*, *J* = 6.3)	$(CH_3)_3C$–N(3,3′)
67.6 (*d*, *J* = 8.4), 67.9 (*d*, *J* = 8.1)	62.4 (*d*, *J* = 2.4), 63.0 (*d*, *J* = 3.1)	C(5,5′)
123.3 (*d*, *J* = 0.6), 123.7 (*d*, *J* = 0.8)	124.0 (*d*, *J* = 1.2), 124.5 (*d*, *J* = 1.0)	C(4″,4‴)
129.0 (*d*, *J* = 5.0), 130.0 (*d*, *J* = 4.7)	130.6 (*d*, *J* = 1.6), 132.3 (*d*, *J* = 1.7)	C(6″,6‴)
130.8 (*dd*, *J* = 4.9, 3.8), 131.5 (*dd*, *J* = 4.7, 3.5)	133.0 (*dd*, *J* = 3.0, 0.9), 133.4 (*dd*, *J* = 3.0, 0.9)	C(1″,1‴)
138.2, 139.1	137.8 (*d*, *J* = 4.8), 140.3 (*d*, *J* = 6.2)	C(3″,3‴)
141.2, 141.8	143.6 (*d*, *J* = 1.8), 144.5 (*d*, *J* = 1.7)	C(5″,5‴)
150.40 (*dd*, *J* = 5.2, 1.8), 150.42 (*dd*, *J* = 5.1, 3.9)	147.0 (*dd*, *J* = 9.9, 0.7), 147.8 (*dd*, *J* = 14.6, 0.6)	C(2″,2‴)

In the ^{31}P-NMR spectrum of **7**, two *s* were observed at δ 68.0 and 70.2 that correspond to two nonequivalent uncoupled P-atoms. Although the possible effects due to rehybridization at the P-atom cannot be discounted, this observation strongly supports a coupling mechanism in which the lone electron pair on the P-atom is involved.

Chiral 1,3,2-Oxazaphospholidines. In order to address the question as to whether the configuration at the P-atom is important in the transmission of coupling information in **1a**, the synthesis of chiral analogues of **1a** was required. The synthesis of chiral oxazaphospholidines of both trivalent [12] and pentavalent [13] P starting from enantiomerically pure ephedrine, serine, or prolinol is known.

The reductive amination of (1*R*,2*S*)-norephredine (**8**) with isobutyraldehyde (**9**) and $NaBH_4$ gave the *N*-(2-methylpropyl)-substituted derivative (1*R*,2*S*)-**10** (81%, after column chromatography) [14] (*Scheme 2*). The phosphorochloridite (4*S*,5*R*)-**11** was prepared by the reaction of (1*R*,2*S*)-**10** with PCl_3 using Et_3N as an acid acceptor. In the

Scheme 2



(1R,2S)-**8** $R^1 = Me$, $R^2 = H$, $R^3 = Ph$, $R^4 = H$

(1S,2R)-**8** $R^1 = H$, $R^2 = Me$, $R^3 = H$, $R^4 = Ph$

10

(4S,5R)-**11** $R^1 = Me_2CHCH_2$, $R^2 = Me$, $R^3 = H$, $R^4 = Ph$, $R^5 = H$

(4R,5S)-**11** $R^1 = Me_2CHCH_2$, $R^2 = H$, $R^3 = Me$, $R^4 = H$, $R^5 = Ph$

13a $R^1 = t$-Bu, $R^2 = R^3 = R^4 = R^5 = H$

13b $R^1 = Me_2CHCH_2$, $R^2 = Me$, $R^3 = H$, $R^4 = Ph$, $R^5 = H$

(4S,5R)-**12** $R^1 = Me_2CHCH_2$, $R^2 = Me$, $R^3 = H$, $R^4 = Ph$, $R^5 = H$

(4R,5S)-**12** $R^1 = Me_2CHCH_2$, $R^2 = H$, $R^3 = Me$, $R^4 = H$, $R^5 = Ph$

^{31}P-NMR spectrum of (4*S*,5*R*)-**11**, a broad *s* was observed at δ 174, *i.e.* in the region expected for a phosphorochloridite [15]. Similarly, in the ^{1}H-NMR spectrum of (4*S*,5*R*)-**11**, several resonances appeared as broad *s*. The observed broadness of the resonances can be explained either by a ring-inversion process occurring near the NMR time scale (spectrum observed near the coalescence temperature) or that a small quantity of dissolved acidic impurity (HCl) is causing rapid epimerization (inversion of configuration at the P-atom). That the former explanation is correct is supported by the fact that the reaction of (4*S*,5*R*)-**11** with the dilithium biphenyldiolate **3a** gave a mixture of only two diastereoisomers (*vide infra*).

The bis[oxazaphospholidine] (4*S*,5*R*)-**12** was prepared as a diastereoisomeric mixture by the reaction of (4*S*,5*R*)-**11** with the dilithium biphenyldiolate **3b**. In the ^{31}P-NMR

spectrum of crude (4*S*,5*R*)-**12**, 2 *singlet* resonances at δ 136.1 (major) and 137.0 (minor) in a 2.3:1 ratio were consistent with a mixture of two diastereoisomers that differ in axial configuration, *i.e.*, (*R**,*R**,*R**)- and (*R**,*S**,*R**)-**12**[5][6]). An identical 2.3:1 diastereoisomeric ratio for crude (4*R*,5*S*)-**12** was determined, which was obtained by the reaction of (4*R*,5*S*)-**11** with the dilithium biphenyldiolate **3b**. Identical ratios are expected because (4*R*,5*S*)- and (4*S*,5*R*)-**12** bear enantiomeric relationships to one another. This interpretation is further substantiated by the fact that the major diastereoisomers of (4*R*,5*S*)- and (4*S*,5*R*)-**12** that can be isolated by recrystallization from MeOH/Et_2O have equal and opposite optical rotations (see *Exper. Part*).

In the ^{31}P-NMR spectrum of the major, isolated diastereoisomer of (4*R*,5*S*)-**12**, a *s* was observed at δ 136.1. In the ^{1}H-NMR spectrum taken immediately upon dissolution in (D_6)benzene, a *d* was observed at δ 5.00 that was assigned to the methine proton at C(5) of the oxazaphospholidine ring. Additionally, a *d* at δ 5.15 was assigned to the corresponding methine proton of the minor diastereoisomer. A major/minor diastereoisomer ratio of > 20:1 was determined by the integration of the corresponding peak areas in the

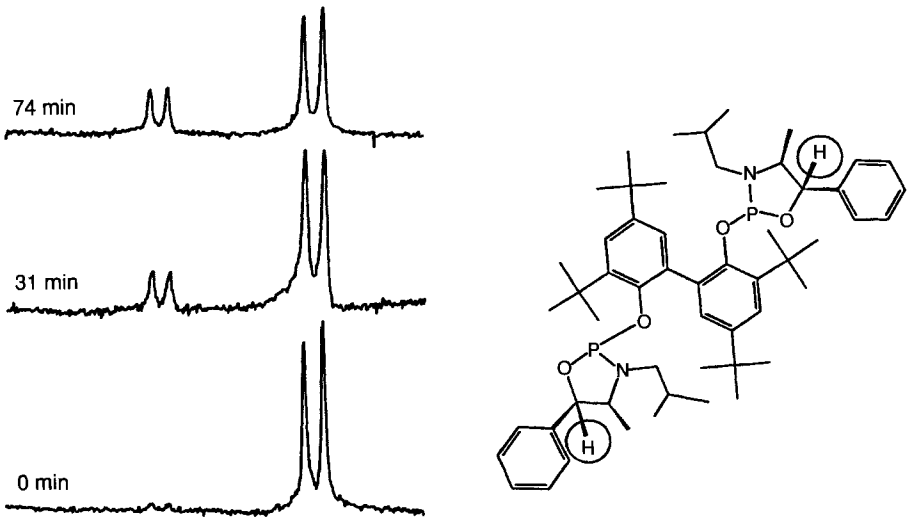


Fig. 2. *^{1}H-NMR Spectrum of (4*R*,5*S*)-***12*** as a function of time*

^{1}H-NMR spectrum. Monitoring the change in the ^{1}H-NMR spectrum with time (*Fig. 2*) led to a decrease in the major *d* at δ 5.00 with a corresponding increase in size of the minor *d* at δ 5.15. After 74 min, a 2:1 equilibrium ratio of diastereoisomers was obtained similar to that obtained by integration of the appropriate resonances of the ^{31}P-NMR spectrum of the crude reaction mixture (*vide supra*). These observations are reasonably

[5]) The diastereoisomeric ratio was determined by integration of the appropriate peak areas in the ^{31}P-NMR spectrum. Caution, however, must be exercised, because the relaxation times of nonequivalent P-atoms are often significantly different, see [16].

[6]) The convention for assignment of the configuration at the P-atoms and of the configuration given in *Footnote 1* is used; the absolute configuration of the C-atoms in the oxazaphospholidine ring is not indicated, because they are fixed and dependent upon the starting norephedrine (= 2-amino-1-phenylpropanol; **8**).

explained by the equilibration of the (*R*,R*,R**)- and (*R*,S*,R**)-**12** atropisomers. The process observed corresponds to the restricted rotation about the central single bond connecting the biphenyl system. The isolation of an atropisomer at room temperature *with only a single* ortho-*substituent on each aryl ring* is quite rare [17]. Aside from the large size of the substituted oxazaphospholidine rings, the buttressing effect of the *t*-Bu substituent *ortho* to the oxazaphospholidine ring no doubt plays a significant role [18]. The observed 2:1 ratio of diastereoisomers at equilibrium corresponds to a standard free energy difference ($\Delta G°$) of 0.4 kcal/mol between diastereoisomers. Furthermore, the observed 2:1 ratio of diastereoisomers in the crude reaction mixture reflects the thermodynamic equilibrium of the atropisomers rather than kinetic product control.

Strong evidence for the above explanation of the observation of (*R*,R*,R**)- and (*R*,S*,R**)-**12**, which differ only by the axial configuration due to hindered rotation about the single bond of the biphenyl system, is provided by the reaction of the dilithium biphenyldiolate **3b** with racemic phosphoramidite *rac*-**11** (prepared by mixing equimolar quantities of (4*S*,5*R*)- and (4*R*,5*S*)-**11**). In the ^{31}P-NMR spectrum of the product mixture, the 2 *s* observed previously at δ 136.1 and 137.0 were observed along with a new *AB* '*q*' at δ 135.9. The new *AB* system can reasonably be assigned to the nonequivalent P-atoms of (*R*,R*,S**)-**12** in which the configurations of the P-atoms are different. The observed ^{7}J(P,P) of 36 Hz is similar to that of **1a**. The absence of this diastereoisomer in the ^{31}P-NMR spectrum of the crude product of the reaction of either enantiomerically pure (4*S*,5*R*)- or (4*R*,5*S*)-**11** with **3b** provides further evidence that both (4*S*,5*R*)- and (4*R*,5*S*)-**11** are single diastereoisomers (*vide supra*).

The question remains as to whether seven-bond P,P coupling is occurring in the two diastereoisomers of **12** that possess NMR-equivalent homotopic P-atoms, *i.e.*, (*R*,R*,R**)- and (*R*,S*,R**)-**12** that contain a proper C_2 axis of rotation. This question was resolved by the examination of the ^{13}C-NMR spectrum of (4*R*,5*S*)-**12**. In the ^{13}C-

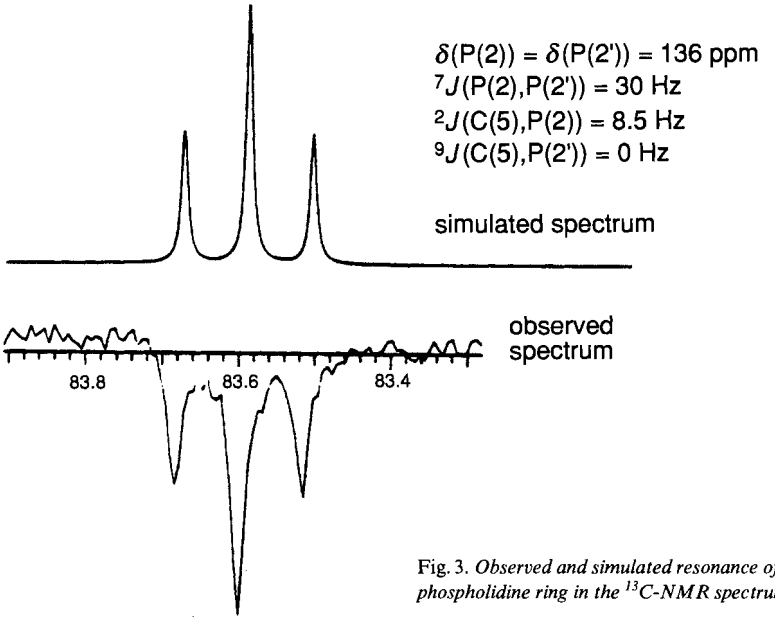


Fig. 3. *Observed and simulated resonance of C(5) of the oxazaphospholidine ring in the ^{13}C-NMR spectrum of (4S,5R)-***12**

NMR spectrum of (4*R*,5*S*)-**12**, a *m* (apparent *t*) was observed at δ 84.3 that was assigned to C(5) of the oxazaphospholidine ring. This observation is readily explained if C(5) is two-bond coupled to the oxazaphospholidine P-atom (^2J(C(5),P(2′)) = 8.5 Hz) that is further virtually coupled to the P-atom of the other oxazaphospholidine ring (^7J(P(2),P(2′)) = 30, ^9J(C(5),P(2′)) = 0 Hz; δ(P(2)) = δ(P(2′)) = 136 ppm). An alternate explanation for the observed *t* is ^2J(C(5),P(2)) and ^9J(C(5),P(2′)) being of equal magnitude, but this appears highly unlikely. The calculated spin-simulated spectrum, which assumed a J(P,P) of 30 Hz, was identical to that observed (*Fig. 3*). Quite interestingly, a *m* was observed at δ 83.9 for the minor diastereoisomer of **12** (*vide supra*). The observed *m* in the ^{13}C-NMR spectrum of the minor diastereoisomer of (4*R*,5*S*)-**12** is similarly explained by the fact that the P-atoms of each oxazaphospholidine ring are virtually coupled to each other with ^7J(P(2),P(2′)) = 30 Hz. As expected, identical observations were made in the ^{13}C-NMR spectrum of the enantiomeric (4*S*,5*R*)-**12**.

The above observations provide strong evidence that seven-bond P,P coupling occurs in all three diastereoisomers of **12**. *The observed P,P coupling is both independent of the configuration of the chirality axis and the configuration of the chiral P-centers.* This must be the case because P,P coupling was observed for all three diastereoisomers. This independence of P,P coupling upon the absolute configuration at the P-centers implies also the independence of the observed coupling upon the orientation of the lone electron pair on P *provided that the conformations of the diastereoisomers are similar in solution.* This suggests that the proposed through-space coupling mechanism may involve transmission of coupling information through the lone electron pair on either the O- or the N-atom similar to that proposed by *Goddard et al.* [10]. However, this supposition that the heteroatom lone electron pairs are involved in the transmission of coupling information remains speculative at present [10d].

X-Ray Crystal Structure. Sterically hindered trivalent P-ligands are capable of providing unique coordination spheres for transition-metal-mediated reactions. Indeed, sterically hindered dibenzo[*d,g*][1,3,2]dioxaphosphocines and dibenzo[*d,f*][1,3,2]dioxaphosphepines [19] have recently been claimed to be superior ligands in transition-metal-catalyzed hydroformylation reactions [20]. Particularly interesting is the design of sterically encumbered ligands to either impart kinetic stabilization to coordinately unsaturated complexes or to control the reactivity of metal complexes [21].

Quite recently, *Floriani* and coworkers reported the synthesis of metal complexes utilizing an interesting class of sterically hindered calixarenes functionalized with the

Table 2. *Crystal and Data Collection Parameters for* **13a**

Formula	$C_{40}H_{66}Cl_2N_2O_4P_2Pt$	d_{calc}	1.263 g·cm^{-3}
Formula weight (g·mol^{-1})	966.916	Crystal size	0.72 × 0.36 × 0.12 mm
Crystal system	monoclinic	Temp.	298 K
Space group	$P2_1/c$ (# 14) centro-symmetric	Diffractometer type	*Nonius CAD4*
		Radiation	Cu$K\alpha$ (λ = 1.5418 Å)
Z	4	Scan width	1.4°
Cell parameters	a = 20.683 (2) Å	No. of reflections measured	4773
	b = 17.850 (2) Å	No. of reflection used in	
	c = 14.109 (2) Å	analysis $I > 2\sigma(I)$	4036
	β = 102.63 (1) deg	Data range	4–116°
	V = 5083 Å^3	R	0.068

N-(*tert*-butyl)-1,3,2-oxazaphospholidine ring system [22]. In a preliminary communication, we reported the synthesis and spectral characterization of the first Pd^{II} and Pt^{II} complexes of **1a** [6]. As previously reported [6], the Pt^{II} complex **13a** was prepared by the reaction of **1a** with dichloro(cycloocta-1,5-diene)platinum(II). Based upon the small two-bond P,P coupling (^2J(P(2),P(2')) = 26.7 Hz) and large one-bond P,Pt couplings (^1J(P(2),Pt) = 5667.2 and ^1J(P(2'),Pt) = 5668.1 Hz) observed in the ^{31}P-NMR spectrum of **13a**, a *cis*-arrangement of the P-atoms was suggested [23] [24]. Upon attainment of suitable crystals by recrystallization from toluene/hexane, an X-ray structure of **13a** was obtained (*Table 2*) that confirmed the proposed *cis*-geometry of the P donor atoms (*Figs. 4* and *5*).

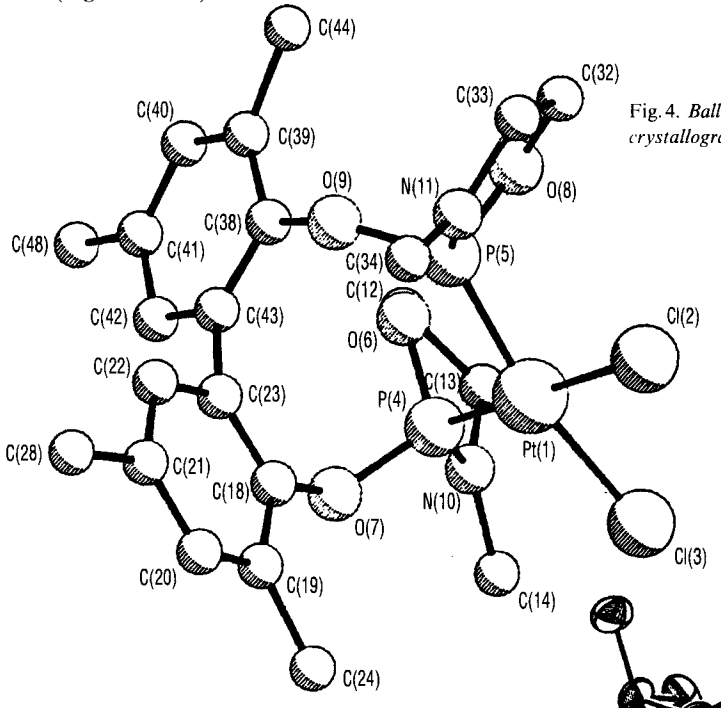


Fig. 4. *Ball and stick view of* **13a** *showing the crystallographic numbering scheme* (arbitrary)

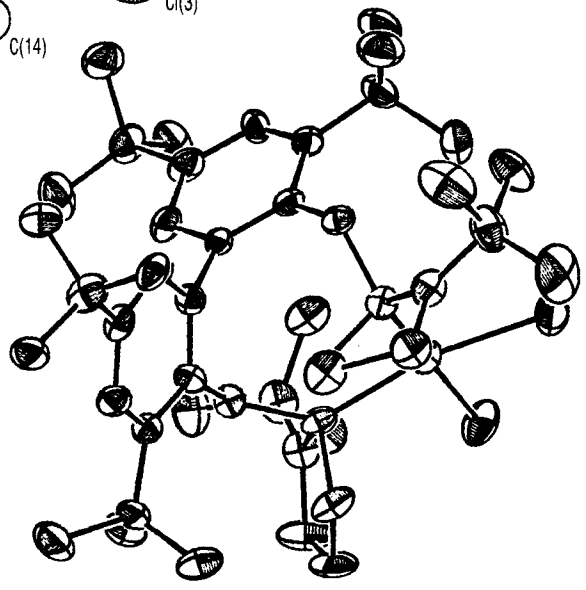


Fig. 5. *ORTEP view of* **13a**

The coordination sphere of the Pt-atom in **13a** is nearly planar as expected for a four-coordinate d^8 Pt^{II} complex [25]. The P(4), P(5), Cl(2), and Cl(3) atoms lie in a plane with the Pt-atom situated at a distance of 0.138 Å above this plane (for numbering, see *Fig. 4*). The distortion from planarity is pyramidal, which is in contrast to the often observed tetrahedral distortion in $[Pt^{II}Cl_2(PR_3)_2]$ compounds [26–28]. The angle between the planes comprising the atoms Cl(2)–Pt(1)–Cl(3) and P(4)–Pt(1)–P(5) is 10.2°. The observed Pt–Cl bond distances (d(Pt(1),Cl(2)) = 2.365(6) and d(Pt(1),Cl(3)) = 2.323(6) Å) are in the expected 2.305–2.376 Å region reported in the literature [29] (see *Table 3*). The observed P–Pt bond distances (d(Pt(1),P(4)) = 2.218(6) and d(Pt(1),P(5)) = 2.207(5) Å), which are known to be dependent on the steric bulk of the P-ligand [26] [29], is similarly found in the expected 2.141–2.295 Å region. The corresponding P(4)–Pt(1)–P(5) bond angle is 95.0° (*Table 4*).

The relative configuration of the oxazaphospholidine ligand in **13a** is *R*,R*,S**, which is the same as in the uncomplexed ligand **1a**. Quite interestingly, the two oxaza-

Table 3. *Selected Bond Distances* [Å] *for* **13a**

Pt(1)–Cl(2)	2.365 (6)	N(10)–C(13)	1.46 (3)	C(21)–C(28)	1.58 (3)	C(38)–C(43)	1.39 (3)
Pt(1)–Cl(3)	2.323 (6)	N(10)–C(14)	1.52 (3)	C(22)–C(23)	1.42 (3)	C(39)–C(40)	1.42 (3)
Pt(1)–P(4)	2.218 (6)	N(11)–C(33)	1.50 (3)	C(23)–C(43)	1.49 (2)	C(39)–C(44)	1.56 (3)
Pt(1)–P(5)	2.207 (5)	N(11)–C(34)	1.47 (3)	C(24)–C(25)	1.57 (3)	C(40)–C(41)	1.40 (3)
P(4)–O(6)	1.58 (1)	C(12)–C(13)	1.56 (3)	C(24)–C(26)	1.61 (3)	C(41)–C(42)	1.39 (2)
P(4)–O(7)	1.65 (1)	C(14)–C(15)	1.53 (4)	C(24)–C(27)	1.57 (4)	C(41)–C(48)	1.56 (3)
P(4)–N(10)	1.64 (2)	C(14)–C(16)	1.60 (4)	C(28)–C(29)	1.52 (3)	C(42)–C(43)	1.41 (3)
P(5)–O(8)	1.60 (1)	C(14)–C(17)	1.49 (4)	C(28)–C(30)	1.52 (4)	C(44)–C(45)	1.55 (3)
P(5)–O(9)	1.64 (1)	C(18)–C(19)	1.39 (2)	C(28)–C(31)	1.57 (4)	C(44)–C(46)	1.57 (3)
P(5)–N(11)	1.63 (2)	C(18)–C(23)	1.39 (2)	C(32)–C(33)	1.45 (4)	C(44)–C(47)	1.56 (3)
O(6)–C(12)	1.50 (3)	C(19)–C(20)	1.39 (3)	C(34)–C(35)	1.54 (3)	C(48)–C(49)	1.52 (4)
O(7)–C(18)	1.42 (2)	C(19)–C(24)	1.52 (3)	C(34)–C(36)	1.57 (3)	C(48)–C(50)	1.55 (4)
O(8)–C(32)	1.42 (3)	C(20)–C(21)	1.39 (3)	C(34)–C(37)	1.58 (3)	C(48)–C(51)	1.49 (4)
O(9)–C(38)	1.41 (2)	C(21)–C(22)	1.40 (3)	C(38)–C(39)	1.36 (2)		

Table 4. *Selected Bond Angles* [°] *for* **13a**

Cl(2)–Pt(1)–Cl(3)	85.9 (2)	Pt(1)–P(4)–N(10)	127.3 (6)	O(8)–P(5)–N(11)	94.9 (8)
Cl(2)–Pt(1)–P(4)	174.4 (2)	O(6)–P(4)–O(7)	110.7 (7)	O(9)–P(5)–N(11)	97.8 (7)
Cl(2)–Pt(1)–P(5)	86.4 (3)	O(6)–P(4)–N(10)	98.1 (7)	P(4)–N(10)–C(13)	110.0 (1)
Cl(3)–Pt(1)–P(4)	91.9 (2)	O(7)–P(4)–N(10)	104.1 (7)	P(4)–N(10)–C(14)	135.0 (1)
Cl(3)–Pt(1)–P(5)	168.7 (3)	Pt(1)–P(5)–O(8)	105.1 (5)	C(13)–N(10)–C(14)	115.0 (2)
P(4)–Pt(1)–P(5)	95.0 (2)	Pt(1)–P(5)–O(9)	129.2 (6)	P(5)–N(11)–C(33)	112.0 (1)
Pt(1)–P(4)–O(6)	102.8 (5)	Pt(1)–P(5)–N(11)	119.8 (5)	P(5)–N(11)–C(34)	127.0 (2)
Pt(1)–P(4)–O(7)	112.5 (4)	O(8)–P(5)–O(9)	104.0 (6)	C(33)–N(11)–C(34)	121.0 (2)

Table 5. *Selected Torsion Angles* [°] *for* **13a**

O(6)–P(4)–N(10)–Cl(3)	14.2 (1.4)	O(8)–P(5)–N(11)–C(33)	0.8 (1.5)
P(4)–N(10)–Cl(3)–Cl(2)	–31.3 (1.9)	P(5)–N(11)–C(33)–C(32)	–7.1 (2.2)
P(4)–O(6)–Cl(2)–Cl(3)	–27.9 (1.7)	P(5)–O(8)–C(32)–C(33)	–11.5 (2.4)
N(10)–P(4)–O(6)–Cl(2)	9.5 (1.3)	N(11)–P(5)–O(8)–C(32)	6.3 (1.6)
O(6)–Cl(2)–Cl(3)–N(10)	35.7 (2.0)	O(8)–C(32)–C(33)–N(11)	11.0 (2.5)

phospholidine rings in **13a** have different ring conformations in the solid-state structure. One five-membered oxazaphospholidine ring is in an envelope conformation with O(8)–P(5)–N(11)–C(33) lying in a plane and C(32) at a distance of 0.15 Å to this plane. The other five-membered ring exists in a twist conformation with C(12) lying 0.23 Å below and C(13) lying 0.34 Å over the plane defined by P(4)–O(6)–N(10). The sum of the absolute values of the torsion angles, which is indicative of the degree of ring pucking for a particular conformation [30], for the envelope ($\Sigma|\omega| = 36.7°$) and twist ($\Sigma|\omega| = 118.6°$) are significantly different (*Table 5*). The torsion angle defined by the planes of the aryl rings is 79°, which is considerably smaller than the 100.2° found in the free ligand [3]. Given the posit that trigonal-planar geometry is achieved when the sum of the bond angles exceeds 355° [31], the N-atoms in both oxazaphospholidine rings approach planarity. A similar planar geometry has been found in related five-membered ring systems containing a P-adjacent to an N-atom [32–34]. The sum of the bond angles about both P-atoms (297 and 311°) indicates a geometry intermediate between pyramidal and tetrahedral and is larger than that of the free ligand (*ca.* 292°). The observed geometry about both P-atoms suggests a significant amount of s character in the orbital containing the lone electron pair used in bonding to Pt^{II} that is consistent with the observed large J(P,Pt) (*vide supra*) [35]. The crystal packing in the unit cell is apparently determined by *van der Waals* contact, and no short intermolecular distances are observed (*Fig. 6*).

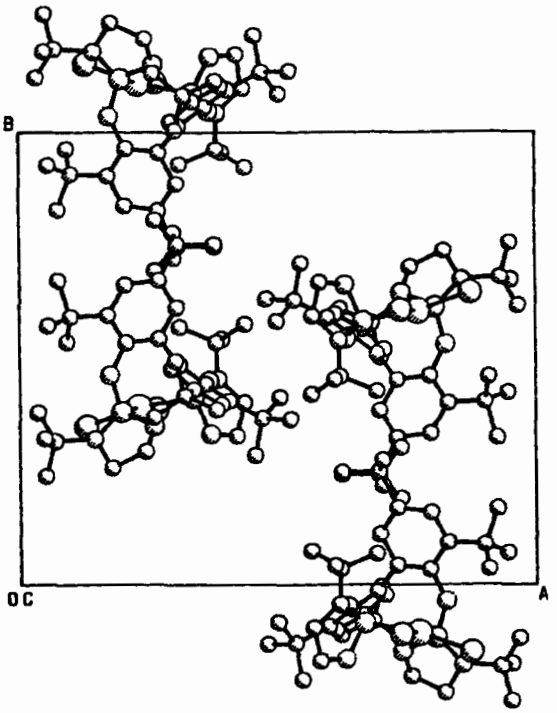


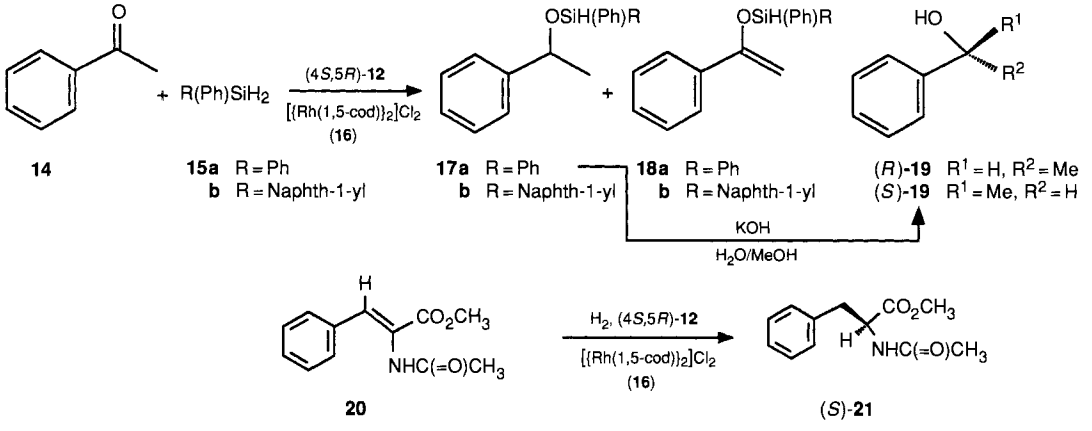
Fig. 6. *Projection along the crystallographic* c *axis showing the crystal packing of* **13a**

The chiral Pt^{II} complex **13b** was obtained by the reaction of the chiral oxazaphospholidine (4*S*,5*R*)-**12** with dichloro(1,5-cyclooctadiene)platinum(II). In the ^{31}P-NMR spectrum of **13b**, a *s* was observed at δ 76.7 with the corresponding ^{195}Pt satellites (^1J(P,Pt) = 5538.1 Hz). Although a crystal structure of **13b** was not obtained, the similarity of the ^1J(P,Pt) coupling constant to that observed for **13a** strongly suggests the *cis*-arrangement of the P-atoms of the ligand in **13b**.

Asymmetric Hydrosilylation and Hydrogenation. The crystal structure of **13a** suggests that the chiral analogues **12** would be useful as chiral auxiliaries in transition-metal-catalyzed reactions. The oxazaphospholidine P-atoms are coordinated in a *cis*-fashion to the Pt-atom with the biaryl system effectively shielding approach of any reagent from this direction. Both the stereogenic P- and C-atoms of both oxazaphospholidine rings would be in the vicinity of any reaction taking place in the coordination sphere of the metal, and a significant degree of asymmetric induction would be expected to occur.

Initially, the Rh(I)-catalyzed hydrosilylation of ketones was investigated [36] [37]. To an equimolar solution of acetphenone (**14**) and diphenylsilane (**15a**) in toluene were added 0.6 mol-% of an *in situ*-formed catalyst prepared from (cycloocta-1,5-diene)rhodium(I) chloride dimer **16** and the major enantiomerically pure diastereoisomer of (4*S*,5*R*)-**12** that was obtained by recrystallization. After 160 min, the reaction mixture consisted of

Scheme 3



(1-phenylethoxy)diphenylsilane (**17a**) silyl enol ether **18a** in a ratio of 4.6:1, as determined by GLC analysis. The formation of enol ethers during the hydrosilylation of **14** was previously noted by *Corriu* and *Moreau* [38]. Removal of the silyl group of **17a** with KOH in H_2O/MeOH gave (*S*)-phenethyl alcohol ((*S*)-**19**) in 9% enantiomeric exess (ee). The ee was determined after formation of a derivative with isopropyl isocyanate followed by GLC using a *Chirasil*-L-*Val* column. Quite interestingly, catalyzed hydrosilylation of **14** with (naphth-1-yl)phenylsilane (**15b**), which was previously shown by both *Kagan* and coworkers [39] and *Corriu* and *Moreau* [36a] to produce alcohols in better optical yield than trisubstituted silanes, gave the alcohol (*R*)-**19**, of opposite absolute configuration in 15.8% ee.

The change in absolute configuration of **19** produced by the hydrosilylation of **14** with **15a** and **15b** may be due to the fact that in the case of hydrosilylation with **15b**, two stereogenic atoms are produced, *i.e.*, the alcohol C-atom and the Si-atom. In this case, additional pertubations upon the stereoselective formation of the transition-state structure are expected in addition to that caused by the chiral ligand (double stereodifferentiation [40]). Caution must be observed with this interpretation, however, because time-dependent ^{1}H-NMR studies on (4*R*,5*S*)-**12** suggest that **12** may not remain enantiomerically pure during the catalyst preparation due to equilibration on the (*R**,*R**,*R**)-**12** and (*R**,*S**,*R**)-**12** atropisomers. Further studies that both fully characterize catalysts made from **12** and examine their stability in solution are needed.

The enantioselective reduction of α,β-unsaturated α-amino acids has been extensively studied, and over one hundred examples of this reduction have been reported in the literatur [41]. Mechanistic studies, notably those of *Halpern* [42], have investigated the structure of the various intermediates involved in the Rh^I-catalyzed hydrogenation of α-acetamidocinnamic acid. We now hydrogenated methyl α-acetamidocinnamate (**20**) in EtOH in the presence of 0.5 mol-% of a catalyst solution prepared from **16** and the major diastereoisomer of (4*S*,5*R*)-**12**. Methyl (*S*)-*N*-acetylphenylalaninate (**21**) was isolated in 40.4% ee, albeit the conversion of the starting material was low (29%) due to deactivation of the catalyst during the reaction by an unidentified mechanism. Although the ee's obtained using **12** as a chiral ligand are low, both the optimization of the reaction conditions in the present systems and exploration of other transition-metal-catalyzed reactions are expected to yield fruitful results. Notably, a higher ee was obtained using **12** as a ligand compared to less sterically demanding bis[dioxaphospholane] ligands studied by *Wink et al.* [43]. These authors suggested a more crowded environment at the metal as one factor for improvement of the chiral induction.

Experimental Part

General. Reagents were purchased from commercial laboratory-supply houses. Solvents were dried prior to use. Tetrahydrofuran (THF), Et_2O, toluene, and benzene were distilled prior to use from a deep-blue soln. of sodium ketyl under N_2. Reactions were carried out in dried apparatus under Ar using standard inert atmosphere and *Schlenk* techniques. GLC: 50-m *Chirasil*-L-*Val* column on *Carlo-Erba-HRGC-5300* GLC. Column chromatography (CC): *Woelm* alumina *N* (act. IV), *ICN Biomedicals* alumina *N* (act. I), and *Merck* silica gel *60* (70–230 mesh). Flash chromatography (FC) [44]: *Merck 9385* silica gel *60* (200–400 mesh). Prep. HPLC: *Waters-PREP-500A* HPLC. M.p.: open capillary tubes; uncorrected. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra: *Bruker-300-FT* or *Varian-XL-200-FT* NMR spectrometer; ^{31}P-NMR were obtained with full ^{1}H decoupling; δ in ppm relative to tetramethylsilane (^{1}H) or 85% H_3PO_4 (external; ^{31}P) where a positive sign is downfield from the standard, *J* in Hz. Elemental analyses were performed by Analytical Research Services, *Ciba-Geigy Corp.*

2-Chloro-3-methyl-1,3,2-oxazaphospholidine (**4b**). To a soln. of 13.8 g (0.1 mol) of PCl_3 in 150 ml of CH_2Cl_2 cooled with an acetone/dry-ice bath to −60° was added dropwise within 15 min a soln. of 7.5 g (0.1 mol) of 2-(methylamino)ethanol and 20.24 g (2.0 mol) of Et_3N in 50 ml of CH_2Cl_2. The mixture was warmed to r.t., then heated at reflux for 2 h, and stirred 18 h at r.t. After removal of the solids by filtration, the solvent was evaporated, the residue dissolved in 250 ml of toluene, the mixture filtered through a bed of *Celite*, the solvent evaporated, and the residue distilled: 3.92 g (28%). Colorless liquid. B.p. 62°/10 Torr. ^{1}H-NMR ($CDCl_3$): 2.77 (*d*, $^3J(CH_3,P) = 17.5$, MeN); 3.19 (*m*, 2 H–C(4)); 4.49 (br. *m*, 2 H–C(5)). ^{31}P-NMR ($CDCl_3$): 170.0. MS: 139, 141 ($M^{+\cdot}$). Anal. calc. for C_3H_7ClNOP: C 25.83, H 5.06, N 10.04; found: C 25.72, H 5.05, N 9.96.

3,3′-Dimethyl-2,2′-{[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diyl]bis(oxy)}bis[1,3,2-oxazaphospholidine] (**1b**). Modification of the original procedure using NaH [3]: To a soln. prepared from 13.8 ml (22 mmol) of 1.6M BuLi in hexanes and 50 ml of Et_2O was added dropwise a soln. of 4.10 g (10 mmol) of 3,3′,5,5′-

tetra(*tert*-butyl)-1,1′-biphenyl-2,2′-diol in 40 ml of THF at a rate that maintained the reaction temp. between 25 and 30°. The mixture was heated at 30° for 1 h. To the cooled mixture at 0–5° was added dropwise a soln. of 3.07 g (22 mmol) of **4b** in 10 ml of Et_2O. The mixture was stirred for 40 h at r.t., and then the turbid mixture was filtered through *Hyflo*. The residue was triturated twice with 100 ml of MeOH to give 2.95 g (48%) of a white crystalline solid. M.p. 161.5–162.5°. ^{1}H-NMR ($CDCl_3$): 1.27, 1.29, 1.32, 1.33 (4 *s*, 18 H, *t*-Bu); 1.41, 1.43, 1.44 (3 *s*, 18 H, *t*-Bu); 1.93, 1.97 (2 *d*, 3 H, MeN); 2.20, 2.22 (2 *d*, 3 H, MeN); 2.87 (complex *m*, 2 H); 3.07 (complex *m*, 2 H); 4.08 (complex *m*, 2.5 H); 4.36 (complex *m*, 1.5 H); 6.96 (*d*, 0.5 H); 7.05 (*d*, 0.5 H); 7.15 (*d*, 0.5 H); 7.23 (*d*, 0.5 H); 7.38 (complex *m*, 2 H); the total integration of the individual peak areas was consistent with a diastereoisomer mixture. ^{31}P-NMR ($CDCl_3$): 131.4 (*d*, upfield half of *AB* '*q*', ^7J(P,P) = 17.1); 135.0 (*d*, downfield half of *AB* '*q*'); 132.9 (*s*); 134.0 (*s*). Anal. calc. for $C_{34}H_{54}N_2O_4P_2$: C 66.21, H 8.82, N 4.54, P 10.04; found: C 66.25, H 8.86, N 4.55, P 10.15.

3,3′-Bis(1,1-dimethylethyl)-2,2′-{[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diyl]bis(oxy)}bis-[1,3,2-oxazaphospholidine] (**1a**). As described for **1b**, **1a** was prepared from 17.2 ml (27.5 mmol) of 1.6M BuLi in hexanes, 5.13 g (12.5 mmol) of 3,3′,5,5′-tetra(*tert*-butyl)-1,1′-biphenyl-2,2′-diol, and 4.99 g (27.5 mmol) of **4a** in 60 ml of Et_2O (18 h at r.t.). The residue was recrystallized twice from MeOH: 5.40 g (62%) of white crystalline solid. M.p. 179–181°. Identical in every respect to compound previously reported [3].

3,3′-Bis(1,1-dimethylethyl)-2,2′-{[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diyl]bis(oxy)}bis-[1,3,2-oxazaphospholidine]-2,2′-dithione (7). A soln. of 2.0 g (2.9 mmol) of (**1a**) and 0.2 g (6.3 mmol) of sulfur in 15 ml of chlorobenzene was heated at 80° under N_2. After 15 h, the reaction was complete (TLC: no starting material left). The solvent was evaporated and the residue recrystallized from 15 ml of heptane: 1.7 g (77%) of a white solid. M.p. 182–185°. ^{1}H-NMR (200 MHz, (D_6)benzene): 1.48, 1.49, 1.52, 1.54 (4 *s*, 36 H, *t*-Bu); 1.83, 1.95 (2 *s*, 18 H, *t*-BuN); 2.75 (complex *m*, 4 H); 3.50 (complex *m*, 3 H); 4.14 (complex *m*, 1 H); 7.58 (*d*, 1 H); 7.78 (*dd*, 1 H); 7.82 (*dd*, 1 H); 7.98 (*d*, 1 H). ^{31}P-NMR ((D_6)benzene): 68.0, 70.2. Anal. calc. for $C_{40}H_{66}N_2O_4P_2S_2$: C 62.8, H 8.7, N 3.7; found: C 62.8, H 8.9, N 3.8.

(−)-(1R,2S)-2-[(2-Methylpropyl)amino]-1-phenylpropanol ((1*R*,2*S*)-**10**). To a soln. of 15.12 g (0.1 mol) of (−)-(1*R*,2*S*)-norephedrine in 100 ml of benzene were added 9.1 ml (0.1 mol) of isobutyraldehyde. The mixture was heated at reflux for 15 min and then evaporated. The viscous liquid in 60 ml of MeOH and 5 ml of H_2O was treated with 2.0 g (53 mmol) of $NaBH_4$ portionwise within 15 min. The mixture was stirred for 2 h at r.t. and then evaporated. The resultant residue was dissolved in H_2O, the aq. soln. extracted with Et_2O (3 × 50 ml), the combined Et_2O extract dried ($MgSO_4$) and evaporated, and the residue purified by CC (180 g of silica gel, Et_2O): 16.7 g (81%) of a white crystalline solid. M.p. 36.8–37.5°. $[\alpha]_D^{22} = -9.65$ ($c = 0.508$, $CHCl_3$). IR (CCl_4): 3600, 3430 (OH, NH). ^{1}H-NMR ($CDCl_3$): 0.80 (*d*, Me); 0.94 (overlapping *d*, $(CH_3)_2CHCH_2$); 1.72 (*m*, $(CH_3)_2CHCH_2$); 2.45, (*dd*, 1 H, $(CH_3)_2CHCH_2$); 2.57 (*dd*, 1 H, $(CH_3)_2CHCH_2$); 2.89 (*dq*, H–C(2)); 3.91 (br. *s*, NH, OH); 4.73 (*d*, H–C(1)); 7.30 (complex *m*, Ph). Anal. calc. for $C_{13}H_{21}NO$: C 75.32, H 10.21, N 6.76; found: C 75.23, H 10.23, N 6.85.

(+)-(1S,2R)-2-[(2-Methylpropyl)amino]-1-phenylpropanol ((1*S*,2*R*)-**10**). As described for (1*R*,2*S*)-**10**, (1*S*,2*R*)-**10** was prepared from 15.12 g (0.1 mol) of (+)-(1*S*,2*R*)-norephedrine, 9.1 ml (0.1 mol) of isobutyraldehyde in 100 ml of toluene, and 2.0 g (53 mmol) of $NaBH_4$ 60 ml of MeOH and 5 ml of H_2O. The residue was purified by CC (180 g of silica gel, MeOH/CH_2Cl_2): 15.81 g (76%) of a white crystalline solid. M.p. 41–44°. Identical spectral properties to (1*R*,2*S*)-**10**.

(4S,5R)-2-Chloro-4-methyl-3-(2-methylpropyl)-5-phenyl-1,3,2-oxazaphospholidine ((4*S*,5*R*)-**11**). As described for **4b**, (4*S*,5*R*)-**11** was prepared from 10.88 g (79 mmol) of PCl_3, 16.40 g (79 mmol) of (1*R*,2*S*)-**10**, and 15.96 g (2.0 mol) of Et_3N in 200 ml of CH_2Cl_2 (1 h at reflux temp.). The residue was purified by distillation: 18.34 g (86%) of a colorless liquid. B.p. 125–128°/0.05 Torr. $[\alpha]_D^{22} = -56.54$ ($c = 1.873$, $CHCl_3$). IR (CCl_4): 985 (POC, stretch). ^{1}H-NMR ($CDCl_3$): 0.71 (br. *m*, Me); 1.01 (overlapping *d*, $(CH_3)_2CHCH_2$); 2.00 (*m*, $(CH_3)_2CHCH_2$); 2.76 (br. *m*, 1 H, $(CH_3)_2CHCH_2$); 2.92 (*m*, 1 H, $(CH_3)_2CHCH_2$); 3.72 (*m*, H–C(4)); 5.88 (br. *m*, H–C(5)); 7.35 (complex *m*, Ph). ^{31}P-NMR ($CDCl_3$): 174.0. Anal. calc. for $C_{13}H_{19}ClNOP$: C 57.46, H 7.05, N 5.16; found: C 56.71, H 7.20, N 5.29 (no correct analysis for C was obtained, but all spectral properties were fully consistent with the structure proposed).

(4R,5S)-2-Chloro-4-methyl-3-(2-methylpropyl)-5-phenyl-1,3,2-oxazaphospholidine ((4*R*,5*S*)-**11**). As described for **4b**, (4*R*,5*S*)-**11** was prepared from 10.07 g (73 mmol) of PCl_3, 15.20 g (73 mmol) of (1*S*,2*R*)-**10**, and 14.8 g (150 mmol) of Et_3N in 200 ml of CH_2Cl_2 (1 h at reflux temp.). The residue was purified by distillation: 7.54 g (40%) of colorless liquid. B.p. 135–137°/0.1 Torr. Identical spectral properties to (4*S*,5*R*)-**11**.

(4S,4′S,5R,5′R)-4,4′-Dimethyl-3,3′-bis(2-methylpropyl)-5,5′-diphenyl-2,2′-{[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diyl]bis(oxy)}bis[1,3,2-oxazaphospholidine] ((4*S*,5*R*)-**12**). As described for **1b**, (4*S*,5*R*)-**12** was prepared from 17.4 g (64 mmol) of (4*S*,5*R*)-**11**, 11.89 g (29 mmol) of 3,3′,5,5′-tetra(*tert*-butyl)-1,1′-biphenyl-2,2′-diol, 40 ml (64 mmol) of 1.6M BuLi in hexanes, and 100 ml of Et_2O. The residue was triturated with MeOH followed by two recrystallizations from Et_2O/MeOH: 11.24 g (44%) of a white crystalline solid. M.p.

147.5–148.5°. $[\alpha]_D^{22} = +191.45$ ($c = 1.06$, CH_2Cl_2). IR (KBr): 980 (POC, stretch). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.47 (*d*, 6 H CH_3–C(4,4′)); 0.83 (overlapping *d*, 2 $(CH_3)_2CHCH_2$); 1.24 (*s*, 18 H, *t*-Bu); 1.42 (*s*, 18 H, *t*-Bu); 1.73 (*m*, 2 $(CH_3)_2CHCH_2$); 2.39 (*m*, 2 H, 2 $(CH_3)_2CHCH_2$ (*A*)); 2.83 (*m*, 2 H, 2 $(CH_3)_2CHCH_2$ (*B*); 3.62 (*dq*, 2 H, H–C(4,4′)); 4.83 (*d*, 2 H, H–C(5,5′)); 7.06 (*m*, 4 arom. H). ^{13}C-NMR (diastereoisomer in (D_6)benzene, 50 MHz; assignments of selected C's from APT and DEPT experiments; second-order spectrum because of virtual coupling to P, therefore, the observed multiplicity is reported): major isomer: 16.1 (*t*), 20.7 (*t*), 21.0 (*t*), 29.4 (*t*), 31.4 (*t*), 31.7, 35.9, 39.5, 51.3 (*t*), 57.4 (*t*), 84.3 (*t*, C(5) of oxazaphospholidine ring), 123.7, 127.3, 127.6, 127.9, 129.2 (*t*), 134.6 (*t*), 139.4 (*t*), 140.4 (*t*); minor isomer: 15.4 (*t*), 20.6 (*t*), 21.0 (*t*), 28.9 (*t*), 31.2 (*t*), 31.8, 35.8, 39.5, 50.8 (*t*), 57.3 (*t*), 83.9 (*t*, C(5) of oxazaphospholidine ring), 124.0, 127.3, 127.6, 127.9, 129.5 (*t*), 133.6 (*t*), 139.1 (*t*), 140.0 (*t*), 143.0, 150.7 (*t*). ^{31}P-NMR ($CDCl_3$): 135.6. Anal. calc. for $C_{54}H_{78}N_2O_4P_2$: C 73.61, H 8.92, N 3.18, P 7.03; found: C 73.36, H 8.86, N 3.30, P 7.05.

(4R,4′R,5S,5′S)-4,4′-Dimethyl-3,3′-bis(2-methylpropyl)-5,5′-diphenyl-2,2′-{[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diyl]bis(oxy)}bis[1,3,2-oxazaphospholidine] ((4*R*,5*S*)-**12**). As described for **1b**, (4*R*,5*S*)-**12** was prepared from 2.72 g (10 mmol) of (4*R*,5*S*)-**11**, 2.05 g (5 mmol) of 3,3′,5,5′-tetra(*tert*-butyl)-1,1′-biphenyl-2,2′-diol, 4 ml (10 mmol) of 2.5M BuLi in hexanes, and 25 ml of THF. The residue was triturated with 20 ml of MeCN followed by recrystallization from Et_2O/MeOH: 0.63 g (14%) of a white crystalline solid. M.p. 147–149°. $[\alpha]_D^{22} = -191.99$ ($c = 1.04$, CH_2Cl_2). ^{31}P-NMR, ^{13}C-NMR, and ^{1}H-NMR: identical to those of (4*S*,5*R*)-**12**. Anal. calc. for $C_{54}H_{78}N_2O_4P_2$: C 73.61, H 8.92, N 3.18; found: C 73.6, H 8.8, N 3.2.

*^{1}H-NMR Equilibration Experiment for (4R,5S)-***12**. A 50 mg sample of (4*R*,5*S*)-**12** was dissolved into 0.5 ml of (D_6)benzene. After dissolution, the ^{1}H-NMR was obtained immediately on a *Jeol-FX-90-Q* spectrometer (90 MHz) at a probe temp. of 26°. The *d*'s at 5.00 and 5.15 were monitored as a function of time (*Fig. 2*).

Dichloro{(4S,4′S,5R,5′R)-4,4′-dimethyl-3,3′-bis(2-methylpropyl)-5,5′-diphenyl-2,2′-{[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diyl]bis(oxy)}bis[1,3,2-oxazaphospholidine]}platinum(II) (**13b**). To a mixture of 440 mg (0.5 mmol) of (4*S*,5*R*)-**12** and 190 mg (0.5 mmol) of dichloro(cycloocta-1,5-diene)platinum(II) cooled with an ice-bath were added dropwise 5 ml of benzene. The mixture was allowed to warm to r.t. and the heterogeneous mixture stirred at r.t. for 72 h (→homogeneous). The solvent was evaporated and the residue triturated with hexane (3 × 5 ml): 550 mg (96%) of white powder. M.p. 230–233° (sealed tube *in vacuo*). $[\alpha]_D^{22} = -205.35$ ($c = 0.748$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.67 (*d*, 6 H, CH_3–C(4,4′)); 0.89 (*s*, 18 H, *t*-Bu); 0.95 (*d*, 6 H, $(CH_3)_2CHCH_2$); 1.02 (*d*, 6 H, $(CH_3)_2CHCH_2$); 1.60 (*s*, 18 H, *t*-Bu); 2.00 (*m*, 2 H, $(CH_3)_2CHCH_2$); 3.46 (*m*, 2 H, H–C(4,4′)); 3.69 (*m*, 4 H, $(CH_3)_2CHCH_2$); 4.98 (*d*, 2 H, H–C(5,5′)); 6.85 (*d*, 2 H); 7.03 (*m*, 6 H); 7.31 (*m*, 6 H). ^{31}P-NMR ($CDCl_3$): 76.7 (^1J(P,Pt) = 5538.1); ^{195}Pt satellites observed at 54.0 (*s*), 99.5 (*s*). Anal. calc. for $C_{54}H_{78}Cl_2N_2O_4P_2Pt$: C 56.54, H 6.85, N 2.44; found: C 56.83, H 6.77, N 2.37.

Asymmetric Hydrosilylation Reactions. a) *Diphenylsilane.* To a soln. of 1.17 ml (10 mmol) of **14**, 1.86 ml (10 mmol) of **15a**, and 0.5 ml of dodecane (internal standard) in 11 ml of toluene were added 3 ml of a deep-red soln. prepared separately by mixing 15 mg (0.0609 mmol) of **16** and 64 mg (0.0726) of the major diastereoisomer of (4*S*,5*R*)-**12** in 10 ml of toluene. The color of the mixture slowly changed to yellow within 2 min during which time the temp. rose to 40°, and a relatively strong evolution of gas began. After 160 min, the mixture contained 78% of **17a** and 17% of **18a** (GLC analysis). To this mixture was added a mixture of 5 ml of aq. 2N KOH and 7 ml of MeOH. The mixture was extracted with Et_2O (3 × 3 ml), the combined Et_2O extract dried ($MgSO_4$), the solvent evaporated, and the residue dissolved in hexane. A precipitate that formed was removed by filtration and then the solvent evaporated. The ee of the (*S*)-**19** formed (9%) was determined by GLC (*Chirasil*-L-*Val*, 50 m), after formation of a derivative with 2-propyl isocyanate, by comparison of retention times to authentic samples prepared from both (*R*)- and (*S*)-**19**.

b) *(Naphth-1-yl)phenylsilane.* The procedure used for hydrosilylation with **15a** was repeated using 1.17 ml (10 mmol) of **14**, 2.31 g (10 mmol) of **15b**, 0.5 ml of dodecane (internal standard), 3 ml of the catalyst soln. as prepared above, and 11 ml of toluene. After 220 min (*ca.* 90% conversion), the mixture contained 71.5% of **17b** and 7.5% of **18b**. After hydrolysis and formation of the derivative with 2-propyl isocyanate, the ee of the (*R*)-**19** obtained was 15.8%, as determined by GLC (*Chirasil*-L-*Val* column).

Asymmetric Hydrogenation. To a soln. of 550 mg (2.5 mmol) of **20** in 20 ml of EtOH were added 2 ml of catalyst soln. prepared as above. The reaction vessel (*Schlenk* tube) was evacuated and filled with H_2 3 times. The resultant mixture was stirred under H_2 at 1 atm/r.t. for 16.7 h (29% conversion). The solvent was evaporated and the ee of the (*S*)-**21** formed was 40.4% as determined by GLC (*Chirasil*-L-*Val* column).

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