Preparation and Properties of (S,S)-[Ti((R,R)-cyclacene)Cl₂], a Chiral Strapped Bent Metallocene

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The ligand (1R,2R)-*trans*-1,2-bis(1-indenylmethyl)cyclopentane has been prepared, and its dilithio salt was allowed to react with TiCl₄·2THF; after reduction of this product, the complex (S,S)-[Ti((R,R)-cyclacene)Cl₂] was isolated. The *trans*-1,2-dimethylenecyclopentane group joining the two tetrahydroindenyl groups induces the formation of one chiral diastereomer. The crystal structure shows that the two tetrahydroindenyl groups are not symmetrically disposed although the ¹H NMR spectrum at various temperatures indicates a symmetric structure, at least on an NMR time scale. Circular dichroism spectra are recorded for the complex. The possible origins of the unsymmetrical structure are discussed in terms of the strap size.

Derivatives of the species [M(Cp)₂Cl₂] (M = Ti(IV), Zr(IV), Hf(IV)), where Cp is the cyclopentadienyl ligand, have found increasing application for stoichiometric and catalytic transformations of organic substrates. Among these applications are asymmetric catalytic hydrogenation of olefins,[1] catalytic hydrosilation of esters,[2a] asymmetric production of allylic amines,[2b] and, perhaps most notably, the isotactic polymerization of propylene[3] and related stereoregular polymerizations.[4] Aside from the production of isotactic polypropylene where a racemic catalyst will suffice, all of the enantioselective reactions require one enantiomer of the catalyst or metal-based reagent. The most effective of the enantioselective reagents are those which employ the ethylenebis(tetrahydro-1-indenyl) ligand in the chiral complexes of the type 1. The titanium and

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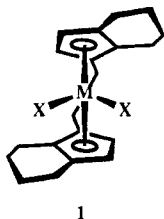
zirconium complexes of this type were first reported by Brintzinger,[5] who separated the meso and racemic forms of 1 and separated the enantiomers of the racemic form. Many other chiral strapped bent metallocenes have been reported subsequently,[6] but in nearly all cases the products obtained in the preparation of these species consist of a mixture of racemic and meso forms. As a result, the desired racemic isomer has to be either separated initially or the racemic–meso mixture has to be irradiated to its approximate photostationary state before separation. Generally, the separation is tedious and results in low yields of the desired racemic isomer. After isomer separation, there remains the problem of resolving the racemic isomer into its enantiomers, a procedure which is not always simple. Finally, after separation and resolution, there is the observation that, in the case of some titanium complexes, racemization occurs in ambient light.[5] Although these are not insurmountable problems, it would be advantageous if the isomer separation step, the resolution step, and the photochemical lability could be circumvented by the use of an appropriate ligand.

We,[7] and others,[8,9] have attempted to achieve these objectives by the use of chiral ligands analogous to the ligand in 1. These chiral ligands were expected to complex in a preferred absolute configuration about the metal. The three chiral ligands that have been described are shown as 2,[7] 3,[8] and 4.[9] The (S,S)-chiracene, which is most

S,S-chiracene

2   3   4
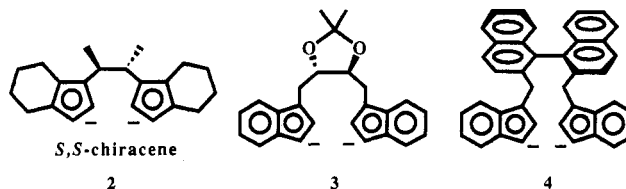
directly related to the ligand in 1, gives mixtures of isomers of both its titanium and zirconium complexes, and the titanium species required photochemical interconversion in order to obtain the desired diastereomerically pure C₂ isomer.[7] The ligand 3 gave only the meso isomer for the

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zirconium complex and probably also for the titanium analog.[8] In addition it possesses the acid-sensitive acetonide group. Ligand 4 does give the desired chiral isomers for both its titanium and zirconium complexes but has an unexpected characteristic where the preferred arrangement of the two bound indenyl ligands is such that they are not (C_2) symmetrically disposed. For the titanium dichloride complex the barrier to conformational interconversion between the equivalent C_1 isomers is high $(\Delta G^* \sim 13$ kcal/mol). Thus each of these ligands has its own problems and we were prompted to search for other analogous chiral ligands which might obviate the undesirable aspects associated with the previous ligands. This paper describes the preparation of the precursor to the chiral ligand $(R,-R)$-cyclacene (5) and the characterization of its titanium complex (S,S)-[Ti$((R,R)$-cyclacene)Cl₂] (6). As we show, this system may have advantages over previously described complexes.

R,R-cyclacene   S,S-[Ti(R,R-cyclacene)Cl₂]

5   6
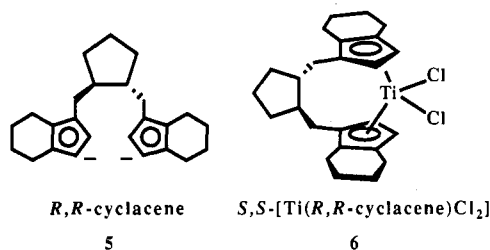
Ligand Precursor Synthesis

The starting point for synthesis of the ligand was the excellent diastereoselective synthesis[10] of di-$(1R,2S,5R)$-menthyl $(1S,2S)$-trans-1,2-cyclopentanedicarboxylate (7) from the dianion of (−)-dimenthyl succinate and the ditosylate of 1,3-dihydroxypropane. Reduction of 7 gave,

7   8   9   10
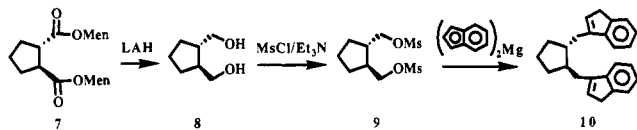
after careful distillation, the diol 8 (92% yield), which was converted to its dimesylate 9 (90% yield). We found that the most efficient method of converting 9 into the desired product 10 was by use of the bis(indenyl)magnesium[11] reagent in THF solution. The desired product was obtained in 83% yield from 9 or 40% overall yield from (−)-dimenthyl succinate as an oil. It consisted of only the stable double-bond isomer shown in 10. The use of the bis(indenyl)magnesium reagent, which was used by us for the synthesis of (S,S)-chiracene,[7] appears to be generally a more satisfactory reagent for the synthesis of bis(indene) species. Thus we found that the use of indenyllithium for the reaction with the ditosylate of 8 gave a mixture of products of which the desired product 10 was present in only 43% yield. The rest of the material consisted of spiro-annulated indene (20%) and unidentified volatile and polymeric materials.

(S,S)-[Ti$((R,R)$-cyclacene)Cl₂]

The dilithio salt of 10 was allowed to react with TiCl₄·2THF under high-dilution conditions in THF solution to give the bis(indenyl) product, which, upon reduction with PtO₂/H₂, gave (S,S)-[Ti$((R,R)$-cyclacene)Cl₂] as the sole isomer product in 20% yield as long red crystals. No other monomeric isomers of the bis(indenyl) complex or
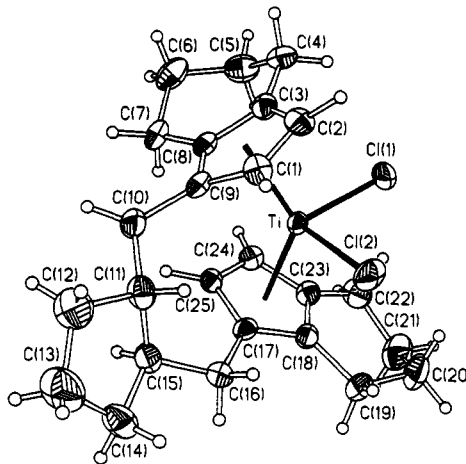
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Figure 1. Molecular structure and labeling scheme for (S,S)-[Ti$((R,R)$-cyclacene)Cl₂] (6) drawn with 40% probability ellipsoids.

Table I. Structure Determination Summary

Crystal Data	
empirical formula	$C_{25}H_{32}Cl_2Ti$
color	dark red
cryst size	$0.28 \times 0.30 \times 0.52$ mm
cryst system	orthorhombic
space group	$P2_12_12_1$
unit cell dimenss	$a = 8.462$ (2) Å
	$b = 12.524$ (3) Å
	$c = 20.921$ (4) Å
V	2217.2 (9) Å³
Z	4
fw	451.3
D(calc)	1.352 g/cm³
abs coeff	6.36 cm⁻¹
Data Collection	
diffractometer	Siemens P4
radiation	Mo Kα ($\lambda = 0.71073$ Å)
temp	299 K
monochromator	highly oriented graphite crystal
2θ range	4.0–51.0°
scan type	modified Ω
std reflcns	3 measd every 197 reflcns
no. of reflcns collcd	2764
no. of indpdt reflcns	2740
no. of obsd reflcns	2018 ($F > 4.0\sigma(F)$)
Solution and Refinement	
refinement method	full-matrix least-squares
quant minimized	$\sum w (F_o - F_c)^2$
absolute struct	$\eta = 1.12$ (10)
no. of params refined	254
final R indices (obsd data)	$R = 4.20\%$, $R_w = 4.71\%$
R indices (all data)	$R = 6.38\%$, $R_w = 5.24\%$
goodness-of-fit	1.03
largest and mean Δ/σ	0.405, 0.021
data-to-param ratio	7.9:1
largest diff peak	0.27 e Å⁻³
largest diff hole	−0.26 e Å⁻³

the cyclacene complex were detected by ¹H NMR spectroscopy.

A single-crystal X-ray diffraction structure of the complex is shown in Figure 1, crystallographic data are listed in Table I, and selected bond lengths and angles are provided in Table III. Although bond lengths and angles are unexceptional, the structure does not possess a C_2 axis. The tetrahydroindenyl ligands are twisted so that one ring projects at one of the chloro ligands while the other is twisted away from the other chloro ligand. The structure is reminiscent of that found for the titanium complex of ligand 4.

The ¹H NMR spectrum of (S,S)-[Ti$((R,R)$-cyclacene)Cl₂] in CD₂Cl₂ at 25 °C, however, indicates that on an ¹H NMR

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	$U(eq)^a$
Ti	2662 (1)	3740 (1)	3780 (1)	31 (1)
Cl(1)	808 (2)	2403 (1)	3567 (1)	56 (1)
Cl(2)	863 (2)	4802 (1)	4354 (1)	61 (1)
C(1)	3814 (5)	3771 (4)	4805 (2)	42 (1)
C(2)	3120 (6)	2760 (4)	4729 (2)	44 (1)
C(3)	3990 (5)	2202 (4)	4260 (2)	38 (1)
C(4)	3836 (6)	1055 (4)	4054 (2)	50 (1)
C(5)	4807 (7)	845 (4)	3465 (3)	65 (1)
C(6)	6466 (6)	1283 (5)	3528 (3)	63 (1)
C(7)	6467 (5)	2510 (4)	3586 (2)	45 (1)
C(8)	5192 (5)	2875 (4)	4033 (2)	35 (1)
C(9)	5083 (5)	3875 (4)	4373 (2)	36 (1)
C(10)	6309 (6)	4749 (4)	4378 (3)	48 (1)
C(11)	5752 (6)	5903 (4)	4457 (2)	47 (1)
C(12)	7008 (8)	6573 (5)	4792 (3)	85 (1)
C(13)	6874 (9)	7671 (6)	4550 (4)	101 (1)
C(14)	5624 (7)	7708 (4)	4048 (3)	64 (1)
C(15)	5377 (6)	6536 (3)	3845 (2)	45 (1)
C(16)	3720 (5)	6398 (4)	3552 (2)	44 (1)
C(17)	3366 (5)	5359 (4)	3226 (2)	36 (1)
C(18)	1872 (5)	5094 (4)	2947 (2)	39 (1)
C(19)	400 (6)	5760 (4)	2924 (3)	53 (1)
C(20)	-971 (6)	5132 (5)	2664 (3)	76 (1)
C(21)	-570 (7)	4481 (6)	2084 (3)	83 (1)
C(22)	737 (6)	3653 (5)	2225 (3)	61 (1)
C(23)	2014 (5)	4112 (4)	2627 (2)	39 (1)
C(24)	3583 (5)	3742 (4)	2722 (2)	38 (1)
C(25)	4415 (5)	4534 (4)	3065 (2)	36 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(500 MHz) time scale, the molecule is symmetrical. Thus, for example, the Cp protons consist of two sharp doublets whereas a C_1 structure would show four Cp proton signals. On cooling of the solution to 60 °C, all proton signals remain sharp and there is no evidence of broadening. These observations admit two possible explanations: either the molecule exists as a C_2 symmetric structure in solution and the observed C_1 structure is a result of crystal packing or the molecule prefers to exist in a C_1 structure which undergoes rapid conformational interchange between two equivalent C_1 structures. This process involves the interchange of the positions of the two tetrahydroindenyl groups by rotation via a C_2 symmetric structure. A consideration of a scale molecular model of the molecule suggests that the C_1 structure is more stable than the symmetrical C_2 structure, which appears to represent the transition state for the interconversion. If the C_1 structure is indeed preferred, as we believe, then the barrier to interconversion is low unlike the case of the analogous complex formed with the ligand 4.[9] We note that Brintzinger[12] was the first to observe this phenomenon with an analogous titanium complex which contained a trimethylene strap. In the crystal, this complex displays a similar unsymmetrical C_1 structure, but in solution, the ¹H NMR spectrum indicated that on an NMR time scale the two tetrahydroindenyl ligands are equivalent.

The preparation of [Ti((S,S)-chiracene)Cl₂] gives a mixture of isomers from which the species (R,R)-[Ti((S,-S)-chiracene)Cl₂] can be isolated. The absolute configuration about the metal center in this complex is opposite to that of (S,S)-[Ti((R,R)-cyclacene)Cl₂]. This difference should be reflected in the circular dichroism spectra of the two complexes, which are shown in Figure 2. It will be noted that the circular dichroism spectra are considerably different although in an overall sense the two spectra have

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Table III. Selected Bond Distances and Angles

Bond Distances (Å)

Ti–Cl(1)	2.337 (2)	C(7)–C(8)	1.500 (6)
Ti–Cl(2)	2.351 (2)	C(8)–C(9)	1.443 (6)
Ti–C(1)	2.355 (4)	C(9)–C(10)	1.508 (7)
Ti–C(2)	2.366 (5)	C(10)–C(11)	1.530 (7)
Ti–C(3)	2.446 (5)	C(11)–C(12)	1.525 (8)
Ti–C(8)	2.457 (4)	C(11)–C(15)	1.539 (7)
Ti–C(9)	2.401 (4)	C(12)–C(13)	1.469 (9)
Ti–C(17)	2.411 (5)	C(13)–C(14)	1.491 (10)
Ti–C(18)	2.522 (5)	C(14)–C(15)	1.542 (7)
Ti–C(23)	2.518 (5)	C(15)–C(16)	1.540 (7)
Ti–C(24)	2.347 (4)	C(16)–C(17)	1.500 (7)
Ti–C(25)	2.330 (4)	C(17)–C(18)	1.431 (6)
Ti–CNT(1)	2.083 (4)	C(17)–C(25)	1.403 (6)
Ti–CNT(2)	2.108 (4)	C(18)–C(19)	1.500 (7)
C(1)–C(2)	1.404 (7)	C(18)–C(23)	1.406 (7)
C(1)–C(9)	1.410 (6)	C(19)–C(20)	1.504 (8)
C(2)–C(3)	1.412 (6)	C(20)–C(21)	1.500 (10)
C(3)–C(4)	1.505 (7)	C(21)–C(22)	1.545 (8)
C(3)–C(8)	1.404 (6)	C(22)–C(23)	1.484 (7)
C(4)–C(5)	1.504 (8)	C(23)–C(24)	1.421 (6)
C(5)–C(6)	1.513 (8)	C(24)–C(25)	1.413 (6)
C(6)–C(7)	1.542 (8)		

Bond Angles (deg)

Cl(1)–Ti–Cl(2)	93.9 (1)	C(12)–C(11)–C(15)	104.1 (4)
CNT(1)–Ti–CNT(2)	131.2 (2)	C(11)–C(12)–C(13)	107.6 (5)
CNT(1)–Ti–Cl(1)	106.3 (2)	C(12)–C(13)–C(14)	109.1 (6)
CNT(1)–Ti–Cl(2)	107.2 (2)	C(13)–C(14)–C(15)	105.1 (5)
CNT(2)–Ti–Cl(1)	107.1 (2)	C(11)–C(15)–C(14)	103.5 (4)
CNT(2)–Ti–Cl(2)	105.0 (2)	C(11)–C(15)–C(16)	117.5 (4)
C(2)–C(1)–C(9)	109.3 (4)	C(14)–C(15)–C(16)	109.8 (4)
C(1)–C(2)–C(3)	107.8 (4)	C(15)–C(16)–C(17)	117.4 (4)
C(2)–C(3)–C(4)	128.8 (4)	C(16)–C(17)–C(18)	124.3 (4)
C(2)–C(3)–C(8)	108.4 (4)	C(16)–C(17)–C(25)	128.4 (4)
C(4)–C(3)–C(8)	122.6 (4)	C(18)–C(17)–C(25)	106.9 (4)
C(3)–C(4)–C(5)	110.8 (4)	C(17)–C(18)–C(19)	128.1 (4)
C(4)–C(5)–C(6)	111.9 (5)	C(17)–C(18)–C(23)	108.8 (4)
C(5)–C(6)–C(7)	111.7 (4)	C(19)–C(18)–C(23)	122.8 (4)
C(6)–C(7)–C(8)	110.6 (4)	C(18)–C(19)–C(20)	111.2 (4)
C(3)–C(8)–C(7)	123.3 (4)	C(19)–C(20)–C(21)	113.8 (5)
C(3)–C(8)–C(9)	108.0 (4)	C(20)–C(21)–C(22)	111.8 (5)
C(7)–C(8)–C(9)	128.1 (4)	C(21)–C(22)–C(23)	111.7 (5)
C(1)–C(9)–C(8)	106.5 (4)	C(18)–C(23)–C(22)	123.2 (4)
C(1)–C(9)–C(10)	126.0 (4)	C(18)–C(23)–C(24)	107.3 (4)
C(8)–C(9)–C(10)	126.1 (4)	C(22)–C(23)–C(24)	129.3 (4)
C(9)–C(10)–C(11)	118.3 (4)	C(23)–C(24)–C(25)	107.9 (4)
C(10)–C(11)–C(12)	110.8 (4)	C(17)–C(25)–C(24)	108.9 (4)
C(10)–C(11)–C(15)	117.4 (4)		
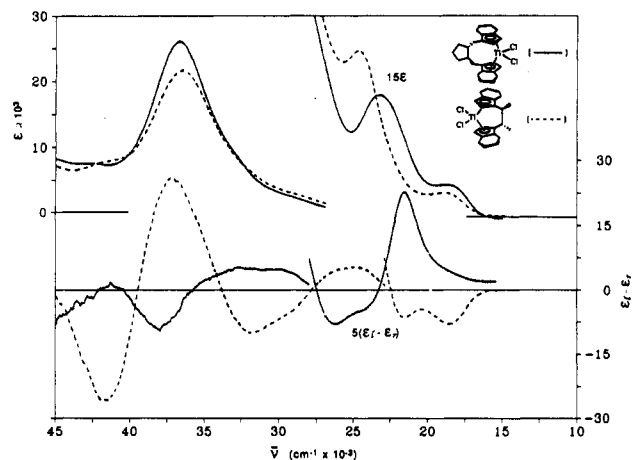
Figure 2. Electronic absorption and circular dichroism spectra of (S,S)-[Ti((R,R)-cyclacene)Cl₂] (6) and (R,R)-[Ti((S,S)-chiracene)Cl₂] in THF solution.

opposite signs in about the same regions.

Discussion

Our initial objective of designing a chiral strapped ligand which would give a single chiral diastereomer of the bent

metallocene has been met by the use of (R,R)-cyclacene precursor, but the product does not appear to have the desired C_2 symmetric structure. We found that chloroform solutions of (S,S)-[Ti((R,R)-cyclacene)Cl₂], despite some slight decomposition, are stable to room light and remain isomerically pure, which fulfilled the other objective of this work.

The ligand effects which determine the stereochemistry of metallocenes are clearly subtle. Thus, the ligand **3** which resembles cyclacene gives only the meso diastereomer with zirconium and probably titanium whereas cyclacene produces the chiral (S,S)-isomer exclusively. Presumably, this difference in behavior reflects subtle differences in steric interactions emanating from the bridging groups, which may lead to different preferences for the geometry about the metal. The metallocene isomers from ligands **2–4** and **10** are obtained preparatively, however, and may not represent the thermodynamic preferences. For example, during the metalation of **10**, a single diastereomer could arise from the kinetic preference for formation of the (S,S)-monomer, whereas unfavorable ligand geometries may be required for the other diastereomeric monomers, resulting only in polymers, the major side products of the reaction. Given that the ligand **4** also gives unsymmetrical chiral complexes and chiracene gives C_2 symmetric species for the chiral isomer, it appears that extending the strap beyond two carbon atoms will lead to unsymmetrical arrangements of the bis(indenyl) or tetrahydroindenyl groups when bound to a metal. This effect probably arises from the fact that straps larger than two carbon atoms tend to expand the Cp-tilt angle in the C_2 structure and this angle is best accommodated by twisting the structure to one of its C_1 conformers.

The C_1 structure is not ideal for asymmetric synthesis since the two coordination positions where the substrate could bind are structurally different. On the other hand, none of these C_1 chiral molecules has been tested for enantioselection and there is no a priori reason to reject them for this purpose. We shall report on the use of (S,S)-[Ti((R,R)-cyclacene)Cl₂] and of the chiracene analog in asymmetric catalysis shortly.

Experimental Section

The NMR spectra were obtained on GE GN 500, GE QE 300, and Chicago built 500-MHz spectrometers. Chemical shifts are referenced against internal CHCl₃ (δ 7.26) or CHDCl₂ (δ 5.32). UV–visible spectra were recorded on a Varian-Carey 2400 spectrometer. Circular dichroism spectra were measured with a Jasco J-600 instrument. The following solvents were distilled under nitrogen immediately before use: tetrahydrofuran (THF) from potassium, methylene chloride from calcium hydride, and diethyl ether from lithium aluminum hydride (LAH). Triethylamine was distilled from calcium hydride. Manipulations of air- or moisture-sensitive compounds were carried out under argon atmosphere using Schlenk techniques. In the case of the metallocene preparations, filtration and washings of **11** could be conducted in air, as could filtrations and crystallizations of **6**. The adduct TiCl₄·2THF was prepared by an established procedure.[13]

(1S,2S)-trans-1,2-Bis(hydroxymethyl)cyclopentane (8). A solution of di-(1R,2S,5R)-menthyl (1S,2S)-trans-1,2-cyclopentanedicarboxylate[10] (**7**) (22.8 g, 52.5 mmol) in dry ether (75 mL) was added dropwise over 50 min to a stirred suspension of LAH (4.20 g, 110.7 mmol) in dry ether (300 mL) under argon. The mixture was stirred overnight at ambient temperature and then ice-cooled and quenched by the sequential dropwise addition of H₂O (4.20 mL), 15% aqueous NaOH (4.20 mL), and H₂O (12.60 mL). The cooling bath was removed after the initial vigorous gas evolution had subsided. The resultant mixture, a white precipitate

in a clear supernatant, was refluxed for a few minutes, cooled, and filtered. The white precipitate was further extracted with boiling ether (2 × 100 mL) and the combined filtrates dried (Na₂SO₄ and K₂CO₃). After filtration the ether was removed and the residue distilled, yielding (1S,2S)-trans-1,2-bis(hydroxymethyl)cyclopentane (**8**) (6.29 g, 92%), a viscous colorless oil [bp₂.₅ 122–126 °C (lit.[14] (racemic mixture) bp₂₄ 127–129 °C)]. ¹H NMR (300 MHz, CDCl₃): δ 4.21 (s, 2 H), 3.74 (br d, J = 9.6 Hz, 2 H), 3.38–3.30 (m, 2 H), 1.90–1.74 (m, 4 H), 1.63–1.52 (m, 2 H), 1.34–1.17 (m, 2 H).

(1S,2S)-trans-1,2-Bis((mesyloxy)methyl)cyclopentane (9). A solution of methanesulfonyl chloride (2.47 mL, 31.9 mmol) in dry CH₂Cl₂ (5 mL) was added dropwise over 10 min to a vigorously stirred solution of (1S,2S)-trans-1,2-bis(hydroxymethyl)cyclopentane (**8**) (1.88 g, 14.4 mmol) and dry Et₃N (6.10 mL, 43.8 mmol) in dry CH₂Cl₂ (25 mL) immersed in a –35 °C dry ice/ethanol bath under argon. The stirred mixture was maintained at –30 °C (±5 °C) for 30 min and then allowed to warm to 0 °C over 30 min and poured into ice water (75 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (50 mL). The combined organic layers were washed with ice cold 10% aqueous HCl (2 × 50 mL), ice cold saturated aqueous NaCl (35 mL), ice cold saturated aqueous NaHCO₃ (2 × 50 mL), and H₂O (50 mL) and dried (MgSO₄). After filtration the solvent was removed and the residue, a yellow oil (4.12 g), dissolved in a little benzene was passed through a short plug of neutral alumina (8.0 g, Brockmann I) eluting with benzene yielding (1S,2S)-trans-1,2-bis((mesyloxy)methyl)cyclopentane (**9**) (3.68 g, 89%), a colorless oil which solidified when all of the solvent had been removed. ¹H NMR (500 MHz, CDCl₃): δ 4.20–4.14 (m, 4 H), 3.02 (s, 6 H), 2.18–2.10 (m, 2 H), 1.93–1.82 (m, 2 H), 1.71–1.62 (m, 2 H), 1.51–1.42 (m, 2 H).

(1R,2R)-trans-1,2-Bis(1-indenylmethyl)cyclopentane (10). Dry THF (25 mL) was quickly added to solid bis(indenyl)magnesium[11] (4.61 g, 18.1 mmol) under argon and the warm yellow-orange mixture stirred vigorously. After a few minutes (1S,2S-trans-1,2-bis((mesyloxy)methyl)cyclopentane (**9**) (3.68 g, 12.9 mmol) dissolved in dry THF (5 mL) was added dropwise sufficiently rapidly to maintain reflux. The mixture was stirred an additional 5 min and then refluxed for 3.5 h. After cooling, the brown reaction mixture was quenched by the addition of saturated NH₄Cl (50 mL). The reaction mixture was poured into H₂O (85 mL) and extracted with hexane/ether (2/1, 2 × 100 mL). The combined organic layers were washed with H₂O (2 × 100 mL) and dried (MgSO₄). After filtration the solvents were removed by rotary evaporator, and then the excess indene was removed under higher vacuum (0.2 mmHg, bath temperature 115 °C). The residue, a viscous dark red-orange oil (4.05 g), dissolved in a little hexane was passed through a short basic alumina column (25.0 g, Brockmann I) eluting with hexane, yielding (1R,2R)-trans-1,2-bis(1-indenylmethyl)cyclopentane (**10**) (3.49 g, 83%) as a light yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.43 (d, J = 7.3 Hz, 2 H), 7.33–7.15 (m, 6 H), 6.17 (br s, 2 H), 3.34–3.14 (m, 4 H), 2.80–2.68 (m, 2 H), 2.49–2.36 (m, 2 H), 2.10–1.98 (m, 2 H), 1.92–1.80 (m, 2 H), 1.64–1.54 (m, 2 H), 1.40–1.28 (m, 2 H).

(S,S)-[Ti((1R,2R)-trans-1,2-bis(1-indenylmethyl)cyclopentane)Cl₂] (11). A solution of (1R,2R)-trans-1,2-bis(1-indenylmethyl)cyclopentane (**10**) (2.350 g, 7.20 mmol) in THF (40 mL) was cooled to –78 °C and then was treated dropwise by syringe with a solution of n-butyllithium in hexane (9.5 mL, 1.6 M, 15.2 mmol) over 15 min. The red-brown solution was stirred at –78 °C for 1.25 h, warmed to room temperature, and transferred by cannula into a constant-addition dropping funnel. The solution volume was 70 mL. From a separate Schlenk flask, a solution of TiCl₄·2THF (2.404 g, 7.20 mmol) in THF (50 mL) was transferred into a second constant-addition dropping funnel and the solution similarly diluted to 70 mL. The two solutions were added dropwise simultaneously to a 1000-mL 3-neck flask containing THF (50 mL) at room temperature over a period of 2.5 h. The resulting dark brown solution was stirred for a further 17 h and then flushed with dry HCl gas for 30 s, during which the color did not change significantly. The solvents were removed under reduced pressure, the residue was slurried with ether (2 × 20 mL),

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and the slurry again was evaporated to dryness (to ensure complete removal of THF). The residue was slurried with ether (50 mL), filtered out, and washed with ether (50 mL). The solid was washed with aqueous HCl (4 N, 2 × 25 mL), H$_2$O (2 × 10 mL), EtOH (2 × 5 mL), ether (6 × 5 mL), and pentane (2 × 5 mL) and was finally dried under a steam of nitrogen gas. The dark green solid (1.084 g, 34%) was used in this form for hydrogenation. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.79 (d, *J* = 8.8 Hz, 2 H), 7.45 (pseudo-t, *J* = 7.7 Hz, 2 H), 7.38 (d, *J* = 8.7 Hz, 2 H), 7.29 (t, *J* = 7.4 Hz, 2 H), 6.57 (d, *J* = 3.2 Hz, 2 H), 5.17 (d, *J* = 3.1 Hz, 2 H), 3.39–3.34 (m, 2 H), 3.21 (d, *J* = 16.7 Hz, 2 H), 2.23–2.17 (m, 4 H), 1.75–1.70 (m, 2 H), 1.66–1.60 (m, 2 H).

(*S*,*S*)-[Ti((1*R*,2*R*)-*trans*-1,2-bis((tetrahydro-1-indenyl)-methyl)cyclopentane)Cl$_2$] (6). A solution of (*S*,*S*)-[Ti-((1*R*,2*R*)-*trans*-1,2-bis(1-indenylmethyl)cyclopentane)Cl$_2$] (11) (1.071 g, 2.42 mmol) and a suspension of PtO$_2$ (0.033 g, 0.145 mmol) in CH$_2$Cl$_2$ (100 mL) was stirred in a Parr pressure hydrogenator under 60 atm of H$_2$ gas for 19.5 h. The resulting red solution was filtered through a cotton plug and the solvent removed in vacuo. The red oily residue was extracted with acetone (50 mL), the extract was filtered through Celite, and the solvent was removed in vacuo. A second extraction was performed with boiling hexane (200 mL) and the filtered solution again evaporated to dryness. The red solid residue was chromatographed on a column of silanized silica gel (EM Science, 70-230 mesh, 25 g, 1/9 benzene/hexane eluent) and then crystallized from CH$_2$Cl$_2$/hexane (1/6, 35 mL) by gentle warming on a steam bath to remove CH$_2$Cl$_2$, followed by cooling to room temperature. An initial crop of 6 (0.293 g) was produced that was washed with pentane (2 × 5 mL). Successive crystallizations of the evaporated supernatant produced further crops that when combined gave a total mass

of 6 (0.635 g, 58%) as long red needles. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ 6.20 (d, *J* = 2.9 Hz, 2 H), 5.52 (d, *J* = 2.9 Hz, 2 H), 3.17–3.11 (m, 2 H), 2.79–2.71 (m, 4 H), 2.55–2.49 (m, 4 H), 2.46–2.40 (m, 2 H), 2.04–1.97 (m, 2 H), 1.87–1.83 (m, 2 H), 1.80–1.73 (m, 2 H), 1.68–1.60 (m, 6 H), 1.58–1.53 (m, 2 H), 1.50–1.43 (m, 2 H). Anal. Calcd for C$_{25}$H$_{32}$Cl$_2$Ti: C, 66.53; H, 7.15; Cl, 15.71. Found: C, 66.78; H, 7.05; Cl, 15.72. [α]$^{25}_{436}$ = −2240° (10 cm, c = 2.5 mg/100 mL, CHCl$_3$).

Crystal Structure Determination. Crystallographic data are collected in Table I. A dark red specimen possessed *mmm* Laue symmetry, and systematic absences in the diffraction data uniquely identified the orthorhombic space group *P*2$_1$2$_1$2$_1$. No correction for absorption was required ($T_{max/min}$ = 1.05). The structure was solved by direct methods and refined with all non-hydrogen atoms anisotropic. Hydrogen atoms were treated as idealized contributions. All computations used Siemens SHELXTL PLUS (VMS) software (G. Sheldrick, Siemens Analytical X-Ray Instruments, Madison, WI). Atomic Coordinates are given in Table II, and selected bond distances and angles are in Table III.

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Synthesis, Characterization, and Structure of Acetylenic Gallium Dialkylphosphides Having the Formula [(*t*-Bu)(Me$_3$SiC≡C)GaPR$_2$]$_2$ (R = Et, *i*-Pr, *t*-Bu)

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Reactions of the gallium acetylide [(*t*-Bu)$_2$GaC≡CSiMe$_3$]$_2$ and 2 equiv of the phosphines R$_2$PH (R = Et, *i*-Pr, *t*-Bu) in toluene at 140 °C give the acetylenic gallium dialkylphosphide dimers [(*t*-Bu)-(Me$_3$SiC≡C)GaPR$_2$]$_2$ (61–81%) as cis and trans isomers. Single-crystal X-ray analysis of colorless cubes obtained from a cold hexane solution of cis- and trans-[(*t*-Bu)(Me$_3$SiC≡C)GaPEt$_2$]$_2$ shows the crystals to be trans-[(*t*-Bu)(Me$_3$SiC≡C)GaPEt$_2$]$_2$ (monoclinic, *P*2$_1$/*n* (No. 14); *a* = 10.023 (6) Å, *b* = 16.271 (9) Å, *c* = 12.292 (8) Å, β = 113.91 (5)°, *V* = 1833 (2) Å^3, *Z* = 4). Dimer formation occurs via Ga–P bonding in a planar Ga$_2$P$_2$ ring. The ^{13}C{^{1}H} and ^{13}C NMR spectra of these dimers also give evidence for a gallium–phosphorus bridge.

Introduction

Monomeric, dimeric, and trimeric alkylgallium dialkylphosphides are currently being investigated as potential single-source precursors for the metal–organic chemical vapor deposition (MOCVD) of gallium phosphide (GaP) semiconducting films.[1–4] Source compounds featuring Et, *i*-Pr, and *t*-Bu alkyl groups are of interest since it has been demonstrated that lower film growth temperatures can be achieved with precursors having β-hydrogens which facilitate hydrocarbon elimination.[4] Prior to 1986, the only example of a dimeric alkylgallium dialkylphosphide compound was [Me$_2$GaPPh$_2$]$_2$.[5] However, in recent years, many of these dimers have been prepared and several have been structurally characterized.[1,2] In this

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