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Article

Synthesis and Resolution of (*R**,*R**)-(±)-1,1,4,7,10,10-Hexaphenyl-1,10-diarsa-4,7-diphosphadecane: New Ligand for the Stereoselective Self-Assembly of Dicopper(I), Disilver(I), and Digold(I) Helicates

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Diphenylvinylarsine oxide reacts with 1,2-bis(phenylphosphino)ethane in the presence of potassium *tert*-butoxide to give the anti-Markovnikov product (*R**,*R**)-(±)/(*R**,*S**)-1,1,4,7,10,10-hexaphenyl-1,10-diarsa-4,7-diphosphadecane dioxide-1*AsO*,10*AsO*, which, upon reduction with $HSiCl_3/NEt_3$ in boiling acetonitrile, affords in 84% overall yield the di(tertiary arsine)–di(tertiary phosphine) (*R**,*R**)-(±)/(*R**,*S**)-diphars. After separation of the diastereomers by fractional crystallization, the (*R**,*R**)-(±) form of the ligand was resolved by metal complexation with (+)-di(μ-chloro)bis[(*R*)-1-[1-(dimethylamino)ethyl]-2-phenyl-C^2,*N*]dipalladium(II): (*R*,*R*)-diphars, mp 87–88 °C, has $[\alpha]_D^{21} = -18.6$ (*c* 1.0, CH_2Cl_2); (*S*,*S*)-diphars has $[\alpha]_D^{21} = +18.4$ (*c* 1.0, CH_2Cl_2). The crystal and molecular structures of the complexes (*M*)-$[M_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$ (M = Cu, Ag, Au) have been determined: $[M\text{-}(S_{Cu},S_{Cu})]$-(–)-$[Cu_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 16.084(3)$ Å, $b = 18.376(3)$ Å, $c = 29.149(6)$ Å, $Z = 4$; $[M\text{-}(S_{Ag},S_{Ag})]$-(+)-$[Ag_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$, triclinic, $P1$, $a = 12.487(2)$ Å, $b = 12.695(4)$ Å, $c = 27.243(4)$ Å, $\alpha = 92.06°$, $\beta = 95.19°$, $\gamma = 98.23°$, $Z = 2$; $[M\text{-}(S_{Au},S_{Au})]$-(–)-$[Au_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 16.199(4)$ Å, $b = 18.373(4)$ Å, $c = 29.347(2)$ Å, $Z = 4$. In the copper(I) and gold(I) helicates, each ligand strand completes 1.5 turns of an *M* helix in a parallel arrangement about the two chiral MAs_2P_2 stereocenters of *S* configuration. The unit cell of the silver(I) complex contains one molecule each of the parallel helicate of *M* configuration and the conformationally related double α-helix of *M* configuration in which each ligand strand completes 0.5 turns of an *M* helix about two metal stereocenters of *S* configuration. Energy minimization calculations of the three structures with use of the program SPARTAN 5.0 gave results that were in close agreement with the core structures observed.

Introduction

A variety of double-stranded di- and oligonuclear metal helicates and other interesting structural motifs is now available through self-assembly of semirigid oligo-2,2′-bipyridines and related ligands with kinetically labile metal ions, such as univalent copper and silver.[1−5] Geometric constraints within these ligands, especially when partially coordinated, induce helicate formation with metal ions disposed to tetrahedral coordination. Freely flexible ligands of the type L−L′−L′−L containing aliphatic carbon or aliphatic carbon−ether backbones and prochiral (ether, thioether) or chiral (amine, phosphine, arsine) donor stereocenters, however, can generate both chiral (R_M*,R_M*)-(±) or achiral (R_M*,S_M*) diastereomers of helicates of the type $M_2(L{-}L'{-}L'{-}L)_2$, depending upon whether the helicities of the two newly created metal stereocenters are the same (chiral) or opposite (achiral), respectively.[6] Tetrahedral complexes of the type

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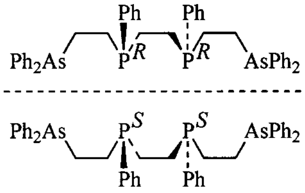
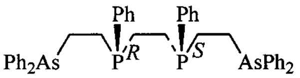
(6) For tetrahedral spiro stereocenters of the type M(L−L′)$_2$, *Chemical Abstracts* indexing practice is to assign the Cahn−Ingold−Prelog (CIP) descriptors *R* or *S*.[7]

10.1021/ic010988d CCC: $22.00

$[M(diphos)_2]^+$ and $[M(phars)_2]^+$ (M = Cu(I), Ag(I), Au(I)) undergo rapid rearrangements between diastereomers, with redistribution rates increasing in the order gold(I) < copper(I) < silver(I); metal stereocenter inversion rates decrease in the order copper(I) > gold(I) > silver(I).[8] Chiral MP_4 and MAs_2P_2 groups of these types are therefore suitable for thermodynamic self-assembly of di- and oligonuclear metal helicates and other interesting structural motifs. Asymmetric induction in helicates of semirigid ligands was achieved first by incorporation of enantiopure α-methyl-2-pyridylmethanol spacer groups within the helicating ligand,[9] and similar approaches have since furnished additional examples of enantioselective syntheses of double- and triple-stranded di- and oligonuclear metal helicates.[2-4] For fully flexible ligands, the ability to separate or resolve diastereomers of the type $(R_M{}^*,R_M{}^*)$-(±)/$(R_M{}^*,S_M{}^*)$-$[M_2(L-L'-L'-L)_2]$ will depend on the configurational stabilities of the donor stereocenters (if present) and the strengths of the two types of metal−donor atom bonds, M−L and M−L′, the making and breaking of which provide intra- and intermolecular routes to interconversions between diastereomers and racemization. Recent work in our laboratory has shown that the stereoselective self-assembly of double-stranded dinuclear helicates of the type (*M*)-$[M_2(tetraphos)_2](PF_6)_2$ (M = Ag(I) and Au(I)) can be achieved with the highly flexible tetra(tertiary phosphine) (*S*,*S*)-$Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$, (*S*,*S*)-tetraphos.[10] In these complexes, two molecules of the (*S*,*S*) ligand bind stereospecifically to two metal ions to give dinuclear metal helicates of *M* helicity,[2-4,11] in which each metal stereocenter has the *S* configuration.[6] The silver complex crystallizes with one molecule each of the double α-helix conformer and the parallel helix conformer of the double-stranded helicate in the unit cell; crystals of the gold complex contain only the parallel helix form. For copper(I), the mononuclear metal complex (*S*)-(+)-[Cu{(*R*,*R*)-tetraphos}]PF_6 was isolated.[10] For double-stranded dinuclear metal complexes containing symmetrical ligands, the side-by-side or parallel arrangement of the ligand strands about the tetrahedral metal stereocenters produces an achiral complex containing a σ plane in which the metal configurations are *R* and *S*: this arrangement has been referred to as side-by-side helicate.[2] When the ligand strands themselves are chiral and enantiomerically pure, as in the conformationally labile D_2 complexes $[M_2\{R,R)\text{-tetraphos}\}_2](PF_6)_2$ (M = Ag(I), Au(I)),[9] both double α-helix and side-by-side helix conformers are possible: we refer henceforth to the latter as parallel helicates to distinguish them from the achiral side-by-side helicates derived from achiral ligands. The parallel helicate is the structural motif of certain proteins, where two polypeptide α-helices are held together by hydrogen bonding in a parallel arrangement.[12] Here, we report the syntheses and crystal and molecular structures of the complexes [*M*-(S_M,S_M)]-$[M_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$ (M = Cu(I), Ag(I), Au(I)), where (*R*,*R*)-diphars is the coordinated form of (*S*,*S*)-$Ph_2AsCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2AsPh_2$.[13]



(*R**,*R**)-(±)-diphars



(*R**,*S**)-(±)-diphars

Results and Discussion

Synthesis, Separation of Diastereomers, and Resolution of Ligand. Whereas base-catalyzed additions of secondary phosphines to vinyl-substituted tertiary phosphines provide efficient routes to a variety of di- or oligotertiary phosphines,[14] secondary phosphine additions to vinyl-substituted tertiary arsines do not proceed under similar conditions. For these reactions, the arsenic must be activated by oxidation or by coordination to a metal ion.[15] Thus, 2 equiv of diphenylvinylarsine *oxide* reacted with 2 equiv of bis(phenylphosphino)ethane[16] in THF in the presence of a small quantity of potassium *tert*-butoxide to give in high yield the *diarsine−dioxide* (Scheme 1). The latter quantitatively rearranges into the sparingly soluble *diphosphine−dioxide* when heated in chloroform in the presence of a trace of trichlorosilane (Scheme 2). This is seen in the $^{31}P\{^1H\}$ NMR spectrum of the compound by a shift in the ^{31}P resonance from −16.15 (racemic) and −16.52 (meso) to 42.05 (meso) and 42.35 (racemic). When a mixture of the diarsine−dioxide and an excess of triethylamine and trichlorosilane in acetonitrile is heated for 24 h, however (typical conditions for the reduction of a tertiary phosphine oxide),[17] the desired di(tertiary arsine)−di(tertiary phosphine) is obtained in high yield after a workup involving addition of aqueous sodium hydroxide to the reaction mixture, removal of acetonitrile, and extraction of the product into dichloromethane. Yield of (*R**,*R**)-(±)/

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[13] As a consequence of the Cahn−Ingold−Prelog (CIP) rules for specifying absolute configuration, an apparent inversion at phosphorus takes place upon coordination of a *P*-chiral tertiary phosphine to an element of higher atomic number than 12.[7]

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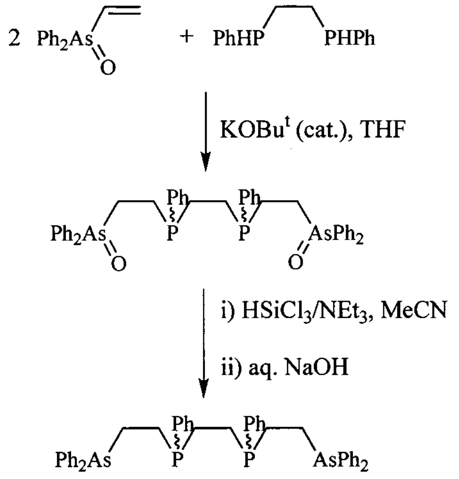
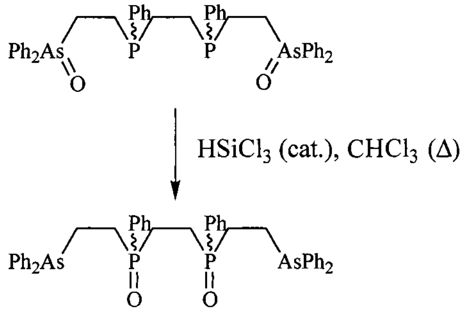
Scheme 1



Scheme 2

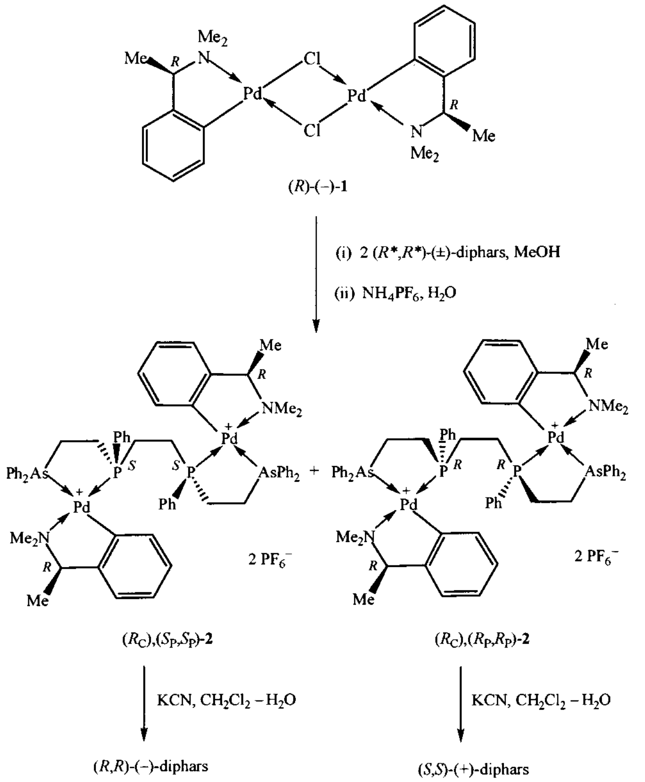


(*R**,*S**)-diphars: 84% (60/40 mixture). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −15.7 (60%), −16.1 (40%). The (*R**,*R**)-(±)/(*R**,*S**) = 60/40 mixture was heated for 2 h at 150 °C to convert it into a 1/1 mixture for fractional crystallization [$E_{inv}(PR_3)$ ~120−130 kJ mol^{-1}].[18]

The 1/1 mixture of (*R**,*R**)-(±)/(*R**,*S**)-diphars was separated by fractional crystallization from dichloromethane−ethanol. The sparingly soluble (*R**,*S**) diastereomer, mp 242 °C, was recovered in ~88% yield (δ_P −15.7). Concentration of the mother liquor afforded (*R**,*R**)-(±) material of ~90% diastereomeric excess (de), which was enriched to 98% de by selective extraction into *n*-hexane (Soxhlet apparatus). Total (*R**,*R**)-(±)-diphars recovered: 76% having mp 104 °C (δ_P −16.09). Additional (*R**,*R**)-(±)-diphars was obtained by heating the (*R**,*S**) diastereomer for 2 h at 150 °C and fractionally crystallizing the resulting 1/1 mixture of diastereomers as described previously.

The (*R**,*R**)-(±)-diphars was resolved as indicated in Scheme 3. Equimolar quantities of the *racemate* and the resolving complex (*R*)-(−)-**1** were suspended in methanol, and the mixture was stirred until complete dissolution of the two solids had occurred. The addition of an aqueous solution of ammonium hexafluorophosphate to the almost colorless solution brought about the precipitation of (R_C),(R_P,R_P)/(R_C),(S_P,S_P)-**2**, a colorless solid (84% yield). The mixture was separated by suspension in a small volume of chloroform, whereupon (R_C),(R_P,R_P)-**2** preferentially dissolved. The chloroform-insoluble fraction, after recrystallization from dichloromethane−ethanol, afforded transparent prisms of configurationally homogeneous (R_C),(S_P,S_P)-**2** (δ_P 63.5) having $[\alpha]_D^{21}$ = −51.1 (*c* 1.0, CH_2Cl_2). Yield: 48% (96% of possible). The chloroform-soluble diastereomer (R_C),(R_P,R_P)-**2** (δ_P 62.5), after recrystallization from dichloromethane−ethanol, crystallized as colorless plates and had $[\alpha]_D^{21}$ = +20.7 (*c* 1.0, CH_2Cl_2). Yield: 44% (88% of possible).

Scheme 3



The liberation of the enantiomer of the phosphine−arsine from the individual palladium diastereomer in each case was achieved by dissolving the complex in dichloromethane and exposing the solution to aqueous potassium cyanide. When the reaction was complete (~6 h at 20 °C), the phosphine−arsine was recovered from the organic phase and subjected to chromatography on a short column of silica with dichloromethane as eluent, the eluate concentrated, and the pure enantiomer recovered by the addition of ethanol. Thus, (R_C),(R_P,R_P)-**2** afforded (*S*,*S*)-diphars, colorless needles, mp 87−88 °C, $[\alpha]_D^{21}$ = +18.4 (*c* 1.0, CH_2Cl_2); (R_C),(S_P,S_P)-**2** gave (*R*,*R*)-diphars, mp 87−88 °C, $[\alpha]_D^{21}$ = −18.6 (*c* 1.0, CH_2Cl_2). The purity of each enantiomer was confirmed by in situ preparation of each diastereomer of the complex from the liberated arsine−phosphine and (*R*)-(−)-**1**: the absence of the signal for the *other* diastereomer of the complex in the ^{31}P{^{1}H} NMR spectrum indicated >99.5% enantiomeric excess of the phosphine−arsine in each case.

Metal Complexes. The addition of (*S*,*S*)-diphars to [Cu(MeCN)$_4$]PF$_6$ in dichloromethane gave a solution from which (−)-[Cu_2{(*R*,*R*)-diphars}$_2$](PF_6)$_2$ crystallized upon addition of ethanol. The slow evaporation of dichloromethane from a dichloromethane−ethanol solution of the complex gave prisms of the complex suitable for X-ray crystallography. The analogous silver complex was prepared in a two-phase

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Table 1. Crystal Data and Experimental Parameters for the X-ray Structure Analyses

	[M-(S_{Cu},S_{Cu})]-(−)-[Cu_2{(R,R)-diphars}$_2$](PF_6)$_2$	[M-(S_{Ag},S_{Ag})]-(+)-[Ag_2{(R,R)-diphars}$_2$](PF_6)$_2$	[M-(S_{Au},S_{Au})]-(−)-[Au_2{(R,R)-diphars}$_2$](PF_6)$_2$
molecular formula	$C_{84}H_{84}As_4Cu_2F_{12}P_6$	$C_{84}H_{84}Ag_2As_4F_{12}P_6$	$C_{84}H_{84}As_4Au_2F_{12}P_6$
fw, g mol^{-1}	1934.19	2022.83	2201.03
space group	$P2_12_12_1$ (No. 19)	$P1$	$P2_12_12_1$ (No. 19)
cryst syst	orthorhombic	triclinic	orthorhombic
a, Å	16.084(3)	12.487(2)	16.199(4)
b, Å	18.376(3)	12.695(4)	18.373(4)
c, Å	29.149(6)	27.243(4)	29.347(2)
α, deg		92.06(2)	
β, deg		95.19(1)	
γ, deg		98.23(2)	
V, Å^3	8616(2)	4251.3(2)	8734(3)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.49	1.58	1.67
cryst size, mm^3	0.41 × 0.10 × 0.06	0.15 × 0.10 × 0.02	0.33 × 0.19 × 0.19
μ, cm^{-1}	39.7	70.7	96.4
instrument	Rigaku AFC6R	Rigaku AFC6R	Rigaku AFC6R
radiation	Cu Kα	Cu Kα	Cu Kα
no. of unique reflns	7069	12601	7142
no. of reflns obsd	4925 ($I > 2.0\ \sigma$(I))	9216 ($I > 2.0\ \sigma$(I))	6272 ($I > 2.0\ \sigma$(I))
2θ range, deg	120.2	120	120.1
scan technique	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
scan width (deg)	1.30 + 0.30 tanθ	1.30 + 0.30 tanθ	1.30 + 0.30 tanθ
temperature (°C)	23 ± 1	23 ± 1	23 ± 1
structural refinement	teXsan[31]	XTAL3.4[30]	teXsan[31]
final R, R_w	0.045, 0.054	0.062, 0.080	0.035, 0.041

system involving (S,S)-diphars in dichloromethane and silver(I) nitrate−ammonium hexafluorophosphate in water. The product, (+)-[Ag_2{(R,R)-diphars}$_2$](PF_6)$_2$, was isolated as colorless rosettes from dichloromethane−ethanol. The similar reaction between (S,S)-diphars and $Et_4N[AuBr_2]/NH_4PF_6$ afforded (−)-[Au_2{(R,R)-diphars}$_2$](PF_6)$_2$, which crystallized as long colorless prisms from dichloromethane−ethanol. For each metal, use of (R*,R*)-(±)-diphars produced the identical, but racemic, complex, viz. (±)-[M_2{(R*,R*)-diphars}$_2$](PF_6)$_2$ (M = Cu(I), Ag(I), Au(I)), which in each case was evident from a comparison of the $^{31}P\{^1H\}$ NMR spectra of the two forms of the complex.

Crystal and Molecular Structures. Crystal data, information relating to data collection, and refinement details for [M-(S_{Cu},S_{Cu})]-(−)-[Cu_2{(R,R)-diphars}$_2$](PF_6)$_2$, [M-(S_{Ag},S_{Ag})]-(+)-[Ag_2{(R,R)-diphars}$_2$](PF_6)$_2$, and [M-(S_{Au},S_{Au})]-(−)-[Au_2{(R,R)-diphars}$_2$](PF_6)$_2$ are given in Table 1. The copper complex crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19). The structure of the cation in the copper complex is shown in Figure 1, and selected distances and angles are given in Table 2. The structure is that of a parallel double helix in which each ligand strand completes 1.5 turns of an M helix. Both tetrahedral metal ion stereocenters have the S configuration. The central ten-membered ring containing the two copper ions has the chiral twist-boat−chair−boat (TBCB) conformation, which is of δ helicity. The Cu···Cu distance is 6.005(3) Å.

Crystals of [M-(S_{Au},S_{Au})]-(−)-[Au_2{(R,R)-diphars}$_2$](PF_6)$_2$ are isomorphous with those of the copper complex. Selected angles and distances in the cation are given in Table 2. The average metal−donor atom bond lengths are longer than those in the copper complex, however, viz. Au−As 2.59 Å versus Cu−As 2.43 Å and Au−P 2.35 Å versus Cu−P 2.28 Å. The metal−metal distance in the gold complex is 5.862(3) Å; in (S,S)-(−)-[Au_2{(R,R)-tetraphos}$_2$](PF_6)$_2$·CH_2Cl_2, it is 6.244(2) Å.[10]

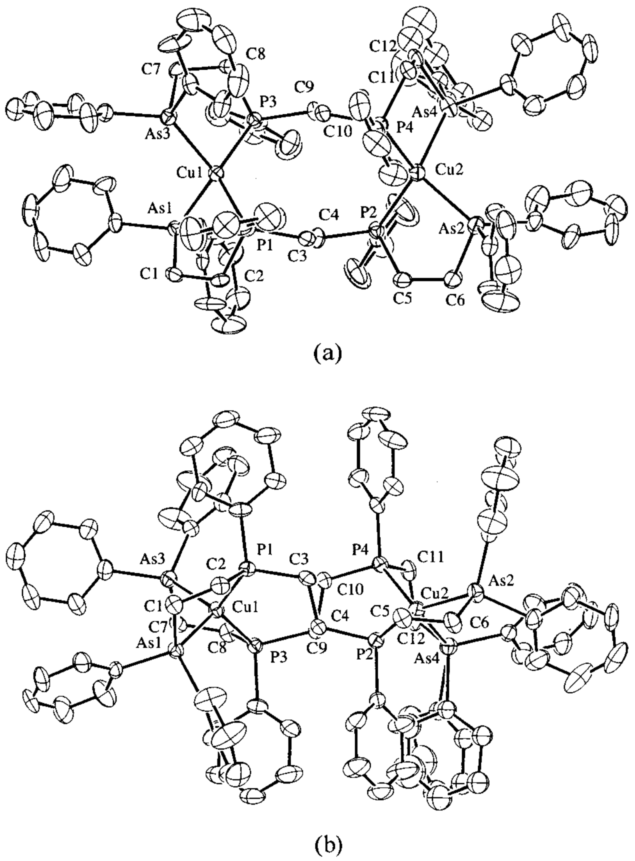
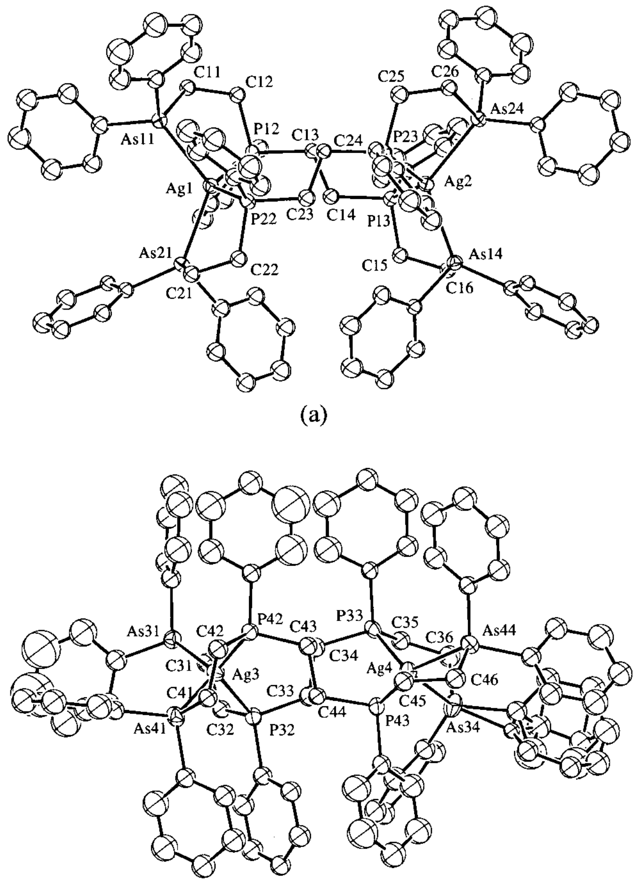


Figure 1. Cation of [M-(S_{Cu},S_{Cu})]-(−)-[Cu_2{(R,R)-diphars}$_2$](PF_6)$_2$ viewed perpendicular to plane of parallel helix (a) and in plane of parallel helix (b).

Complex (+)-[Ag_2{(R,R)-diphars}$_2$](PF_6)$_2$ crystallizes in the space group $P1$, with one molecule each of the double α-helix conformer and the parallel helix conformer of the helicate and associated anions in the unit cell (Figure 2). Selected distances and angles in the two conformers of the cation are given in Table 3. In each conformer, the metal



(a)

(b)

Figure 2. Double α-helix (a) and parallel helix (b) conformers of $[M\text{-}(S_{Ag},S_{Ag})]$-(+)-$[Ag_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[M\text{-}(S_{Cu},S_{Cu})]$-(−)-$[Cu_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$ and $[M\text{-}(S_{Au},S_{Au})]$-(−)-$[Au_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$

Copper Complex		Gold Complex	
Cu(1)−As(1)	2.397(2)	Au(1)−As(1)	2.543(1)
Cu(1)−As(3)	2.423(2)	Au(1)−As(3)	2.594(2)
Cu(1)−P(1)	2.267(4)	Au(1)−P(1)	2.353(3)
Cu(1)−P(3)	2.255(3)	Au(1)−P(3)	2.333(3)
Cu(1)···Cu(2)	6.005(3)	Au(1)···Au(2)	5.862(3)
Cu(2)−As(2)	2.438(2)	Au(2)−As(2)	2.586(2)
Cu(2)−As(4)	2.463(2)	Au(2)−As(4)	2.637(3)
Cu(2)−P(2)	2.304(4)	Au(2)−P(2)	2.375(3)
Cu(2)−P(4)	2.286(4)	Au(2)−P(4)	2.343(3)
As(1)−Cu(1)−As(3)	112.94(8)	As(1)−Au(1)−As(3)	111.72(5)
As(1)−Cu(1)−P(1)	89.0(1)	As(1)−Au(1)−P(1)	85.59(8)
P(1)−Cu(1)−P(3)	124.8(1)	P(1)−Au(1)−P(3)	129.7(1)
As(1)−Cu(1)−P(3)	120.5(1)	As(1)−Au(1)−P(3)	123.33(7)
As(3)−Cu(1)−P(1)	122.7(1)	As(3)−Au(1)−P(1)	123.66(8)
As(3)−Cu(1)−P(3)	89.5(1)	As(3)−Au(1)−P(3)	85.82(9)
As(2)−Cu(2)−As(4)	109.70(9)	As(2)−Au(2)−As(4)	107.53(5)
As(2)−Cu(2)−P(2)	88.6(1)	As(2)−Au(2)−P(2)	85.84(9)
P(2)−Cu(2)−P(4)	118.0(1)	P(2)−Au(2)−P(4)	124.1(1)
As(2)−Cu(2)−P(4)	129.5(1)	As(2)−Au(2)−P(4)	131.85(8)
As(4)−Cu(2)−P(2)	128.5(1)	As(4)−Au(2)−P(2)	128.03(8)
As(4)−Cu(2)−P(4)	87.2(1)	As(4)−Au(2)−P(4)	84.01(8)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[M\text{-}(S_{Ag},S_{Ag})]$-(+)-$[Ag_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$

Double α-Helicate		Parallel Helicate	
Ag(1)−As(11)	2.578(2)	Ag(3)−As(31)	2.606(3)
Ag(1)−As(21)	2.601(2)	Ag(3)−As(41)	2.608(3)
Ag(1)−P(12)	2.475(4)	Ag(3)−P(32)	2.508(6)
Ag(1)−P(22)	2.490(5)	Ag(3)−P(42)	2.495(6)
Ag(2)−As(14)	2.608(3)	Ag(4)−As(34)	2.620(4)
Ag(2)−As(24)	2.586(3)	Ag(4)−As(44)	2.606(3)
Ag(2)−P(13)	2.478(5)	Ag(4)−P (33)	2.452(6)
Ag(2)−P(23)	2.465(5)	Ag(4)−P(43)	2.452(6)
Ag(1)···Ag(2)	6.567(2)	Ag(3)···Ag(4)	5.802(3)
As(11)−Ag(1)−As(21)	122.1(1)	As(31)−Ag(3)−As(41)	121.3(1)
As(11)−Ag(1)−P(12)	85.4(1)	As(31)−Ag(3)−P(32)	84.1(2)
As(11)−Ag(1)−P(22)	120.9(1)	As(31)−Ag(3)−P(42)	127.6(2)
As(21)−Ag(1)−P(12)	127.8(1)	As(41)−Ag(3)−P(32)	115.7(2)
As(21)−Ag(1)−P(22)	85.0(2)	As(41)−Ag(3)−P(42)	84.1(2)
P(12)−Ag(1)−P(22)	120.3(2)	P(32)−Ag(3)−P(42)	128.3(2)
As(14)−Ag(2)−As(24)	121.7(1)	As(34)−Ag(4)−As(44)	103.6(1)
As(14)−Ag(2)−P(13)	84.1(1)	As(34)−Ag(4)−P(33)	84.2(2)
As(14)−Ag(2)−P(23)	128.0(1)	As(34)−Ag(4)−P(43)	129.9(2)
As(24)−Ag(2)−P(13)	121.1(2)	As(44)−Ag(4)−P(33)	127.4(2)
As(24)−Ag(2)−P(23)	84.9(1)	As(44)−Ag(4)−P(43)	85.3(2)
P(13)−Ag(2)−P(23)	121.1(2)	P(33)−Ag(4)−P(43)	129.0(2)

ion stereocenters have the *S* configuration. The central ten-membered ring in each case has the chiral twist-boat−chair−boat (TBCB) conformation,[19] which is of λ helicity in the double α-helix conformer and δ in the parallel helix conformer. For the double α-helix, the left-handed twist of ~60° of the chiral TBCB ring combines constructively with the two twists of similar magnitude for the two chiral AgP_4 stereocenters of *S* configuration to give an overall twist of ~180° in the *M* direction. This is reflected in the C−C−P−C torsion angles between the central carbon−carbon bonds of the ten-membered ring and the adjacent phosphorus−carbon bonds of the terminal five-membered chelate rings, which are ~180° for the double α-helix conformer and ~90° for the parallel helix conformer. Each of the four chiral terminal five-membered chelate rings in the double α-helix conformer has the δ conformation, which results in idealized D_2 symmetry for the cation. In the parallel helix conformer, the helicities of the terminal pairs of five-membered rings are opposed to one another (one pair δ, the other λ), which reduces the overall idealized symmetry of the helicate ion from D_2 to C_2. The Ag···Ag distance in the double α-helix conformer is 6.567(2) and 5.802(3) Å in the parallel helix conformer, which compare with the values of 6.859(3) and 6.072(4) Å in the corresponding conformers of $[M\text{-}(S_{Ag},S_{Ag})]$-(−)-$[Ag_2\{(R,R)\text{-tetraphos}\}_2](PF_6)_2$.[10]

NMR Spectra. The $^{31}P\{^1H\}$ NMR spectrum of (−)-$[Cu_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$ in acetonitrile-d_3 at 295 K exhibits a sharp singlet at δ_P 12.3 and a broad, almost coalesced, resonance centered at δ_P 10.4. When the sample is cooled to 236 K, the signal at δ_P 12.3 remains sharp (but shifted to δ_P 13.8), and the broad resonance is resolved into three singlets (δ_P 8.4, 9.4, 12.2) of approximately equal intensity. The singlet has been assigned to the mononuclear copper complex (*S*)-$[Cu\{(R,R)\text{-diphars}\}]PF_6$, and the three low-temperature resonances have been assigned to the three most stable conformers of the dicopper(I) helicate, viz. the double α-helix, the parallel helix, and the intermediate containing the achiral boat−chair−boat (BCB) conformation of the ten-membered ring (Figure 9).[19] The spectrum of (+)-$[Ag_2\{(R,R)\text{-diphars}\}_2](PF_6)_2$ in acetonitrile-d_3 contains a broad doublet at δ_P 10.3 ($^1J_{PAg}$ = 322 Hz), which does not sharpen

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[19] Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7047. Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.

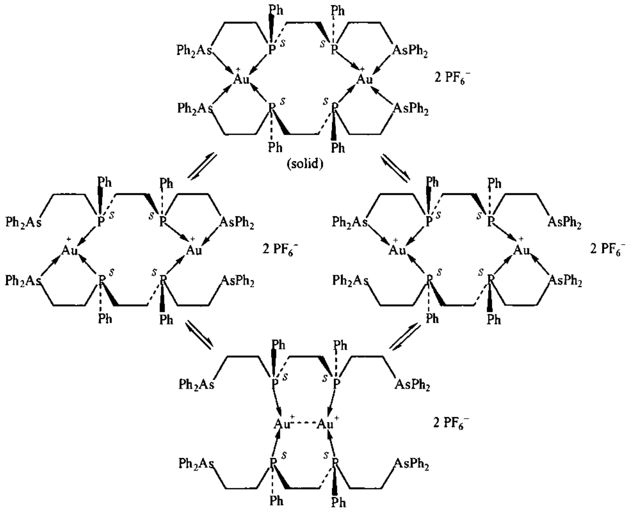

Figure 3. Fluxional behavior of [M-(S_{Au},S_{Au})]-(−)-[Au_2\{(R,R)-diphars\}$_2$]-(PF_6)$_2$.

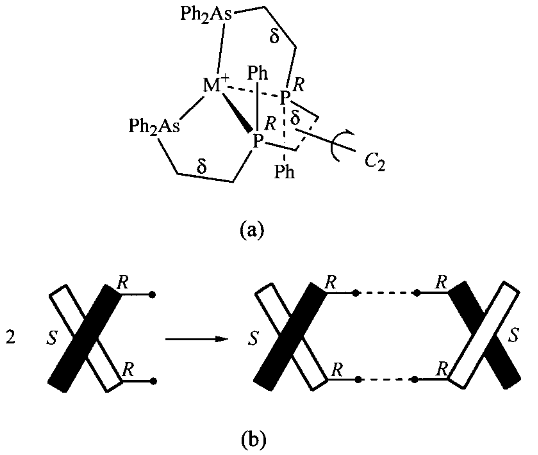

Figure 4. Stereospecific coordination of (S,S)-diphars to M^+ to give a chiral metal chelate of S configuration (a) and dimerization of hypothetical building block (b).

when the solution is cooled to 236 K. For (−)-[Au_2\{(R,R)-diphars\}$_2$](PF_6)$_2$ in dichloromethane-d_2, singlets are observed at δ_P 37.4 and 45.0 at 295 K in the intensity ratio 5:1. The signal at δ_P 45.0 at 295 K in this complex corresponds to the value of δ_P 44.6 at 183 K for [Au_2(μ-dppe)$_2$](ClO_4)$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) in the same solvent,[20] in which each diphosphine is considered to bridge two two-coordinate gold ions to form a ten-membered ring, although similar complexes have gold−gold interactions in the solid state (Au···Au ~2.9 Å).[21] For [Au_2(μ-dppe)$_3$](ClO_4)$_2$, however, which is believed to contain a three-coordinated gold center, a singlet resonance is observed at δ_P 37.0 in dichloromethane-d_2 at 183 K. (The four-coordinate tetrahedral complex [Au(dppe)$_2$]SbF_6·Me_2CO exhibits a singlet resonance at δ_P 20.8 in chloroform-d_1.[22]) We accordingly assign the more intense resonance at δ_P 37.4 in the spectrum of (−)-[Au_2\{(R,R)-diphars\}$_2$](PF_6)$_2$ to a species containing three-coordinate gold in which one arsenic only from each ligand strand is coordinated, and the minor peak at δ_P 45.0 to a two-coordinate gold species related to [Au_2(μ-dppe)$_2$]-(ClO_4)$_2$ in which none of the arsenic donors is coordinated (Figure 3). Because of the slower ligand exchange rate for the diphars−gold complex compared to that of the dppe complex, sharp NMR spectra were observed at higher temperatures for the diphars complex. Coordination of the terminal arsenic donor to the gold in the diphars complex is thus competitive with metal−metal bond formation in solution, with the three-coordinated cation being considerably more stable than the two-coordinate cation containing the gold···gold interaction.

Theoretical Modeling

Stereochemical Considerations. The stereospecific coordination of (S,S)-diphars to copper(I) can be rationalized as indicated in Figure 4. (The analogous ligand, (S,S)-tetraphos, does indeed give the mononuclear metal complex (S)-[Cu\{(R,R)-tetraphos\}]PF_6.)[10] Here, the central carbon−carbon bond in the hypothetical mononuclear copper−diphars cation (a) has been cleaved homolytically about the C_2 axis of the molecule to produce a bis(bidentate)copper(I) cation, which can be represented by the chiral crossed-bar helicate building block (b). The positions of the methylene carbon atoms and the *ipso* carbon atoms of the phenyl groups were determined from data calculated for [Cu($Me_2PCH_2CH_2PMe_2$)$_2$]$^+$ with use of the molecular force-field SYBYL.[23] The S configuration of the metal stereocenter is apparent from inspection of the crossed-bar representation of the molecule. For the S configuration of the metal, the calculated distance between the methylene carbon atoms in the hypothetical cation is 3.69 Å; if the phosphorus stereocenters are inverted (and the metal configuration is unaltered), the distance becomes 6.41 Å. Thus, (S,S)-diphars will bind stereospecifically to copper(I) to give a complex of S configuration. Two mononuclear units of this configuration can dimerize to give a double-stranded dinuclear metal helicate of the type (S,S)-[M_2\{(R,R)-diphars\}$_2$]$^{2+}$, in which there is a central ten-membered ring containing the two metal ions.

Molecular Mechanics Calculations. Detailed modeling of the structures of the ions [Cu\{(R,R)-$H_2AsCH_2CH_2P(H)CH_2CH_2P(H)CH_2CH_2AsH_2$\}]$^+$, [Cu\{($R$,$R$)-diphars*\}]$^+$, and [$Cu_2$\{($R$,$R$)-$H_2AsCH_2CH_2P(H)CH_2CH_2P(H)CH_2CH_2AsH_2$\}$_2$]$^{2+}$, [$Cu_2$\{($R$,$R$)-diphars*\}$_2$]$^{2+}$, were carried out with use of the TRIPOS 5.2 force field in the program SPARTAN 5.0. For the mononuclear cation, only the S configuration at the metal is possible (see previous description). There are six possible conformers of the mononuclear cation resulting from inversion of one or more of the three five-membered chelate rings. The conformers have similar energies, and the inversions have little effect on either the energy (maximum energy difference between conformers is 3.0 kcal mol^{-1}) or the

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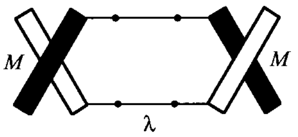
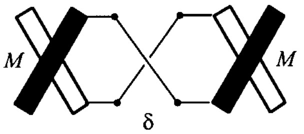
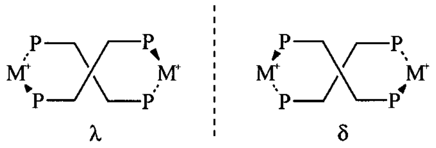


double α-helix
D_2 (*M*)

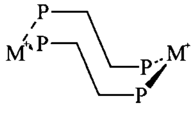


parallel helix
C_2 (*M*)

Figure 5. Schematic representation of double α-helix and parallel helix conformers of [*M*-(S_M,S_M)]-[M_2{(*R*,*R*)-diphars}$_2$]$^{2+}$.

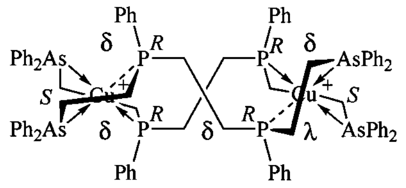


TBCB (C_2)
(a)

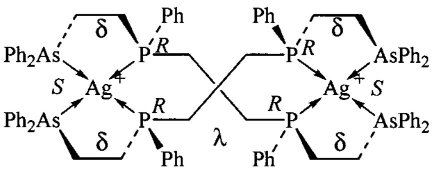


BCB (C_S)
(b)

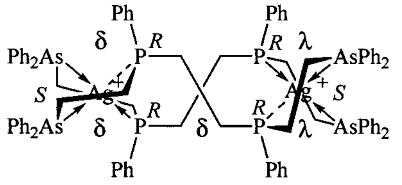
Figure 6. Most stable conformations of the central ten-membered ring in [*M*-(S_M,S_M)]-[M_2{(*R*,*R*)-diphars}$_2$]$^{2+}$: (a) chiral twist-boat–chair–boat (TBCB) and (b) symmetrical boat–chair–boat (BCB).



C_1 (*M*)



D_2 (*M*)



C_2 (*M*)

Figure 7. Stereochemical assignments of chiral elements in solid-state structures of [*M*-(S_M,S_M)]-[M_2{(*R*,*R*)-diphars}$_2$]$^{2+}$ (M = Cu(I), Ag(I)).

geometry of the cation. The C_2 conformer of the mononuclear cation having δ, δ, δ conformations of the three five-membered rings is the most stable (*S* metal). The starting structures for the dinuclear metal cations were generated by varying the configurations of the metal stereocenters (*R* or *S*), the conformation of the ten-membered ring containing the two metal ions (Figure 7), and the conformations of the four terminal five-membered chelate rings (δ or λ). The chiral TBCB conformation of the ten-membered ring is found in the structures of [*M*-(S_M,S_M)]-[M_2{(*R*,*R*)-tetraphos}$_2$](PF_6)$_2$ (M = Ag(I), Au(I)), although, in cyclododecane and its derivatives, the achiral boat–chair–boat (BCB) conformation is preferred.[19] As found for similar calculations on the (*S*,*S*)-tetraphos–copper(I) system,[10] mononuclear metal cations were less stable than dinuclear metal cations, and for the latter, the most stable structures contained two metal stereocenters of *S* configuration. When the central TBCB ring has the λ conformation, its twist reinforces the similar negative twists of the two copper stereocenters of the *S* configuration to give an overall twist of 180° for the helicate in the *M* direction. This is the double α-helix conformer of the helicate (Figure 5). When the central TBCB ring is inverted (to δ), there is a diminution of ~60° in the overall twist in the helicate, which results in the parallel double helix conformer of the helicate. The difference in energy between the double α-helix (central ring λ) and the parallel double helix (central ring δ) conformers is small; the transition structure between the two contains a ten-membered ring in the achiral BCB conformation (Figure 6). The stereochemical assignments of the chiral elements in the cations of the three complexes, taken from the crystal structures, are given in Figure 7. Molecular dynamics calculations using the Osawa conformation searching program of the SPARTAN 5.0 package were conducted on the parallel helicate. The search established that the double α-helicate and the intermediate (achiral BCB ring) could be obtained from the parallel helicate. The mononuclear cations were less stable than the dinuclear metal cations by 16.8–21.2 kcal mol^{-1}. When the calculations were repeated for the silver(I) and gold(I) complexes, similar results were obtained.

Semiempirical Calculations. Modeling of conformers of [Cu{(*R*,*R*)-diphars*}]$^+$ and [Cu_2{(*R*,*R*)-diphars*}$_2$]$^{2+}$ was performed with use of PM3(TM) theory.[24] The differences in energies between the conformers were much closer at this level of theory, and in many cases, the minimization process involved the inversion of terminal five-membered chelate rings, which frequently led to degeneration into the starting structures. All conformers of (*S*)-[Cu{(*R*,*R*)-diphars*}]$^+$ degenerated into the C_2 conformer of the cation having δ, λ, δ conformations of the three five-membered rings. Of the configurational and conformational diastereomers of [Cu_2{(*R*,*R*)-diphars*}$_2$]$^{2+}$, the most stable has *S* configurations at copper, which generate an overall helix of *M* configuration. The steric energies of the configurational diastereomers and conformers of [*M*-(S_{Cu},S_{Cu})]-[Cu_2{(*R*,*R*)-diphars*}$_2$]$^{2+}$ are given in Figure 8. The most stable ten-membered ring conformation in the cation is the TBCB, the helicity of which,

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(24) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

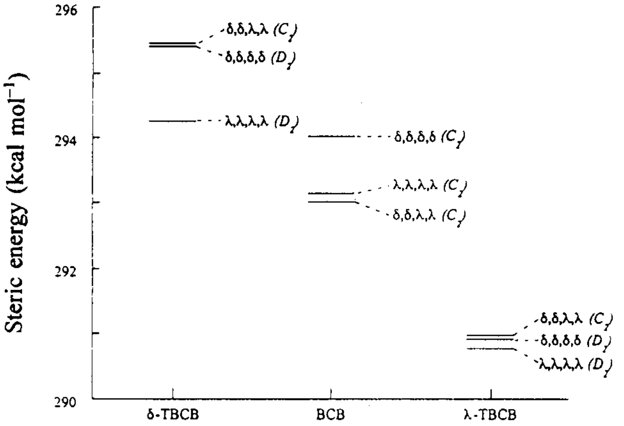

Figure 8. Steric energies of conformational diastereomers of [*M*-(S_{Cu},S_{Cu})]-[Cu_2{(*R*,*R*)-diphars*}$_2$]$^{2+}$.

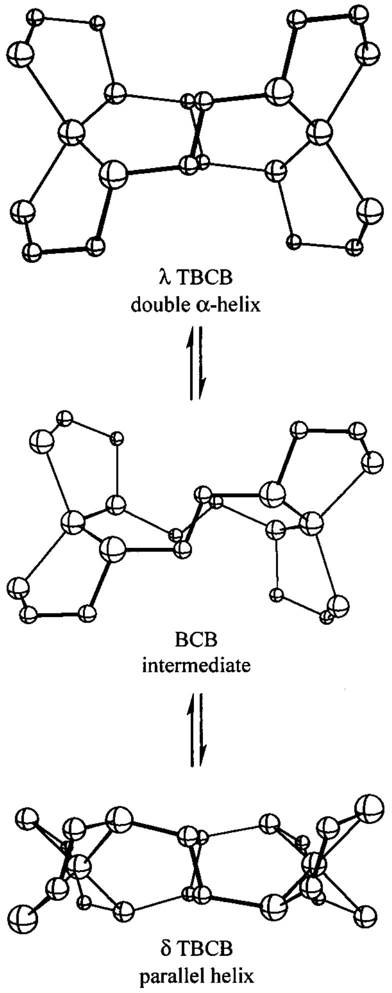

Figure 9. Calculated core structures showing inversion of central ten-membered ring in [*M*-(S_{Cu},S_{Cu})]-[Cu_2{(*R*,*R*)-diphars*)$_2$]$^{2+}$ via intermediate structure containing achiral BCB ring.

in conjunction with the configurations of the four phosphorus stereocenters of *R* configuration, determines the most stable conformer of the helicate, double α-helix (λ-TBCB) or parallel helix (δ-TBCB) (Figure 9). The conformations of the terminal five-membered rings contribute little to the steric energies calculated. The achiral BCB conformation of the ten-membered ring also stabilizes the dinuclear helicate, but a central ring of this conformation has not been observed in the solid state.

Conclusion

The new mixed arsenic−phosphorus donor ligand (*R**,*R**)-(±)/(*R**,*S**)-diphars has been prepared, the diastereomers have been separated, and the (*R**,*R**)-(±) form has been resolved by the method of metal complexation. The (*S*,*S*) enantiomer of the ligand binds stereospecifically to univalent copper, silver, and gold to give double-stranded dinuclear metal helicates of the type [*M*-(S_M,S_M)]-[M_2{(*R*,*R*)-diphars}$_2$]$^{2+}$ (M = Cu(I), Ag(I), Au(I)) in which the two metal stereocenters in each case have the *S* configuration and the overall helicity of the helix is *M*. In each case, the central ten-membered ring containing the two metal ions has the chiral twist-boat−chair−boat (TBCB) conformation, and it is the relationship between the helicity of this ring and the configurations of the two metal stereocenters that determines the conformation of the helicate. When the TBCB ring has the λ conformation, the overall twist of the helicate is maximized by reinforcement of the negative (*S*) twists of the two chiral metal stereocenters: the overall twist of the resulting double α-helix conformer is ~180° in the *M* direction. Inversion of the TBCB ring to the δ conformation reduces the overall *M* twist of the helicate to ~60° and results in the parallel helix conformer of the helicate. The latter conformer was observed in the solid-state structures of copper(I), silver(I), and gold(I) complexes. In this conformer of the helicate, each ligand strand completes ~1.5 turns of an *M* helix around two tetrahedral metal ions of *S* configuration. For silver(I), both the double α-helix and parallel helix conformers of the helicate were found in the unit cell of the crystal. In the double α-helix conformer of the helicate, each ligand strand completes ~0.5 turn of an *M* helix. The overall helicate also completes 0.5 turn of an *M* helix around two tetrahedral metal ions of *S* configuration. The results of molecular mechanics and semiempirical calculations on the relative stabilities of the various conformers of the helicates were in close agreement with the observed structures.

Experimental Section

All chemical manipulations were carried out under argon with use of Schlenk and cannula techniques. NMR spectra were recorded at 295 K on a Varian Gemini 300 spectrometer operating at 300.075 MHz (^{1}H), 121.47 MHz (^{31}P), and 75.462 MHz (^{13}C); chemical shifts are quoted with reference to Me_4Si (^{1}H) and 85% H_3PO_4 (^{31}P). Optical rotations were measured on the specified solutions with a Perkin-Elmer Model 241 spectropolarimeter. Specific rotations are within ±0.05 deg cm^2 g^{-1}. Elemental analyses were performed by staff within the Research School of Chemistry. The resolving agent (*R*)-**1**[25] and the complexes $Et_4N[AuBr_2]$[26] and [Cu-$(MeCN)_4$]PF_6 [27] were prepared by literature procedures.

Molecular Mechanics Calculations. Approximate starting structures for [Cu{(*R*,*R*)-diphars*}]$^+$, [Cu_2{(*R*,*R*)-tetraphos*}$_2$]$^{2+}$,

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[25] Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301. Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876.

[26] Braunstein, P.; Clark, R. J. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1845.

[27] Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

and $[Cu_2\{(R,R)\text{-diphars*}\}_2]^{2+}$ were obtained with use of the SPARTAN 5.0 builder application.[28] The configurations of the metal stereocenters and the conformations of the central 10-membered rings containing the two metal ions and of the terminal five-membered chelate rings in the complexes were varied systematically in order to obtain data for all configurational and conformational diastereomers of the monocations and dications. Geometric optimizations were carried out on each diastereomer and conformer using the molecular mechanics force field SYBYL.[23] Semiempirical calculations were performed on the copper complexes with use of PM3(TM) theory.[24]

Diphenylvinylarsine. A solution of *n*-BuLi in *n*-hexane (56 mL, 1.65 M, 92 mmol) was slowly added to an ice-cold solution of diphenylarsine (21.2 g, 92 mmol) in THF (75 mL). Vinyl bromide (7 mL, 10.6 g, 99 mmol) was then added (over 0.5 h), and the mixture was stirred for 2 h. The solvent was removed in vacuo, and water (100 mL) was added. The product was extracted into dichloromethane (3 × 100 mL) and dried (Na_2SO_4), the extract filtered, and the solvent removed in vacuo to give a yellow oil. Distillation of this material gave the pure product as a colorless oil: bp 110−115 °C (0.02 mmHg), 18.1 g (77%). Anal. Calcd for $C_{14}H_{13}As$: C, 65.6; H, 5.1. Found: C, 65.9; H, 5.3. EI MS and IR data agreed with literature values for the compound.[29]

Diphenylvinylarsine oxide. Aqueous hydrogen peroxide (30%, 30 mL, 260 mmol) was slowly added to an ice-cold solution of diphenylvinylarsine (53.2 g, 208 mmol) in acetone (300 mL). The solution was then heated under reflux for 8 h. The reaction mixture was cooled to room temperature, and water (20 mL) was added. The acetone was removed in vacuo, and the *arsine oxide* was extracted from the water into dichloromethane (3 × 100 mL). The combined organic extracts were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. The residue was recrystallized from dichloromethane−diethyl ether to give colorless needles of the pure product having mp 149 °C. Yield 46.9 g (83%). Anal. Calcd for $C_{14}H_{13}AsO$: C, 61.8; H, 4.8. Found: C, 61.6; H, 4.8. ^1H NMR (acetone-d_6): δ 6.60 (d of d, $^3J_{HHtrans} = 18.4$ Hz, $^2J_{HH} = 1.1$ Hz, 1 H, H_a), 6.73 (d of d, $^3J_{HHcis} = 11.6$ Hz, $^2J_{HH} = 1.1$ Hz, 1 H, H_b), 7.40 (d of d, $^3J_{HHtrans} = 18.4$ Hz, $^3J_{HHcis} = 11.6$, 1 H, H_c), 7.82−7.94 (m, 6 H, unresolved, *o*, *p*-aryl-C*H*), 8.06−8.94 (m, 4 H, unresolved, *m*-aryl-C*H*). EI MS: *m*/*z* 271 amu ($[M - H]^+$).

(*R,*R**)-(±)/(*R**,*S**)-1,1,4,7,10,10-Hexaphenyl-1,10-diarsa-4,7-diphosphadecane Dioxide-*AsO,AsO* ((*R**,*R**)-(±)/(*R**,*S**)-diphars Dioxide).** Diphenylvinylarsine oxide (10.7 g, 40 mmol) and potassium *tert*-butoxide (1.0 g) were added to a solution of 1,2-bis(phenylphosphino)ethane (5.0 g, 20 mmol) in THF (250 mL). The reaction mixture turned deep red, and the product precipitated. After 2 h, the product was isolated and was washed with THF and diethyl ether. Yield 12.9 g (83%). ^1H NMR ($CDCl_3$): δ 1.68−3.24 (br m, 12 H, CH_2), 7.42−8.19 (br m, 30 H, Ar*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.15, −16.52. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.51 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2), 19.87 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2), 23.04 (s, AsCH_2), 23.11 (s, AsCH_2), 25.70 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2), 25.76 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2), 132.78 (s, Ar*C*As), 132.83 (s, Ar*C*As), 135.34 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 6$ Hz, 2 C, PCH_2), 135.22 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 6$ Hz, 2 C, PCH_2). ES MS: *m*/*z* 791 amu ($[M + H]^+$). When a solution of the *diarsine−dioxide* (0.030 g) in $CDCl_3$ (1 mL) containing trichlorosilane (trace) was heated under reflux for 15 min, complete isomerization into the corresponding *diphosphine−dioxide* occurred [$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.05 (meso), 42.35 (racemic)].

(*R,*R**)-(±)/(*R**,*S**)-1,1,4,7,10,10-Hexaphenyl-1,10-diarsa-4,7-diphosphadecane ((*R**,*R**)-(±)/(*R**,*S**)-Diphars).** Trichlorosilane (12.4 mL) was added to an ice-cold solution of (*R**,*R**)-(±)/(*R**,*S**)-diphars dioxide (14.0 g, 17.7 mmol) and triethylamine (14.8 mL) in acetonitrile (400 mL). The mixture was warmed to room temperature and then heated under reflux for 24 h. The reaction mixture was cooled and neutralized with aqueous NaOH (10%, 200 mL), and acetonitrile and volatile silane byproducts were removed in vacuo. Water (200 mL) was added to the residue, and the product was extracted into dichloromethane (3 × 200 mL). The combined organic extracts were dried (Na_2SO_4) and filtered, and the filtrate eluted through a short column of silica using dichloromethane as eluent. The solvent was removed in vacuo to afford the pure product as a colorless powder. Yield 11.3 g (84%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −15.7 (60%), −16.1 (40%).

Separation of the Diastereomers of (*R,*R**)-(±)/(*R**,*S**)-Diphars.** The (*R**,*R**)-(±)/(*R**,*S**)-diphars ~60/40 mixture (7.0 g, 9.2 mmol) was heated for 3 h at 200 °C in order to obtain the 1/1 mixture, which was dissolved in dichloromethane (70 mL), and the solution diluted with ethanol (70 mL). The mixture was set aside for 24 h. Fine transparent crystals of pure (*R**,*S**)-diphars separated from the solution and were filtered off, washed with ethanol, and dried. Yield 3.1 g (88%); mp 242 °C. Anal. Calcd for $C_{42}H_{42}As_2P_2$: C, 66.5; H, 5.6. Found: C, 66.5; H, 5.6. ^1H NMR ($CDCl_3$): δ 1.46−2.01 (br m, 12 H, CH_2), 7.25−7.46 (br m, 30 H, Ar*H*). ^{31}P NMR ($CDCl_3$): δ −15.7. ^{13}C NMR ($CDCl_3$): 22.73 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2), 22.97 (s, 2 C, AsCH_2), 23.83 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2). EI MS: *m*/*z* 758 amu (M^+). Concentration of the filtrate afforded crystalline (*R**,*R**)-(±)-diphars (3.29 g) of ~90% de; further recrystallization of this material did not improve the de. The enriched (*R**,*R**)-(±)-diphars was extracted with *n*-hexane for 20 h in a Soxhlet apparatus. Removal of the solvent from the extract left an oil that slowly solidified, affording (*R**,*R**)-(±)-diphars of ~98% de (2.70 g, 78%). A small portion of the oil was recrystallized from ethanol giving small transparent crystals of the pure diastereomer, which had mp 104 °C. Anal. Calcd for $C_{42}H_{42}As_2P_2$: C, 66.5; H, 5.6; P, 8.2. Found: C, 66.9; H, 5.6; P, 8.6. ^1H NMR ($CDCl_3$): δ 1.81−2.36 (br m, 12 H, CH_2), 7.50−7.82 (br m, 30 H, Ar*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.1. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.76 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2), 22.97 (s, AsCH_2), 24.06 (t, $^1J_{PC} = {}^4J_{PC} = {}^2J_{PC} = 8$ Hz, 2 C, PCH_2), 136.96 (t, $^1J_{PC} = {}^4J_{PC} = 8$ Hz, 2 C, PAr), 139.80 (s, Ar*C*As), 140.15 (s, Ar*C*As). EI MS: *m*/*z* 758 amu (M^+).

Resolution of (*R,*R**)-(±)-Diphars: (R_C),(R_P,R_P)/(R_C),(S_P,S_P)-2.** The resolving agent (*R*)-(−)-**1** (2.1 g, 3.62 mmol) and (*R**,*R**)-(±)-diphars (90% de) (2.7 g, 3.55 mmol) were suspended in methanol (200 mL), and the mixture was stirred until complete solution of solids had occurred (~2 h). Ammonium hexafluorophosphate (1.4 g, 8.5 mmol) in water (10 mL) was then added slowly to the solution with stirring. The diastereomeric palladium hexafluorophosphates precipitated and were filtered off and washed with water, aqueous methanol (90%), methanol, and diethyl ether. Yield 4.7 g (84%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.47(s), 62.52(s), −143.67 (sept, $^1J_{PF} = 710$ Hz, PF_6^-) (1/1 mixture).

Separation of (R_C),(R_P,R_P)/(R_C),(S_P,S_P)-2. Chloroform (30 mL) was added to the mixture of diastereomers (4.7 g), and the mixture was stirred for 24 h. The chloroform-insoluble fraction was filtered off, and the filtrate was collected and evaporated to dryness. The chloroform-insoluble fraction was washed with a small quantity of chloroform and recrystallized from dichloromethane−ethanol to

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(28) *SPARTAN 5.0*, Wavefunction Inc.: Irvine, CA, 1997.

(29) Chooi, S. Y. M.; Siah, S. Y.; Leung, P.-H.; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812.

give large transparent crystals of pure (R_C),(R_P,R_P)-**2**. Yield 2.2 g; mp 210 °C (decomp); $[\alpha]_D^{21} = -51.1$ (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{62}H_{70}As_2F_{12}N_2P_4Pd_2$: C, 47.8; H, 4.5; N, 1.8. Found: C, 47.6; H, 4.4; N, 1.5. ^1H NMR (CD_2Cl_2): δ 1.71 (d, $^3J_{HH} = 6$ Hz, 3 H, CH_3CH), 1.68−2.73 (br m, 12 H, CH_2), 2.62 (s, 3 H, CH_3N), 2.69 (s, 3 H, CH_3N), 3.64 (m, 1 H, C*H*), 6.62−7.26 (br m, 8 H, Ar*H*), 7.44−7.67 (br m, 36 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 62.52. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 26.52 (CH_3CH), 52.29, 52.16 (CH_3N), 77.86 (CH_3CH). ES MS: *m*/*z* 634 (M^{2+}), 1412 amu ($[M + PF_6]^+$). The filtrates were combined, the solvent was removed, and the residue was recrystallized from chloroform−ethanol, affording large transparent prisms of (R_C),(S_P,S_P)-**2**. Yield 2.04 g; mp 168 °C (decomp); $[\alpha]_D^{21} = +20.7$ (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{62}H_{70}As_2F_{12}N_2P_4Pd_2$: C, 47.8; H, 4.5; N, 1.8. Found: C, 47.6; H, 4.4; N, 1.5. ^1H NMR (CD_2Cl_2): δ 1.34 (d, $^3J_{HH} = 6$ Hz, 3 H, CH_3CH), 1.68−2.70 (br m, 12 H, CH_2), 2.67 (s, 3 H, CH_3N), 2.82 (s, 3 H, CH_3N), 4.15 (q, $^3J_{HH} = 6$ Hz, 1 H, C*H*), 6.90−7.16 (br m, 8 H, Ar*H*), 7.43−7.79 (br m, 36 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.47. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 11.76 (CH_3CH), 44.07, 52.71 (CH_3N), 72.75 (CH_3CH). ES MS: *m*/*z* 634 (M^{2+}), 1413 ($[M + PF_6]^+$).

[*R*-(*R,*R**)]-(−)- and [*S*-(*R**,*R**)]-(+)-1,1,4,7,10,10-Hexaphenyl-1,10-diarsa-4,7-diphosphadecane ((*R*,*R*)-(−)- and (*S*,*S*)-(+)-Diphars).** Potassium cyanide (11.4 g) in water (100 mL) was added to a solution of (R_C),(R_P,R_P)-**2** (2.4 g, 3.16 mmol) in dichloromethane (100 mL). The mixture was stirred for 6 h. The dichloromethane fraction was separated, and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were evaporated to dryness, and the residue was purified by chromatography on a short silica column using dichloromethane as eluent. The volume of the eluate was reduced to ∼2 mL, and ethanol (50 mL) was added, causing crystallization of pure (*S*,*S*)-diphars. Yield 1.02 g (92%); mp 87−88 °C; $[\alpha]_D^{21} = +18.4$ (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{42}H_{42}P_2As_2$: C, 66.5; H, 5.6. Found: C, 66.2; H, 5.7.

A similar decomposition of (R_C),(S_P,S_P)-**2** afforded pure (*R*,*R*)-diphars in similar yield having mp 87−88 °C and $[\alpha]_D^{21} = -18.6$ (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{42}H_{42}As_2P_2$: C, 66.5; H, 5.6. Found: C, 66.8; H, 5.6. NMR and MS data were identical with those for (*R**,*R**)-(±)-diphars.

[*M*-(S_{Cu},S_{Cu})]-(−)-[Cu_2\{(*R*,*R*)-Diphars\}$_2$](PF_6)$_2$. The complex $[Cu(MeCN)_4]PF_6$ (0.104 g, 0.28 mmol) was added to a solution of (*S*,*S*)-diphars (0.215 g, 0.28 mmol) in dichloromethane (5 mL). The solution was diluted with ethanol (10 mL) and concentrated until fine transparent crystals of the product separated, which were filtered off and washed with ethanol (5 mL). Yield: 0.23 g (85%); mp 141−142 °C; $[\alpha]_D^{21} = -32.2$ (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{84}H_{84}As_4Cu_2F_{12}P_6$: C, 52.2; H, 4.4. Found: C, 51.9; H, 4.2. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 12.33 (s), 10.40 (br s). ES MS: *m*/*z* 821 ($[M]^{2+}$), 1789 amu ($[M + PF_6]^+$). The $^{31}P\{^1H\}$ NMR spectrum of the complex prepared from (*R**,*R**)-(±)-diphars was identical with that of the enantiomerically pure material.

[*M*-(S_{Ag},S_{Ag})]-(+)-[Ag_2\{(*R*,*R*)-Diphars\}$_2$](PF_6)$_2$. The ligand (*S*,*S*)-diphars (0.118 g, 0.15 mmol) in dichloromethane (5 mL) was added to a solution of silver nitrate (0.026 g, 0.15 mmol) and ammonium hexafluorophosphate (0.040 g, 0.24 mmol) in water (5 mL), and the mixture was stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 3 mL). The combined organic extracts were dried (Na_2SO_4). Filtration, followed by removal of solvent, and recrystallization of the residue from methanol, gave the pure product. Yield: 0.110 g (71%); mp 187 °C; $[\alpha]_D^{21} = +54.2$ (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{84}H_{84}Ag_2As_4F_{12}P_6$: C, 49.9; H, 4.2. Found: C, 49.4; H, 4.0. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 10.29 (d, $^1J_{PAg} = 322$ Hz). ES MS: *m*/*z* 867 ($[M + 2H + 2PF_6]^{2+}$), 1877 amu ($[M - PF_6]^+$). The $^{31}P\{^1H\}$ NMR spectrum of the complex prepared from (*R**,*R**)-(±)-diphars was identical with that of the enantiomerically pure material.

[*M*-(S_{Au},S_{Au})]-(−)-[Au_2\{(*R*,*R*)-Diphars\}$_2$](PF_6)$_2$. The ligand (*S*,*S*)-diphars (0.204 g, 0.26 mmol) was added to a solution of $Et_4N[AuBr_2]$ (0.126 g, 0.26 mmol) in dichloromethane (5 mL). After 2 h, the solvent was removed in vacuo. The product was dissolved in hot aqueous ethanol (15 mL) and filtered, and ammonium hexafluorophosphate (0.066 g) in hot ethanol was added. Slow cooling of the solution to 0 °C afforded fine transparent crystals of the pure product. Yield: 0.20 g (70%); mp 135 °C; $[\alpha]_D^{21} = -19.8$ (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{84}H_{84}As_4Au_2F_{12}P_6$: C, 45.8; H, 3.9. Found: C, 46.0; H, 3.7. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.0, 37.4. ES MS: *m*/*z* 955 ($[M]^{2+}$), 2055 amu ($[M + PF_6]^+$). The $^{31}P\{^1H\}$ NMR spectrum of the complex prepared from (*R**,*R**)-(±)-diphars was identical with that of the enantiomerically pure material.

Supporting Information Available: Additional crystallographic data and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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