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# Stereochemical Consequences of a Parity Restriction on Dynamic Gearing in Tris(9-triptycyl)germanium Chloride and Tris(9-triptycyl)cyclopropenium Perchlorate

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**Abstract:** Crystal and molecular structures of tris(9-triptycyl)germanium chloride (**1**) and tris(9-triptycyl)cyclopropenium (**2**) perchlorate were determined. Crystals of **1** are trigonal, space group $R3c$ (No. 161), with $a = b = 13.090$ (3) Å, $c = 43.58$ (1) Å, $Z = 6$. Crystals of **2** perchlorate are hexagonal, space group $P6_3/m$ (No. 176), with $a = b = 15.145$ (5) Å, $c = 13.617$ (4) Å, $Z = 2$. Both **1** and **2** are located on crystallographic 3-fold rotation axes, with site symmetries $C_3$ for **1** and $C_{3h}$ for **2**. The same symmetries are maintained in solution at room temperature on the NMR time scale. The enantiomers of **1** were separated by HPLC on a column of (−)-poly(triphenylmethyl methacrylate). The racemization barrier for **1** is 19.0 kcal mol$^{-1}$ and the topomerization barrier of **2** is similar in magnitude, as judged by the 22.2 and 23.4 kcal mol$^{-1}$ required for the interconversion of the achiral and DL diastereomers of bis(9-triptycyl)(2,3-dimethyl-9-triptycyl)cyclopropenium ion (**3**). Considering that barriers of less than 5 kcal mol$^{-1}$ need to be overcome to achieve correlated disrotation of 9-triptycyl groups in bis(9-triptycyl)methane and related compounds, these observations show that uncorrelated as well as correlated rotation is mechanically disallowed in a closed cyclic array consisting of an odd number of securely meshed gears, thus providing compelling evidence for the operation of a mechanical (parity) selection rule at the molecular level.

As exemplified by molecular propellers[2] and molecular bevel gears,[3] the torsional motions of two or more chemical rotors may be so strongly coupled that correlated rotation becomes energetically preferred over the independent rotation of the individual groups and may, in appropriately substituted molecules, give rise to phase isomerism.[4] In previous work[3] it had been shown that the 9-triptycyl (Tp) groups in molecules of the type $Tp_2Z$ ($Z = CH_2$, O, CO, etc.) behave as highly mobile (i.e., almost frictionless) and tightly meshed (i.e., securely interlocked) bevel gears, with a gearing trajectory that is virtually flat and that runs along the bottom of a deep and narrow canyon on the potential energy hypersurface. The disrotatory cogwheeling motion in these systems arises from complementary nonbonded interactions between snugly fitting Tp rotors in which the benzene ring of one Tp moiety, acting as a cog in one gear, fits into the V-shaped notch formed by two rings of the other. Indeed, because correlated disrotation in such $Tp_2Z$ systems is favored by 30–40 kcal mol$^{-1}$ over all other internal motions, *mechanical selection rules* (disrotation allowed, conrotation disallowed) in molecular gear systems under steric control can be more strictly obeyed than the selection rules for concerted torsions under orbital symmetry control (such as con- and disrotatory electrocyclic reactions) in which energy differences between allowed and disallowed processes are seldom (if ever) of this magnitude.

**Table I.** Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å$^2$ × 10$^3$) for **1**[a]

| atom | $x$ | $y$ | $z$ | $U$[b] |
|---|---|---|---|---|
| Ge | 0 | 0 | 0 | 28 (1) |
| Cl | 0 | 0 | 506 (1) | 42 (1) |
| C(1) | −2150 (5) | −2566 (5) | 419 (1) | 57 (2) |
| C(2) | −2988 (5) | −3503 (6) | 590 (1) | 76 (3) |
| C(3) | −3448 (5) | −4631 (5) | 497 (2) | 76 (3) |
| C(4) | −3094 (4) | −4846 (4) | 220 (1) | 59 (3) |
| C(4a) | −2269 (4) | −3935 (4) | 45 (1) | 47 (2) |
| C(5) | −2682 (5) | −3779 (5) | −754 (1) | 64 (3) |
| C(5a) | −2022 (4) | −3367 (4) | −487 (1) | 46 (2) |
| C(6) | −2783 (5) | −3007 (6) | −952 (1) | 72 (4) |
| C(7) | −2227 (5) | −1829 (5) | −882 (1) | 61 (3) |
| C(8) | −1594 (4) | −1421 (4) | −610 (1) | 45 (2) |
| C(8a) | −1495 (4) | −2172 (4) | −410 (1) | 38 (2) |
| C(9) | −823 (3) | −1865 (3) | −97 (1) | 33 (2) |
| C(9a) | −1765 (4) | −2763 (4) | 139 (1) | 40 (2) |
| C(10) | −1810 (4) | −4095 (4) | −260 (1) | 53 (2) |
| C(11) | −497 (4) | −3518 (4) | −218 (1) | 49 (2) |
| C(12) | 41 (4) | −2340 (4) | −124 (1) | 38 (2) |
| C(13) | 1213 (5) | −1772 (5) | −54 (1) | 58 (3) |
| C(14) | 1881 (5) | −2301 (5) | −84 (2) | 87 (4) |
| C(15) | 1350 (6) | −3462 (6) | −188 (2) | 90 (4) |
| C(16) | 159 (5) | −4075 (5) | −251 (1) | 70 (3) |

[a] Standard deviations in parentheses. For numbering of atoms, see ref 15. Parameters for hydrogen are given in the supplementary material. [b] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

The present work describes a further test of these rules.[5] If $N$ meshed cogwheels are arranged in a cycle, dynamic gearing (i.e., correlated disrotation through multiples of $2\pi$) is allowed if $N$ is even but disallowed if $N$ is odd.[6] The correlated disrotation of methyl groups in hexamethylbenzene might be cited as a chemical example of the first parity rule,[7] but no example has previously been reported for the second. Thus, although the three *tert*-butyl groups in molecules of the type $(Me_3C)_3ZX$ are brought into close spatial proximity, enantiomerization of the $C_3$ structures

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[1] (a) Princeton University. (b) Osaka University.

[2] (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3198. (b) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (c) Glaser, R.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2777.

[3] Iwamura, H.; Mislow, K. *Acc. Chem. Res.* **1988**, *21*, 175 and references therein.

[4] Correlated rotation imposes a constraint on the *relationship* among the torsion angles of the rotors, even though there are no restrictions on the torsion angle of any one *individual* rotor. With the phase relationship among the rotors fixed, some interconversion pathways among the full set of conformers are blocked. As a result, residual stereoisomers (phase isomers) may be generated.[2,3]

[5] Portions of this work were reported in preliminary communications: (a) Chance, J. M.; Geiger, J. H.; Mislow, K. *J. Am. Chem. Soc.* **1989**, *111*, 2326. (b) Mislow, K. *Chemtracts-Org. Chem.* **1989**, *2*, 151.

[6] Disrotation in an array of $N$ securely meshed cogwheels requires an alternation of clockwise and anticlockwise motions along the gear train. In cyclic gear trains this alternation is possible only if $N$ is even.

[7] This motion is favored at very low temperatures, but uncorrelated rotation is the likely process under normal conditions because the methyl groups are not well meshed. See: Melissas, V.; Faegri, K., Jr.; Almlöf, J. *J. Am. Chem. Soc.* **1985**, *107*, 4640 and references therein. Where such groups *are* well meshed, as in hexaisopropylbenzene and related compounds, the threshold mechanism for conformational interconversion is invariably a stepwise, i.e. uncorrelated, rotation of one side chain at a time.[8] Nevertheless, *all* hexaalkylbenzenes are at least in principle capable of correlated disrotation, even where such pathways might entail the crossing of high-energy regions on the potential energy hypersurface.

[8] (a) Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569. (b) Schuster, I. I.; Weissensteiner, W.; Mislow, K. *Ibid.* **1986**, *108*, 6661. (c) Kahr, B.; Biali, S. E.; Schaefer, W.; Buda, A. B.; Mislow, K. *J. Org. Chem.* **1987**, *52*, 3713.

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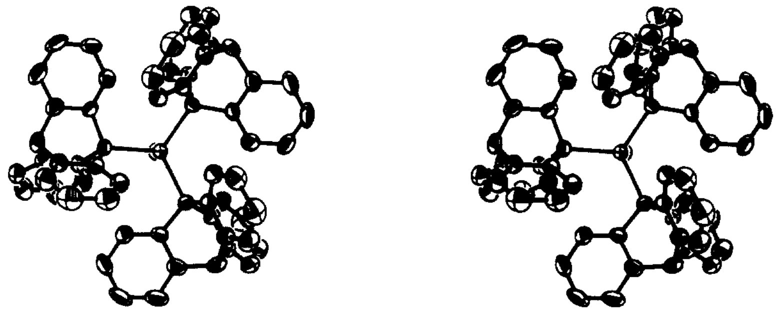

**Figure 1.** Stereoview of the X-ray structure of **1** along the $C_3$ axis, with the chlorine atom located on the far side and with thermal motion ellipsoids (50% probability). Hydrogen atoms are suppressed for clarity.

**Table II.** $^1H$ NMR Spectral Parameters for **1** in $CDCl_3$[a]

| ring no.[b] | chemical shifts[c] H(*n*)[e] | H(*o*)[f] | H(*m*)[g] | H(*p*)[h] | coupling constants[d] $^3J$ | $^4J$ | $^5J$ |
|---|---|---|---|---|---|---|---|
| A | 7.21 (dd) | 6.62 (ddd) | 5.68 (ddd) | 8.08 (d) | $J_{no} = 7.7$<br>$J_{om} = 7.2$<br>$J_{mp} = 7.8$ | $J_{nm} = 1.3$<br>$J_{op} = 0.9$ | |
| B | 7.33 (dd) | 6.80 (ddd) | 5.90 (ddd) | 7.77 (d) | $J_{no} = 7.2$<br>$J_{om} = 7.6$<br>$J_{mp} = 7.5$ | $J_{nm} = 1.4$<br>$J_{op} = 0.9$ | |
| C | 7.43 (ddd) | 7.06 (two overlapping multiplets)[i] | | 9.51 (ddd) | $J_{no} \approx 5.1$<br>$J_{mp} \approx 4.5$ | $J_{nm} \approx 3.8$<br>$J_{op} \approx 4.5$ | $J_{np} < 1.0$ |

[a] 250.1 MHz, ambient temperatures. [b] The relationships of the protons within each ring are known, but the identity of the individual rings is not established. [c] In ppm downfield from TMS. Multiplicities in parentheses. [d] In hertz. [e] Protons nearest to H(10), i.e., H(4), H(5), H(16). [f] Protons ortho to H(*n*), i.e., H(3), H(6), H(15). [g] Protons meta to H(*n*), i.e., H(2), H(7), H(14). [h] Protons para to H(*n*), i.e., H(1), H(8), H(13). [i] Accidental isochrony of two signals, as shown by the relative integrated intensity.

takes place at very low temperatures on the NMR time scale by processes that involve the conrotatory motion of two or all three *tert*-butyl groups,[9] indicative of extremely facile gear slippage.

Realization of the second parity rule at the molecular level evidently requires rotors, such as Tp groups, that are securely meshed. Among molecules of the appropriate type, our first choice for a test of this rule fell on tris(9-triptycyl)germanium chloride, $Tp_3GeCl$ (**1**), which is readily accessible by reaction of TpLi with $GeCl_4$.[10] $Tp_3ZX$ compounds of this type exemplify a novel species of molecular propeller in which each of the three aryl blades is replaced by a three-toothed Tp gear. The axes of the Tp gears in **1** are coextensive with the C(9)–Ge bonds to form a pyramidal array with the Ge atom at the apex. In order to test the second parity rule on a system in which the three Tp bevel gear axes form a coplanar array, we also investigated tris(9-triptycyl)cyclopropenium (**2**) perchlorate ($Tp_3C_3^+ClO_4^-$), in which the extensions of the three coplanar gear axes intersect at the center of the molecule. This compound was readily prepared from bis(9-anthryl)cyclopropenone:[12] double addition of benzyne gave bis(9-triptycyl)cyclopropenone, and addition of TpLi to the latter followed by reaction with $HClO_4$ afforded the perchlorate of **2**.

## Tris(9-triptycyl)germanium Chloride

**Crystal and Molecular Structure.** X-ray data for a crystal of **1** grown from 1-butanol/ethyl acetate were collected at 237 K. The crystals belong to the trigonal system, space group *R*3*c* (No. 161), with $a = b = 13.090$ (3) Å, $c = 43.58$ (1) Å, and $Z = 6$. Final atomic parameters are listed in Table I. The molecule is located on a crystallographic 3-fold axis and therefore has $C_3$ site symmetry (Figure 1).[13] As might be expected from previous experience with $Tp_2Z$ compounds,[3] internal strain in the sterically congested **1** gives rise to substantial structural deformations in the environment of the bridgehead carbon atoms attached to Ge. All four bonds emanating from C(9) are significantly stretched: the Ge–C(9) bond distances are 2.161 (4) Å, as compared with a literature norm of ca. 1.98 Å,[14] and the C(9)–C(8a), C(9)–C(9a), and C(9)–C(12) bond distances[15] are 1.560 (6), 1.586 (5), and 1.544 (8) Å, respectively, as compared with the average C(9)–$C_{ar}$ or C(10)–$C_{ar}$ bond distance of ca. 1.53 Å in triptycene itself (1.523,[16a] 1.534,[16b] 1.526[16c] Å).[17] The Ge–Cl bond distance

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(9) (a) Hounshell, W. D.; Iroff, L. D.; Wroczynski, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 5212. (b) Wroczynski, R. J.; Mislow, K. *Ibid.* **1979**, *101*, 3980.

(10) A compound of this type, $Tp_3SnCl$, had previously been claimed by Ranson and Roberts.[11] These workers had characterized their product by melting point and elemental analysis for carbon and hydrogen, but their report contained no information on the NMR spectrum, nor did it raise the possibility that the Tp rotors might be immobilized. In our hands their procedure led to an ca. 7:1 mixture of $Tp_3SnCl$ and $Tp_3SnBr$ (see Experimental Section) which we were unable to separate by crystallization, TLC, or HPLC.

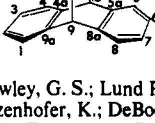
(11) Ranson, R. J.; Roberts, R. M. G. *J. Organomet. Chem.* **1976**, *107*, 295.

(12) Wadsworth, D. H.; Donatelli, B. A. *Synthesis* **1981**, 285. Becker, H.-D.; Andersson, K. *J. Org. Chem.* **1987**, *52*, 5205.

(13) In its symmetry $Tp_3GeCl$ thus resembles molecules of the type $(Me_3C)_3ZX$, which also contain three 3-fold rotors attached to a pyramidal center,[9] and trimesitylmethane, a molecular propeller whose crystallographic and ground-state symmetry is also $C_3$. See: (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2165. (b) Andose, J. D.; Mislow, K. *Ibid.* **1974**, *96*, 2168. (c) Blount, J. F.; Mislow, K. *Tetrahedron Lett.* **1975**, 909.

(14) For example, see: Glockling, F. *The Chemistry of Germanium*; Academic Press: New York, 1969; p 13.

(15) We adopt the IUPAC and Chemical Abstracts numbering for triptycene (9,10-dihydro-9,10-*o*-benzenoanthracene) shown below. See: *Nomenclature of Organic Chemistry*; IUPAC (Organic Chemistry Division), Commission of Nomenclature of Organic Chemistry, prepared by J. Rigaudy and S. P. Klesney; Pergamon Press: Oxford, 1979; Rule A-34.1, p 35.



(16) (a) Hazell, R. G.; Pawley, G. S.; Lund Petersen, C. E. *J. Cryst. Mol. Struct.* **1971**, *1*, 319. (b) Anzenhofer, K.; DeBoer, J. J. *Z. Kristallogr.* **1970**, *131*, 103. (c) Neuman, M. A. *Trans. Am. Cryst. Assoc.* **1970**, *6*, 111.

(17) The stretching of bonds terminating at C(9) in turn leads to a significant *contraction* of the bonds emanating from C(10) (C(10)–C(5a) = 1.494 (8) Å, C(10)–C(4a) = 1.515 (8) Å, and C(10)–C(11) = 1.504 (7) Å). The average values of the C(9)–C and C(10)–C bond lengths, 1.563 and 1.504 Å, thus straddle the normal bond length of 1.53 Å.

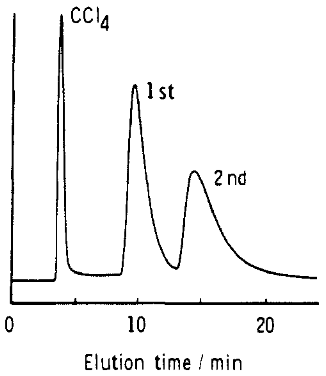


**Figure 2.** Resolution of **1** by chromatography on (−)-poly(triphenylmethyl methacrylate). Eluent: methanol at −30 °C.

of 2.204 (2) Å and the C–Ge–C bond angles of 116.3 (1)° provide further evidence of internal strain near C(9),[18] as does the distortion in the Ge–C(9)–C bond angles (118.3 (3), 114.7 (2), and 111.1 (3)° in Ge–C(9)–C(9a), Ge–C(9)–C(12), and Ge–C(9)–C(8a), respectively). With the exception of C(1)–C(9a)–C(4a), which is markedly compressed (116.5 (4)°), all $C_{ar}$–$C_{ar}$–$C_{ar}$ and internal $C_{ar}$–$C_{ar}$–C(9)/C(10) angles assume more nearly normal values (118–122° and 113–114°, respectively); similarly, with the exception of the abnormally small C(9a)–C(9)–C(12) bond angle (101.8 (4)°), all C–C(9)–C and C–C(10)–C angles assume values (104–107°) that do not differ appreciably from those in triptycene itself (105.3° (mean)[16b]). It thus appears that the most significant structural deformations (bond stretching, bond angle compressions) all center on C(9a), a member of the benzene ring that includes C(1) and that is syn to the Ge–Cl bond (this ring is seen in Figure 1 as farthest from the viewer).[20] The disposition of this ring relative to the Ge–Cl bond forces the hydrogen atom on C(1) against the chlorine atom,[21] and it is this compression[23] that is the most likely source of the deformations near C(9a).

**NMR Structure.** At ambient temperatures the $^{13}C$ and $^1H$ NMR spectra of **1** in $CDCl_3$ solution feature all 20 carbon signals (2 aliphatic, 18 aromatic)[24] and all 13 proton signals (1 aliphatic, 12 aromatic) of the asymmetric Tp unit. Although the identity of the three benzene rings was not established in these experiments, it was possible to assign the three sets of four aromatic proton resonances by NOE difference experiments (Table II): irradiation of the H(10) singlet at δ 5.27 identified the three nearest protons (H(*n*)), irradiation of the H(*n*)'s then identified the three protons ortho to H(*n*) (H(*o*)), and so forth. The $^1H$ NMR spectra of $Tp_3SnCl$ and $Tp_3SnBr$ are nearly identical in appearance with those of **1** (see Experimental Section).

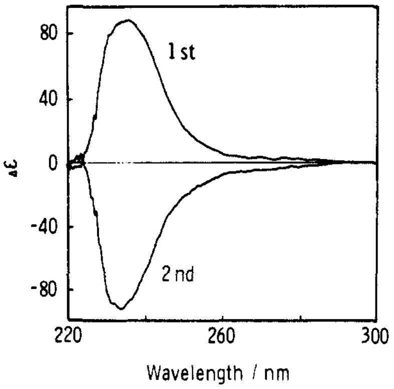


**Figure 3.** CD spectra (methanol, −78 °C) of the first and second chromatographic fractions (see Figure 2) of **1**.

**Table III.** Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for **2** Perchlorate[a]

| atom | *x* | *y* | *z* | $U^b$ |
|---|---|---|---|---|
| C(1) | 8503 (3) | 2435 (3) | 7500 | 53 (2) |
| C(2) | 9128 (3) | 2005 (3) | 7500 | 66 (2) |
| C(3) | 10171 (3) | 2620 (3) | 7500 | 68 (2) |
| C(4) | 10611 (3) | 3665 (3) | 7500 | 57 (2) |
| C(4a) | 9994 (2) | 4101 (3) | 7500 | 46 (1) |
| C(5) | 10381 (2) | 6122 (2) | 5872 (2) | 58 (1) |
| C(5a) | 9874 (2) | 5422 (2) | 6612 (2) | 49 (1) |
| C(6) | 9832 (2) | 6204 (2) | 5101 (2) | 64 (1) |
| C(7) | 8786 (2) | 5581 (2) | 5058 (2) | 60 (1) |
| C(8) | 8269 (2) | 4884 (2) | 5805 (2) | 51 (1) |
| C(8a) | 8816 (2) | 4818 (2) | 6584 (1) | 44 (1) |
| C(9) | 8396 (2) | 4114 (2) | 7500 | 41 (1) |
| C(9a) | 8939 (2) | 3480 (2) | 7500 | 44 (1) |
| C(10) | 10364 (2) | 5233 (3) | 7500 | 52 (1) |
| C(11) | 7270 (2) | 3581 (2) | 7500 | 40 (1) |
| Cl | 6667 | 3333 | 2149 (2) | 82 (1) |
| O(1) | 6667 | 3333 | 3954 (28) | 306 (27) |
| O(2) | 5837 (14) | 2884 (13) | 3062 (22) | 206 (13) |
| O(3) | 5627 (11) | 2781 (8) | 2500 | 173 (13) |

[a] Standard deviations in parentheses. For numbering of atoms, see ref 37. Parameters for hydrogen are given in the supplementary material. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Variable-temperature $^1H$ NMR spectra of **1** in decalin-$d_{18}$[25] showed little change, other than line broadening, up to 120 °C.[26] At higher temperatures some of the peaks began to coalesce, and at 160 °C the most downfield peak had almost disappeared into the baseline. Evidently the $C_3$ conformation of **1** is stably maintained up to ca. 120 °C on the NMR time scale, and this observation suggested the possibility that **1** might be resolvable, at least at low temperatures.

**Resolution and Racemization.** Resolution of **1** was achieved by HPLC on a column of (−)-poly(triphenylmethyl methacrylate),[27] a chiral packing material that has proven its effectiveness in the resolution of a wide variety of compounds.[28] Elution by methanol at −30 °C resulted in clean separation of the enantiomers (Figure 2), whose CD spectra are displayed in Figure 3. It is noteworthy that only partial separation of the enantiomers was achieved by chromatography of **1** on cellulose tris(3,5-dimethylphenylcarbamate),[29] a column material that had proven

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(18) In perchlorotriphenylgermane,[19] a sterically crowded molecular propeller that shares common features with **1**, the Ge–Cl bond length is 2.158 (2) Å, and the C–Ge–C bond angles are 116.3 (3), 116.6 (3), and 105.8 (3)°. However, in contrast to **1** the Ge–C bond lengths are all normal: 1.982 (7), 1.976 (7), and 1.972 (7) Å.

(19) Fajari, L.; Juliá, L.; Riera, J.; Molins, E.; Miravitlles, C. *J. Organomet. Chem.* **1989**, *363*, 31.

(20) The spatial disposition of the three benzene rings in each Tp unit is defined by three torsion angles: Cl–Ge–C(9)–C(9a) = 30.7 (4)° ("syn"), Cl–Ge–C(9)–C(8a) = 151.3 (3)° ("anti"), and Cl–Ge–C(9)–C(12) = −89.5 (3)° ("perpendicular"). The anti rings are the ones that project toward the viewer in Figure 1.

(21) The internuclear C(1)–Cl and H(1)–Cl distances, 3.145 and 2.363 Å, are a good deal shorter than the sums of the corresponding van der Waals radii ($r_w$), 3.52 and 2.75 Å, respectively.[22]

(22) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. The values of $r_w$ taken for chlorine, benzene carbon, and benzene hydrogen are 1.75, 1.77, and 1.00 Å, respectively.

(23) Short intermolecular C–H···Cl contact distances in crystals, such as are observed in **1**,[21] might be thought to indicate the existence of C–H···Cl hydrogen bonds. However, such bonds appear to be significant only in contacts of the type C–H···Cl⁻, in which the dominant interaction term is electrostatic attraction. See: Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

(24) $^{13}C\{^1H\}$ NMR (62.8 MHz) δ 148.28, 147.53, 146.41, 145.42, 144.08, 143.79 (aromatic quaternary carbons), 130.38, 129.46, 129.24, 125.96, 125.18, 124.97, 123.95, 123.60, 122.91, 122.88, 122.57, 122.48 (aromatic C–H carbons), 78.62 (C(9)), 55.66 (C(10)). A tracing of the spectrum is depicted in Figure 5 of ref 5b.

(25) In decalin at room temperature, all but the H(*p*) signals are shifted by no more than 0.08 ppm from the corresponding signals in chloroform whereas all three H(*p*) signals are shifted upfield by more than 0.2 ppm (δ 8.35 (A), 7.95 (B), 9.73 (C)). Evidently this effect is due to differences in solvation at the Ge–Cl dipole end of the molecule.

(26) At this temperature all multiplets, though still well separated, appeared as broad peaks, and only the four resonances of the B ring still showed distant splittings.

(27) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H.; Murata, S.; Noyori, R.; Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971.

(28) Okamoto, Y.; Hatada, K. *J. Liq. Chromatogr.* **1986**, *9*, 369.

more effective than poly(triphenylmethyl methacrylate) in the resolution of decakis(dichloromethyl)biphenyl.[30]

The resolved compound racemizes at −29 °C with a half-life of 3.61 h.[31] The first-order rate constant and $\Delta G^{\ddagger}$ of racemization at that temperature are $5.33 \times 10^{-5}$ s$^{-1}$ and 19.0 kcal mol$^{-1}$. The NMR spectrum of **1** recovered from a solution of **1** in methanol that had been allowed to stand at room temperature for 1 h was unchanged from the original; a racemization mechanism involving solvolysis[32] is therefore safely excluded. This leaves as the only reasonable alternative a mechanism in which the enantiomers are interconverted by internal rotation of the Tp groups.

In contrast to the facile gear slippage ($E_a$ = 6–8 kcal mol$^{-1}$) of the *tert*-butyl groups in molecules such as tri-*tert*-butylmethane and -silane,[9] it takes 19 kcal mol$^{-1}$ to effect slippage of the more securely meshed Tp gears in **1** by the mechanically disallowed conrotation route—clearly manifesting the operation of the second parity rule at the molecular level. Note that in magnitude this barrier is only slightly lower than the 21.1 kcal mol$^{-1}$ gear slippage barrier observed[33] for the interconversion of the DL into the achiral isomer of bis(2-chlorotriptycyl)silane.[34] Although the gear slippage mechanism in $Tp_2CH_2$ has been worked out[35] (in the transition structure two benzene rings within one Tp group are squeezed together and tucked into the expanded notch between two rings in the other group), details of the process responsible for the enantiomerization of **1** are yet to be elucidated.

## Tris(9-triptycyl)cyclopropenium Perchlorate

**Crystal and Molecular Structure.** X-ray data for a crystal of **2** perchlorate grown from acetonitrile were collected at room temperature. The crystals belong to the hexagonal system, space group $P6_3/m$ (No. 176), with $a = b = 15.145$ (5) Å, $c = 13.617$ (4) Å, and $Z = 2$. Final atomic parameters are listed in Table III. The cation (**2**) is located on a site of crystallographic $C_{3h}$ symmetry,[36] but the anion is disordered, and no satisfactory scheme was found to model this disorder by a superposition of tetrahedral perchlorate anions with standard bond lengths and angles.

In the triskelion conformation of **2**, the three Tp groups are rendered equivalent by the 3-fold axis that is normal to and centered on the cyclopropenium ring. Of the three benzene rings within each Tp unit, one (the achirotopic ring) lies in the $\sigma$ plane that also contains the cyclopropenium ring. The other two benzene rings straddle the $\sigma$ plane, which bisects their dihedral angle (120.0°), and are therefore symmetry equivalent (enantiotopic).[37]

The C–C bond length in the cyclopropenium ring, 1.379 (7) Å, falls in the normal range,[38] and so do all the structural parameters of the benzene rings ($C_{ar}$–$C_{ar}$ = 1.374 (7) to 1.393 (5) Å, $C_{ar}$–$C_{ar}$–$C_{ar}$ = 119.1 (3) to 120.8 (5)°). The $C_{ar}$–$C_{ar}$–C(9), $C_{ar}$–$C_{ar}$–C(10), $C_{ar}$–C(9)–$C_{ar}$, and $C_{ar}$–C(10)–$C_{ar}$ bond angles also do not deviate significantly from the corresponding angles in triptycene,[16] and while there is some bond stretching in C(9)–C(8a) (1.555 (5) Å) and C(9)–C(9a) (1.546 (7) Å), with concomitant bond contraction in C(10)–C(4a) (1.515 (7) Å) and C(9)–C(5a) (1.519 (6) Å), this effect is far less pronounced than in the case of **1**. The only notable molecular deformation consists of an in-plane displacement of the Tp group that results in an opening of the C(11)–C(9)–C(9a) angle to 119.2 (3)° from 113.4° in triptycene,[39] a concomitant contraction of the C(11)–C(9)–C(8a)/C(8aA) angles to 109.8 (3)°, and a tilt of the Tp group relative to the cyclopropenium ring (C(9)–C(11)–C(11B) = 154.2 (4)°). This angular displacement (C(9)–C(11) remains normal at 1.477 (6) Å) no doubt serves to relieve some of the strain that is associated with the tight meshing of the Tp gears, and that is manifested in the extraordinary expansion of the central bond angles in compounds of the type $Tp_2Z$.[3]

Table IV. $^1$H and $^{13}$C NMR Spectral Parameters for **2** Perchlorate in $CD_3CN$[a]

| atom no.[b] | chemical shifts[c] | |
|---|---|---|
| | $^1$H | $^{13}$C{$^1$H}[d] |
| 1 | 6.82 (dd) | 128.18, 126.06, 124.50, 123.76 |
| 2 | 5.90 (ddd) | |
| 3 | 6.89 (ddd) | |
| 4 | 7.54 (dd) | |
| 4a | | 146.28, 137.44 |
| 9a | | |
| 5 | 7.84 (dd) | 129.47, 127.06, 126.90, 122.97 |
| 6 | 7.30 (ddd) | |
| 7 | 6.93 (ddd) | |
| 8 | 7.23 (dd) | |
| 8a | | 145.37, 140.62 |
| 5a | | |
| 9 | | 62.01 |
| 10 | 6.01 (s) | 53.56 |
| 11 | | 188.75 |

[a] 500.2 ($^1$H)/125.8 ($^{13}$C) MHz, ambient temperatures. [b] See ref 37. [c] In ppm downfield from TMS. Multiplicities in parentheses. [d] Brackets indicate that signals are assigned as whole sets to the corresponding sets of atoms but are not assigned on an individual basis.

**NMR Structure.** At ambient temperatures the $^{13}$C and $^1$H NMR spectra of **2** perchlorate in $CD_3CN$ solution (Table IV) feature all 15 carbon signals (2 aliphatic, 1 cyclopropenium, 12 benzene)[40] and all 9 proton signals (1 aliphatic, 8 aromatic) of the Tp–C unit. The assignment of the various resonances was greatly facilitated by the fact that the signals due to the carbons and protons of the enantiotopic rings are twice as intense as those of the achirotopic ring. Individual $^1$H NMR resonances were assigned by NOE difference experiments as described for **1**, i.e., by irradiation of the H(10) singlet at $\delta$ 6.01, and so forth. Evidently the $C_{3h}$ structure of **2** is maintained in solution at ambient temperature on the NMR time scale.

Variable-temperature $^1$H NMR spectra of **2** trifluoroacetate in nitrobenzene-$d_5$ showed little change up to 100 °C, other than slight line broadening. At 120 °C the triplet corresponding to

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(29) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Chromatogr.* **1986**, *363*, 173.

(30) Biali, S. E.; Kahr, B.; Okamoto, Y.; Aburatani, R.; Mislow, K. *J. Am. Chem. Soc.* **1988**, *110*, 1917.

(31) Racemization was complete in 10 min at 2 °C.

(32) Methyl-1-naphthylphenylgermanium chloride is optically stable in hydrocarbons, $CCl_4$, or $CHCl_3$, but racemizes in 8 min in THF. See: Carre, F. H.; Corriu, R. J. P.; Thomassin, R. B. *J. Chem. Soc. D* **1968**, 560.

(33) Kawada, Y.; Murata, S.; Iwamura, H. Unpublished results cited in ref 3.

(34) In the corresponding germanes, which appear to be unknown, the diastereomerization barrier would presumably also be somewhat lower because the increase in Tp–Z bond length, from C–Si to C–Ge, would push the Tp groups further apart, thus loosening up the gear system and facilitating gear slippage. By the same argument we presume that the barrier to gear slippage in $Tp_3SiCl$ would be higher, and that in $Tp_3SnCl$ lower, than 19.0 kcal mol$^{-1}$.

(35) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1427.

(36) A stereoview of the X-ray structure of **2** is shown in Figure 1 of ref 5a.

(37) Atom labels in **2** are modified from those in ref 15 by changing C(11), C(12), C(13), C(14), C(15), and C(16) to C(5aA), C(8aA), C(8A), C(7A), C(6A), and C(5A), respectively, in correspondence with the enantiotopic atom labels C(5a), C(8a), etc. The cyclopropenium carbons are C(11), C(11A) [trans to C(1)], and C(11B) [cis to C(1)].

(38) (a) Triphenylcyclopropenium ($r$(av) = 1.373 Å): Sundaralingam, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198. (b) Triphenylcyclopropenium ($r$(av) = 1.377 Å): Borgias, B. A.; Scarrow, R. C.; Seidler, M. D.; Weiner, W. P. *Acta Crystallogr.* **1985**, *C41*, 476. (c) Tris(dimethylamino)cyclopropenium ($r$(av) = 1.363 Å): Ku, A. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 1688. (d) Ferrocenyldiphenylcyclopropenium ($r$(av) = 1.381 Å): Sime, R. L.; Sime, R. J. *Ibid.* **1974**, *96*, 892. (e) Tricyclopropylcyclopropenium ($r$(av) = 1.37 Å) and dicyclopropylphenylcyclopropenium ($r$(av) = 1.359 Å): Moss, R. A.; Shen, S.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J.; Munjal, R. C. *Ibid.* **1986**, *108*, 134. (f) Diphenylhydroxycyclopropenium ($r$(av) = 1.374 Å) and diphenylethoxycyclopropenium ($r$(av) = 1.379 Å): Childs, R. F.; Mahendran, M.; Zweep, S. D.; Shaw, G. S.; Chadda, S. K.; Burke, N. A. D.; George, B. E.; Faggiani, R.; Lock, C. J. L. *Pure Appl. Chem.* **1986**, *58*, 111.

(39) Calculated on the basis of the 105.3° reported for $C_{ar}$–C(9)–$C_{ar}$ in triptycene.[16b]

(40) A tracing of the spectrum is depicted in Figure 6 of ref 5b.

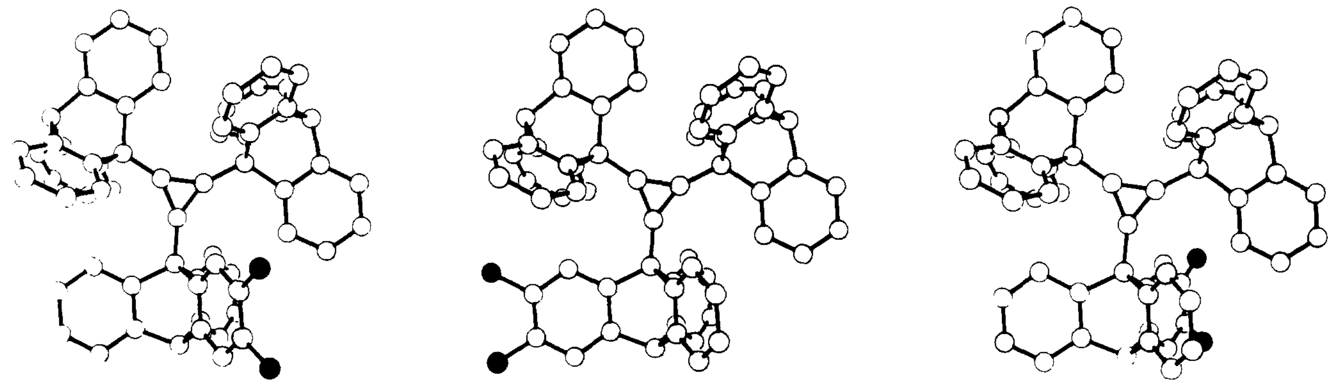

**Figure 4.** Schematic sketches of **3** modeled on the X-ray structure of **2**. Hydrogen atoms are suppressed for clarity. Methyl carbons are indicated by filled circles. Center: achiral **3**. Right and left: DL-**3**.

H(2) at $\delta$ 6.04 had become a broad peak, and at 150 °C the rest of the signals also had become broad peaks, but none had coalesced completely. There was no evidence of decomposition. Given that the signal due to H(3) at $\delta$ 6.98 had not yet coalesced with the signal due to H(6) at $\delta$ 7.41, a lower limit of 21.0 kcal mol$^{-1}$ was calculated[41] for the barrier to rotation of a Tp group. This result suggested the possibility of stereoisomerism in ring-substituted derivatives of **2** on the NMR or even laboratory time scale.

## Stereoisomerism in Ring-Substituted Tris(9-triptycyl) Systems

Phase isomerism in **1** and **2** is excluded because of the parity restriction on dynamic gearing. In the absence of gear slippage, the isomer count in ring-substituted derivatives is therefore straightforwardly derived by conventional combinatorics. For example, there are four nonequivalent substituent positions on each of three nonequivalent benzene rings in each of the three equivalent Tp units of **1**; it follows that there are 12 monochloro and 210 dichloro derivatives for each enantiomer of **1**, or a total of 12 and 210 DL pairs, respectively. Because of the degeneracy introduced by the $\sigma$ plane, the total isomer count in **2** is one-half of the above, 12 monochloro (4 achiral + 4 DL) and 210 dichloro (26 achiral + 92 DL) derivatives.

To demonstrate stereoisomerism in derivatives of **1** we adopted an approach that had proven successful in another context.[8a] Disregarding differences in steric effects between Tp and 2,3-dimethyl-9-triptycyl (Tp*) groups, reaction of an equimolar mixture of TpLi and Tp*Li with GeCl$_4$ should yield a mixture of products in the statistical ratio Tp$_3$GeCl:Tp$_2$Tp*GeCl:TpTp$_2$*GeCl:Tp$_3$*GeCl = 1:3:3:1. But with a 7-fold molar excess of TpLi, the distribution ratio becomes 0.670:0.287:0.041:0.002. Under these conditions, Tp$_3$GeCl and Tp$_3$*GeCl are invisible in the methyl region of the $^1$H NMR spectrum, the former because it contains no methyl groups and the latter because it is only present in trace amounts, while Tp$_2$Tp*GeCl:TpTp$_2$*GeCl = 7:1. This ratio may be even larger if steric effects in TpTp$_2$*GeCl disfavor this derivative relative to Tp$_2$Tp*GeCl. It follows that the latter is effectively isolated for observation. In accord with expectations, the product of the reaction exhibited six methyl singlets, i.e., one pair of 2- and 3-methyl proton signals for each of the three diastereomers of Tp$_2$Tp*GeCl, at $\delta$ 1.88, 1.74, 1.70, 0.56, 0.45, and 0.42. Upon standing 1 week either as solids or in solution, samples that originally showed all three pairs of methyl resonances showed only two pairs at $\delta$ 1.88, 1.74, 0.56, and 0.45; evidently one of the diastereomers is thermodynamically disfavored relative to the other two. Variable-temperature NMR experiments designed to provide an estimate for the barrier to interconversion of the two remaining diastereomers were frustrated by the decomposition of the compound in solution at temperatures above 150 °C. It appears that the approximate coalescence temperature of the resonances at $\delta$ 1.88 and 1.74 and those at $\delta$ 0.56 and 0.45 is in the range of 140–150 °C, so that the interconversion barrier is in the neighborhood of 21 kcal mol$^{-1}$.

Stereoisomerism of this novel type is also exemplified in a derivative of **2**, bis(9-triptycyl)(2,3-dimethyl-9-triptycyl)cyclopropenium (**3**) perchlorate, Tp$_2$Tp*C$_3$$^+$ClO$_4$$^-$, which was prepared by addition of Tp*Li to bis(9-triptycyl)cyclopropenone followed by reaction with HClO$_4$. This derivative exists in three stereoisomeric forms: an achiral isomer (A), in which the labeled (i.e., dimethyl substituted) benzene ring occupies the achirotopic position, and a pair of enantiomers (the D and L isomers), in which this ring occupies the enantiotopic positions (Figure 4). The mixture of diastereomers was characterized by the NMR signals in the methyl region. In 1:1 nitrobenzene-$d_5$/trifluoroacetic acid-$d_1$ at ambient temperature, the $^1$H NMR spectrum of **3** perchlorate features two singlets of equal intensity at $\delta$ 1.95 and 1.00 and two of equal intensity at $\delta$ 2.12 and 1.63 (the corresponding resonances of **3** trifluoroacetate in nitrobenzene-$d_5$ are 1.95, 1.04, 2.13, and 1.64, respectively), with the former pair four times the intensity of the latter. Similarly, the $^{13}$C{$^1$H} NMR spectrum of **3** perchlorate in 1:1 nitrobenzene-$d_5$/trifluoroacetic acid-$d_1$ features two signals of equal intensity at $\delta$ 18.95 and 17.90 and two of equal intensity at $\delta$ 19.23 and 19.06, with the former pair four times the intensity of the latter. This ratio of intensities, which reflects the equilibrium ratio of the two diastereomers, was used as the basis for the configurational assignment. On statistical grounds alone one would expect a DL:A ratio of 2:1, and this is very nearly observed in ring-substituted derivatives of Tp$_2$Z for which this ratio is generally closer to 1.8, indicative of a slight thermodynamic preference for the achiral isomer that may be attributable to the absence of conformations in which the substituted rings come close to one another.[3] In the case of **3**, this situation is exactly reversed: it is now the achiral isomer in which the substituted ring is statically forced into the notch of the neighboring Tp group, whereas the same ring occupies a relatively unencumbered position in the DL isomer. As a result the DL isomer becomes disproportionately favored, leading to a DL:A ratio of 4:1.

At elevated temperatures in nitrobenzene-$d_5$, the two downfield methyl protons at $\delta$ 2.13 and 1.95 in the $^1$H NMR spectrum of **3** trifluoroacetate broadened and coalesced at 170 °C. The resulting singlet at $\delta$ 2.1 sharpened noticeably at 179 °C, the highest temperature reached in this experiment. The two upfield methyl singlets at $\delta$ 1.64 and 1.04 also broadened as the temperature was raised and had practically disappeared into the baseline at 179 °C. A spectrum indistinguishable from the original was recorded after this experiment was concluded; no evidence of decomposition was observed. On the basis on a coalescence temperature of 170 °C for the two downfield protons, $\Delta G^{*}$'s of 23.4 and 22.2 kcal mol$^{-1}$ were calculated[41] for the DL $\rightarrow$ A and A $\rightarrow$ DL interconversions, respectively. These values are close to the lower limit calculated for the homomerization of **2** and probably to the homomerization barrier itself. The detailed pathways of the diastereomerization and homomerization processes are unknown.

The experiments described above do not address questions concerning phase isomerism and gear slippage in systems in which only two (instead of three) meshed Tp's are attached to the cyclopropenium framework; phase isomerism has been demonstrated

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[41] The unequal populations of the exchanging nuclei were accounted for by use of eq 7 in: Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.

thus far only for compounds of the type $Tp_2Z$ in which both Tp's are attached to the same atom.[3] We therefore prepared bis(2,3-dimethyl-9-triptycyl)cyclopropenone (**4**) by double addition of 4,5-dimethylbenzyne to bis(9-anthryl)cyclopropenone. This compound is in principle capable of exhibiting the same A/DL isomerism as the previously studied $Tp_2Z$ derivatives,[3] provided the meshed Tp* groups undergo dynamic gearing that is rapid compared to the interconversion of achiral and DL isomers by gear slippage.

In DMSO-$d_6$ at ambient temperature, the $^1H$ NMR spectrum of **4** in the methyl region features two singlets of equal intensity at δ 2.01 and 1.34, and two of equal intensity at δ 2.05 and 1.55, with the former pair twice the intensity of the latter. The first pair of signals is therefore due to the DL and the second to the achiral isomer. Under these conditions, rapid dynamic gearing evidently occurs with no gear slippage. At elevated temperatures the two signals at δ 2.05 and 2.01 broadened and coalesced at 70 °C and the resulting singlet sharpened as the temperature was raised further. On the basis of this information, $\Delta G^{\ddagger}$'s of 18.6 and 18.1 kcal mol$^{-1}$ were calculated[41] for the DL → A and A → DL interconversions, respectively. From the coalescence at 100 °C of the signals at δ 1.55 and 1.34, $\Delta G^{\ddagger}$'s of 19.0 and 18.5 kcal mol$^{-1}$ were calculated for the same two interconversion processes. Gear slippage in **4** thus requires 18–19 kcal mol$^{-1}$, a barrier that is comparable to the one observed for gear slippage in **1** and that is only slightly lower than the gear slippage barrier in **2** and **3**.

## Conclusion

The mechanical selection rules (disrotation allowed, conrotation disallowed) that govern the motions of meshed macroscopic gears[42] apply also to molecules of the type $Tp_2Z$ in which the two Tp's function as the molecular analogues of meshed three-toothed cogwheels.[3] But whereas the Tp's in these molecules undergo essentially frictionless correlated disrotation (dynamic gearing), with barriers that amount to at most a few kcal mol$^{-1}$, the present work shows that the torsional motion of the same rotors is frozen on the NMR time scale in $Tp_3GeCl$ and $Tp_3C_3^+ClO_4^-$, and thus reduces to the molecular level a corollary of the mechanical selection rules according to which all motion is disallowed in a closed cyclic array consisting of an odd number of securely meshed macroscopic gears.[6] 9-Triptycyl systems are therefore the only molecular gears studied to date that match their mechanical counterparts in both static and dynamic properties, i.e., that follow the same classical mechanical laws as gears in the macroworld.

## Experimental Section

Solution $^1H$ and $^{13}C$ NMR spectra were recorded at ambient temperature on either a Bruker WM-250, JEOL GSX 270, or JEOL GSX 500 spectrometer operating at 250.13, 270.17, and 500.16 MHz, respectively, for $^1H$ and at 62.83, 67.93, and 125.80 MHz, respectively, for carbon. Residual solvent resonances were used as references. Variable-temperature spectra were recorded on a JEOL GSX 270 spectrometer. The sample temperatures were controlled with standard JEOL VT-probe hardware that had been calibrated with a sample of ethylene glycol by use of the van Geet relationship.[43] The CD spectra were measured on a JASCO J-500C CD spectrometer. Mass spectra were measured on a KRATOS MS50 RFA high-resolution mass spectrometer, except for exact mass FAB.[44] Melting points were recorded on either a Thomas-Hoover melting point apparatus or a Electrothermal Digital Melting Point Apparatus and are corrected. A Corning Model 1 pH meter was used to monitor the titration in the $pK_{R^+}$ determination. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Chemicals used were of reagent grade.

**Tris(9-triptycyl)germanium Chloride (1).** A suspension of 9-bromotriptycene[45] (3.03 g, 9.10 mmol) in dry diethyl ether under an argon atmosphere was treated with 1 equiv of 2.5 M *n*-butyllithium in hexane and the mixture was stirred for 2 h at room temperature. $GeCl_4$ (0.22 g, 1.0 mmol) was added via syringe. The reaction mixture was stirred under argon at room temperature for 8 h, quenched with 50 mL of water, and extracted with 100 mL of toluene. The organic layer was dried ($MgSO_4$) and the solvent was removed in the presence of a few grams of silica gel. The crude product mixture on silica was added to the top of a 15 × 2 in. column of silica gel and eluted with 10% $CHCl_3$/hexane to remove bromotriptycene and triptycene. Elution with benzene and crystallization from ethanol/$CHCl_3$/hexane by slow evaporation afforded pure **1** (0.35 g, 0.40 mmol, 40% based on $GeCl_4$) as a white solid: mp 250–260 °C dec; $^1H$ NMR (see Table II); $^{13}C$ NMR (see ref 24); mass spectrum (FAB high resolution), *m/z* 833.2254 (833.2264 calcd for M – Cl = $C_{60}H_{39}{}^{74}Ge$). Anal. Calcd for $C_{60}H_{39}GeCl$: C, 83.02; H, 4.53; Ge, 8.36; Cl, 4.08. Found: C, 82.75; H, 4.63; Ge, 8.69; Cl, 4.38.

A suspension of 9-bromotriptycene (3.33 g, 10.0 mmol) and 9-bromo-2,3-dimethyltriptycene (0.520 g, 1.44 mmol, prepared as described below) in 70 mL of dry ether under an argon atmosphere was treated with 4.60 mL of a 2.50 M hexane solution of *n*-butyllithium. The suspension was stirred for 1.5 h at room temperature and 0.30 mL of $GeCl_4$ (0.56 g, 2.6 mmol) was added. The mixture was stirred at room temperature overnight and 100 mL each of water and toluene were added. The organic layer was collected and dried, and the solvents were removed under reduced pressure to yield a white solid. Chromatography on silica gel with 20% $CHCl_3$/hexane as eluent, followed by rechromatography of the product-containing fraction on silica gel by use of 30% $CHCl_3$/hexane, resulted in the separation of $Tp_3GeCl$ and its 2,3-dimethyl derivatives from the other products. In the second chromatography, earlier fractions contained comparable quantities of each of the three isomers of $Tp_2Tp^*GeCl$ ($^1H$ NMR (DMSO-$d_6$) methyl resonances: δ 1.88 (s), 1.74 (s), 1.70 (s), 0.56 (s), 0.45 (s), 0.42 (s)), while in the later fractions two isomers predominated ($^1H$ NMR methyl resonances (DMSO-$d_6$): δ 1.88, 1.74, 0.56, 0.45) to the almost total exclusion of the third ($^1H$ NMR methyl resonances (DMSO-$d_6$): δ 1.70, 0.42).

**Tris(9-triptycyl)tin Chloride and Bromide.** A 2.5 M solution of *n*-butyllithium in hexane (4.40 mL, 11.0 mmol) was added to a suspension of 9-bromotriptycene[45] (3.67 g, 11.0 mmol) in 60 mL of dry ether under an argon atmosphere. After 4 h at room temperature, stirring was halted to allow the solids (including 9-triptycyllithium) to settle. The supernatant was cannulated off under positive argon pressure, and 120 mL of fresh dry ether was added. Stirring was resumed and $SnCl_4$ (0.32 mL, 0.70 g, 2.7 mmol) was added with a syringe. As the $SnCl_4$ was added, a peach color appeared, became quite bright just as the addition ended, and then faded quickly to a pale yellow. The mixture was left to stir at room temperature under argon for 32 h, at which point 200 mL of distilled water and 200 mL of toluene were added. The undissolved white solid was collected by filtration and dissolved in boiling toluene. The toluene was dried over $MgSO_4$ and filtered through Celite. Removal of the solvent gave the mixture of the two products in a nearly pure state by NMR. Recrystallization from toluene/heptane/$CH_2Cl_2$ or from ethyl acetate/1-butanol gave beautiful clear crystals unchanged in ratio of major to minor components. $^1H$ NMR ($CDCl_3$): major component, δ 9.41 (dd, 3 H), 8.15 (d, 3 H), 7.52 (d, 3 H), 7.47 (dd, 3 H), 7.38 (d, 3 H), 7.27 (d, 3 H), 7.09 (two overlapping dd, 6 H), 6.79 (dd, 3 H), 6.66 (dd, 3 H), 5.88 (ddd, 3 H), 5.72 (ddd, 3 H), 5.35 (s, 3 H); minor component, δ 9.58 (dd), 8.27 (d), 5.83 (dd), 5.34 (s) (other resonances are isochronous with and obscured by the corresponding resonances of the major component). The ratio of major to minor component (7.43:1.00) was determined from the ratio of the integrated areas of the resonances at δ 9.41 and 9.58. The identity of $Tp_3SnBr$ as the minor component was unambiguously established by mass spectrometry and elemental analysis. Mass spectrum (FAB), *m/z* (relative intensity calcd for the isotopic distribution in $C_{60}H_{39}SnBr$/found) 956 (12.3/12.7), 957 (11.3/11.5), 958 (19.8/19.8), 959 (13.2/12.7), 960 (14.2/14.7), 961 (7.3/6.8). Anal. Calcd for $C_{60}H_{39}SnCl$: C, 78.84; H, 4.30; Sn, 12.98; Cl, 3.88. Calcd for $C_{60}H_{39}SnCl_xBr_y$ ($x = 0.8814, y = 0.1186$): C, 78.39; H, 4.28; Sn, 12.91; Cl, 3.40; Br, 1.03. Found: C, 78.06; H, 4.56; Sn, 12.80; Cl, 3.37; Br, 1.47. The previously reported[11] analysis for "$Tp_3SnCl$" (C, 77.7; H, 4.40) is also consistent with a mixture of $Tp_3SnCl$ and $Tp_3SnBr$ of approximately the same composition as our sample.

**Resolution and Racemization of 1.** HPLC of **1** in methanol at –30 °C was performed on a column (25 × 0.46 cm (i.d.)) packed with (–)-poly(triphenylmethyl methacrylate).[27,28] Elution with methanol (1.0 mL min$^{-1}$) at –30 °C yielded well-separated fractions of the two enantiomers (Figure 2). To measure the CD spectra (Figure 3), the eluted fractions were collected in a 1-cm quartz cell cooled to –78 °C and immersed in a quartz Dewar with optical windows.

The racemization of **1** in methanol at –29 ± 1 °C was monitored by observing the decrease in the intensities of the CD maxima over a time interval of 323 min. From the rate constant of racemization, $5.33 \times 10^{-5}$ s$^{-1}$ (correlation coefficient 0.995) and the Eyring equation (assuming a

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(42) Thoughout this paper reference is made to *external gears*, in which the teeth are cut on the outside surfaces of both wheels. See: Candee, A. H. *Introduction to the Kinematic Geometry of Gear Teeth*; Chilton Co.: Philadelphia, 1961; Chapter 1.

(43) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.

(44) Performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-8620177).

(45) Dence, J. B.; Roberts, J. D. *J. Org. Chem.* **1968**, *33*, 1251.

transmission coefficient of unity), the $\Delta G^{\ddagger}$ of racemization at −29 °C was found to be 19.0 kcal mol$^{-1}$. An NMR sample of **1** in $CDCl_3$ was poured into 20 mL of methanol and the solution was allowed to stand for 1 h at room temperature. At the end of this period the solvent was removed under reduced pressure; the NMR spectrum of the residual material was found to be unchanged from the original.

**Bis(9-triptycyl)cyclopropenone.** Bis(9-anthryl)cyclopropenone[12] (0.50 g, 1.2 mmol) was dissolved in 100 mL of 1,2-dichloroethane by heating. After the solution had cooled to room temperature, benzenediazonium-2-carboxylate hydrochloride (0.88 g, 4.8 mmol) and 5 mL of propylene oxide were added and the suspension was refluxed for 2 h.[46] The clear, dark brown solution was cooled, washed with saturated bicarbonate and brine solutions, and dried with anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residual dark oil was titurated with about 2 to 5 mL of diethyl ether, and the resulting yellow solid was collected by filtration to yield 0.3 g (45%) of the desired product. Though relatively pure by NMR, the product can be recrystallized from chloroform/hexane to give colorless, clear crystals that become cloudy upon drying: mp >412 °C; $^1$H NMR ($CDCl_3$) δ 7.58 (d, 6 H), 7.50 (d, 6 H), 7.06 (dd, 6 H), 6.87 (dd, 6 H), 5.56 (s, 2 H). No signal decoalescence was observed when the solution was cooled to −90 °C in acetone-$d_6$. $^{13}$C{$^1$H} NMR ($CDCl_3$) δ 162.91, 161.48 (cyclopropenone carbons), 144.81, 142.06, 126.23, 125.36, 124.09, 123.04 (aromatic carbons), 59.10 (C(9)), 54.06 (C(10)); mass spectrum (high resolution), $m/z$ 558.1963 (558.1984 calcd for $C_{43}H_{26}O$).

**Tris(9-triptycyl)cyclopropenium (2) Perchlorate.**[47] A suspension of 9-bromotriptycene[45] (0.2 g, 0.6 mmol) in 20 mL of dry diethyl ether under an argon atmosphere was treated with a 2.5 M solution of $n$-butyllithium (0.48 mL, 1.2 mmol) and stirred for 5 h. The suspension was allowed to settle (0.5 h), the ether was cannulated away from the deposited white solid, and a solution of bis(9-triptycyl)cyclopropenone (0.13 g, 2.3 mmol) in 30 mL of dry benzene was cannulated onto the precipitate. The mixture was stirred under an argon atmosphere at room temperature for 12 h and quenched by addition of water. The organic phase was washed with saturated bicarbonate and brine and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to leave a white solid. A solution of 7% perchloric acid in acetic anhydride was then prepared as follows: acetic anhydride (100 mL) was cooled to 0 °C and degassed by a stream of argon; similarly degassed ice-cold 70% perchloric acid (10 mL) was then slowly dripped into the stirred anhydride while both solutions were continuously degassed. The white solid was dissolved in ether, degassed as above, and cooled to 0 °C, and 2 mL of the freshly prepared perchloric acid solution was added dropwise to give an immediate milky white precipitate. The solution was filtered and the solid was washed with ether, chloroform, and benzene to give the desired product (between 50 and 140 mg, 24%–67%). Crystals suitable for single-crystal X-ray diffraction were grown over a period of 2 days from a slowly evaporating solution of acetonitrile at 0–20 °C; mp 372–380 °C dec. This solid could be dissolved in acetonitrile/trifluoroacetic acid and the trifluoroacetate salt crystallized out by slow evaporation. This salt is much more soluble than the perchlorate: $^1$H NMR (nitrobenzene-$d_5$) δ 8.03 (d, 6 H, H(5)), 7.70 (d, 6 H, H(8)), 7.41 (dd, 6 H, H(6)), 7.20 (d, 3 H, H(1)), 6.98 (dd, 3 H, H(3)), 6.92 (dd, 6 H, H(7)), 6.23 (s, 3 H, H(10)), 6.04 (dd, 3 H, H(2)). The $^1$H and $^{13}$C{$^1$H} NMR spectral parameters of the perchlorate in acetonitrile are listed in Table IV. Anal. Calcd for $C_{63}H_{39}O_4Cl{\cdot}H_2O$: C, 82.84; H, 4.52; Found: C, 83.14; H, 4.28.

A solution of **2** perchlorate (15.5 mg) in 7.5 mL of standardized NaOH (0.0845 M), 7.1 mL of standardized HCl (0.0904 M), and 22 mL of acetonitrile was titrated with NaOH to give a standard titration curve with the midpoint at pH 8.2 taken to be the $pK_{R^+}$.[49] Back-titration with HCl also gave a standard titration curve, but with the midpoint at pH 7.7. The same results were obtained with the trifluoroacetate of **2**. These values ($pK_{R^+}$ ca. 8) fall into the range obtained for other trialkylcyclopropenium salts.[51]

**9-Bromo-2,3-dimethyltriptycene.** A stirred suspension of 4,5-dimethylanthranilic acid[52] (1.32 g, 8 mmol) in ethanol (12.0 mL) and concentrated HCl (0.8 mL) at 0 °C was treated with isoamyl nitrite (2.0 mL, 17 mmol). The new suspension was then treated with ether (12 mL), filtered, and washed with ether to yield 1.4 g (6 mmol, 83%) of 4,5-dimethylbenzenediazonium-2-carboxylate hydrochloride. A mixture of the hydrochloride (1.34 g, 6.3 mmol), 9-bromoanthracene (0.77 g, 3 mmol), dry 1,2-dichloroethane (50 mL), and propylene oxide (3 mL) was refluxed for 3 h.[46] The clear dark solution was washed with saturated bicarbonate and water, the organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to leave a dark oil. Trituration of the dark oil with acetone gave the product as a pale yellow powder (0.54 g, 1.5 mmol, 50% yield) which was recrystallized from toluene to yield pale yellow chunks: mp 198–201 °C; $^1$H NMR ($CDCl_3$) δ 7.79 (m, 2 H), 7.56 (s, 1 H), 7.36 (m, 2 H), 7.19 (s, 1 H), 7.05 (m, 4 H) (aromatic hydrogens), 5.36 (s, 1 H, H(10)), 2.21 (s, 3 H, $CH_3$), 2.19 (s, 3 H, $CH_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$) δ 145.09, 144.38, 142.38, 141.62, 134.70, 133.67, 126.61, 125.73, 125.68, 124.98, 124.09, 123.28 ($C_{ar}$), 71.69 (C(9)), 53.72 (C(10)), 20.05, 19.73 ($CH_3$). Anal. Calcd for $C_{22}H_{17}Br$: C, 73.14; H, 4.74; Br, 22.12. Found: C, 72.72; H, 4.71; Br, 21.57.

**Bis(9-triptycyl)(2,3-dimethyl-9-triptycyl)cyclopropenium (3) Perchlorate.**[47] A suspension of 9-bromo-2,3-dimethyltriptycene (0.4 g, 0.55 mmol) in 12 mL of dry diethyl ether was stirred under an argon atmosphere and treated with 2.5 M $n$-butyllithium (1.0 mL, 2.5 mmol). After 5 h the suspension was allowed to settle for 30 min and the solvent was cannulated away from the white solid. A solution of bis(9-triptycyl)cyclopropenone (0.12 g, 0.21 mmol) in dry benzene (20 mL) was then cannulated onto the white precipitate which immediately dissolved. The solution was stirred for 12 h and quenched with saturated $H_2NaPO_4$. The organic phase was washed with saturated bicarbonate and brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure to leave a white solid. The solid was dissolved in ether, degassed, and cooled to 0 °C, and 2 mL of a 7% solution of perchloric acid in acetic anhydride, freshly prepared as described above (see **2** perchlorate), was added dropwise to produce a milky white precipitate. The solution was filtered and the solid was washed with ether, chloroform, and benzene to give the product (0.1 g, 0.1 mmol, 48% yield): mp 362–365 °C dec. This solid could be dissolved in an acetonitrile/trifluoroacetic acid mixture and the trifluoroacetate crystallized out by slow evaporation. This salt is much more soluble than the perchlorate which can also be dissolved in nitrobenzene by addition of trifluoroacetic acid: $^1$H NMR (acetonitrile-$d_3$) δ 7.86 (d, 3.6 H), 7.81 (d, 2 H, H(5)), 7.57 (m, 3.0 H, H(4)), 7.30 (m, 7 H), 7.24 (m, 5.4 H, H(6) and H(8)), 6.94 (m, 10 H), 6.69 (s, 1 H, H(7), H(3), and H(1)), 6.04 (s, 1 H, H(10)), 6.03 (s, 1 H, H(10)), 5.94 (t, 2 H, H(2)), 5.90 (s, 1.0 H, H(10)), 2.18 (0.6 H, $CH_3$ in the achiral isomer), 1.95 (2.4 H, $CH_3$ in the DL isomer), 1.64 (s, 0.6 H, $CH_3$ in the achiral isomer), 0.81 (s, 2.4 H, $CH_3$ in the DL isomer); $^1$H NMR (1:1 nitrobenzene-$d_5$/trifluoroacetic acid-$d_1$) δ 7.92 (m, 5.8 H), 7.60 (d, 2 H), 7.55 (m, 7 H), 7.30-7.38 (m, 5.7 H), 7.13–7.24 (m, 3 H), 6.86–6.96 (m, 7.25 H), 6.78 (t, 1.35 H), 6.09 (t, 2 H) (aromatic protons), 6.05 (s, 2 H, H(10)), 5.94 (s, 1 H, H(10)), 2.12 (s, 0.6 H, $CH_3$ in the achiral isomer), 1.95 (s, 2.4 H, $CH_3$ in the DL isomer), 1.63 (s, 0.6 H, $CH_3$ in the achiral isomer), 1.00 (s, 2.4 H, $CH_3$ in the DL isomer). Note: The population values are given as a fraction of one cyclopropenium molecule. Since there are two different molecules in a four-to-one ratio in solution, fractional numbers of protons are obtained. $^{13}$C{$^1$H} NMR (1:1 nitrobenzene-$d_5$/trifluoroacetic acid-$d_1$) δ 189.63, 189.57, 189.32 (cyclopropenium carbons), 146.32, 145.89, 145.85, 143.51, 141.62, 141.56, 141.24, 137.54, 136.34, 135.26, 133.87, 129.93, 129.49, 129.42, 128.13, 126.96, 126.90, 126.84, 126.75, 126.37, 125.85, 125.00, 124.62, 124.43, 124.00, 123.11, 122.89, 122.76, 122.61, 121.94, 117.65, 113.80, 112.78 (the aromatic region would have 90 resonances barring accidental isochronies and proved too complex for complete analysis; only the largest $C_{ar}$ peaks are reported), 62.69, 62.52, 62.19 (C(9)), 54.77, 54.31 (C(10)), 19.23, 19.06 ($CH_3$ in the achiral isomer), 18.95, 17.90 ($CH_3$ in the DL isomer).

**2,3-Bis(2,3-dimethyl-9-triptycyl)cyclopropenone (4).** A suspension of 4,5-dimethylbenzenediazonium-2-carboxylate hydrochloride (0.8 g, 3.7 mmol) in a solution of bis(9-anthryl)cyclopropenone (0.25 g, 0.6 mmol), dry 1,2-dichloroethane (50 mL), and propylene oxide (2 mL) was re-

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(46) This addition procedure was patterned after the one described for the preparation of heptiptycene. See: Luo, J.; Hart, H. *J. Org. Chem.* **1987**, *52*, 4833.

(47) On the basis of a procedure described for the preparation of 3-substituted 1,2-di-*tert*-butylcyclopropenium perchlorates from di-*tert*-butylcyclopropenone.[48]

(48) Ciabattoni, J.; Nathan, E. C., III *J. Am. Chem. Soc.* **1969**, *91*, 4766.

(49) The $pK_{R^+}$, "the $p$H for 50% ionization of carbinol to cation",[50a] has been used as a criterion of stability for cyclopropenium cations relative to their carbinols since they were first synthesized, and there are ample data in the literature that can be used for comparison.[50b]

(50) (a) Breslow, R.; Höver, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168. (b) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011 and references therein.

(51) (a) Tri-$n$-propylcyclopropenium perchlorate ($pK_{R^+}$ 7.2): ref 50a. (b) Tri-*tert*-butylcyclopropenium perchlorate ($pK_{R^+}$ 6.4): ref 48. (c) Tricyclopropylpropenium chloride ($pK_{R^+}$ 9.4): ref 38e.

(52) Prepared by hydrogen peroxide oxidation of the corresponding isatin: (a) Marvel, C. S.; Hiers, G. S. In *Organic Syntheses*, 2nd ed.; Gilman, H., Blatt, A. H., Eds.; John Wiley: New York, 1941; Collect. Vol. 1, p 327. (b) Baker, B. R.; Schaub, R. E.; Joseph, J. P.; McEvoy, F. J.; Williams, J. H. *J. Org. Chem.* **1952**, *17*, 141, 149.

J. Am. Chem. Soc. **1990**, *112*, 3547–3554 3547

fluxed for 3 h.[46] The dark solution was washed with saturated bicarbonate and water, the organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure to leave a dark oil. This oil was chromatographed on silica gel with a mixture of chloroform and hexane. The fractions that showed spots with rf between 0.2 and 0.5 in 100% chloroform on analytical TLC (silica) were combined, the solvent was removed, and the resulting solid was purified by preparatory TLC (silica gel) in $CHCl_3$. A faint blue band at about rf 0.35 was collected and found to be the product. $^1$H NMR ($CDCl_3$) $\delta$ 7.78 (d, 4 H), 7.59 (m and s, 10 H), 7.43 (m, 12 H), 7.32 (s, 6 H), 7.10 (m, 20 H), 6.93 (t, 8 H) (aromatic hydrogens), 5.77 (s, 6 H, H(10)), 2.05 (s, 6 H, $CH_3$ in the achiral isomer), 2.01 (s, 12 H, $CH_3$ in the DL isomer), 1.55 (s, 6 H, $CH_3$ in the achiral isomer), 1.34 (s, 12 H, $CH_3$ in the DL isomer). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$) $\delta$ 162.63, 160.91 (cyclopropenone carbons), 144.66, 142.35, 142.15, 141.85, 141.79, 138.84, 138.60, 133.37, 132.69, 132.31, 125.58, 125.00, 124.76, 124.67, 124.56, 123.36, 122.48, 122.36, 122.30 ($C_{ar}$), 58.36 (C(9)), 53.12 (C(10)), 18.79, 18.32, 18.18 ($CH_3$); mass spectrum (high resolution), $m/z$ 614.2616 (614.2610 calcd for $C_{47}H_{34}O$).

**X-ray Crystallography.** Crystals of **1** were grown from 1-butanol/ethyl acetate by slow evaporation. A truncated trigonal prism of approximately 0.30 × 0.38 × 0.33 mm was chosen for X-ray measurements. The crystals are trigonal, space group $R3c$ (No. 161), with $a = b =$ 13.090 (3) Å, $c = 43.577$ (13) Å, $V = 6466$ (3) Å$^3$, and $d_{calcd} = 1.34$ g cm$^{-1}$ for $Z = 6$ ($C_{60}H_{39}GeCl$, $M = 868.0$). Intensity data were measured at 237 K on a Nicolet R3m diffractometer with $3° < 2\theta < 50°$ ($-h + k + l = 3n$; $k, l \geq 0$) with graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Of 2584 unique reflections 2027 were considered to be observed [$|F_o| > 3\sigma(F_o)$] after applying Lorentz and polarization corrections. The structure was solved in $R3c$ with SHELXTL software. The germanium and chlorine atoms were located in a Patterson map, and the carbon atoms were subsequently located in electron density difference maps. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at standard positions (C–H = 0.96 Å; C–C–H = 120° or 109.5°) and refined isotropically with a riding model. Refinement with 186 least-squares parameters converged at $R = 0.037$ and $R_w = 0.032$.

Crystals of **2** perchlorate were obtained from an acetonitrile solution by slow evaporation. A hexagonal prism of approximately 0.30 × 0.20 × 0.25 mm was chosen for the X-ray measurements. The crystals are hexagonal, space group $P6_3/m$ (No. 176), with $a = b = 15.145$ (5) Å, $c = 13.617$ (4) Å, $V = 2704$ (1) Å$^3$, and $d_{calcd} = 1.10$ g cm$^{-1}$ for $Z = 2$ ($C_{36}H_{39}ClO_4$, $M = 895.5$). Intensity data were measured at room temperature on a Nicolet R3m diffractometer with $3° < 2\theta < 114°$ with graphite monochromated Cu K$\alpha$ radiation ($\lambda = 1.54178$ Å). Of 1281 unique reflections, 1148 were considered to be observed [$|F_o| > 3\sigma(F_o)$] after applying Lorentz and polarization corrections. Three additional reflections (001, 020, and 040) were omitted because $F_o \ll F_{calcd}$ for these reflections, presumably due to extinction. The structure was solved in $P6_3$ with the SHELXTL direct methods software and was refined in $P6_3/m$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at standard positions (C–H = 0.96 Å; C–C–H = 120° or 109.5°) and refined isotropically with use of a riding model. Refinement with 130 least-squares parameters converged at $R = 0.057$ and $R_w = 0.065$. The unit cell contains one independent molecule with crystallographic $C_{3h}$ site symmetry. The perchlorate anion is disordered and no satisfactory scheme was found to model this disorder by a superposition of tetrahedral perchlorate anions with standard bond lengths and angles. This disorder would also mask the molecule of water that is indicated by the elemental analysis.

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**Registry No. 1**, 119480-90-9; **1** (isomer 1), 125829-99-4; **1** (isomer 2), 125830-00-4; **2**, 119503-08-1; **2**·$H_2O$, 125830-04-8; **3** (achiral isomer), 125830-03-7; **3** (DL isomer), 125876-02-0; **4** (achiral isomer), 125829-97-2; **4** (DL isomer), 125876-00-8; $GeCl_4$, 10038-98-9; $Tp_3SnBr$, 125829-98-3; 9-bromotriptycene, 15364-55-3; bis(9-triptycyl)cyclopropenone, 119480-91-0; bis(9-anthryl)cyclopropenone, 78594-10-2; propylene oxide, 75-56-9; 9-bromo-2,3-dimethyltriptycene, 125830-01-5; 4,5-dimethylanthranilic acid, 15089-51-7; 4,5-dimethylbenzenediazonium-2-carboxylate hydrochloride, 39654-49-4; 9-bromoanthracene, 1564-64-3; benzenediazonium-2-carboxylate hydrochloride, 4661-46-5.

**Supplementary Material Available:** Tables of bond lengths and bond angles with standard deviations, anisotropic thermal parameters, and hydrogen atom coordinates with isotropic thermal parameters for **1** and **2** perchlorate (5 pages); tables of observed and calculated structure factors for **1** and **2** perchlorate (14 pages). Ordering information is given on any current masthead page.

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# Chiral Molecular Recognition in the Thermodynamics of Spreading and Transition for Racemic and Enantiomeric Stearoyltyrosine Films

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**Abstract:** Equilibrium spreading thermodynamics, surface pressure vs area isotherms, and surface shear viscosities were measured for ionized monolayer films of the title compounds on an aqueous buffer subphase at pH 6.86. When allowed to equilibrate with their bulk crystalline phases (equilibrium spreading pressures), the racemic and enantiomeric films spread to significantly different surface pressures and displayed clearly defined transitions in their equilibrium spreading pressure vs temperature-phase diagrams at 30.3 and 26.3 °C, respectively. A thermodynamic analysis of the results demonstrates large differences between the racemic and enantiomeric films in terms of their changes in entropy and internal energy as they undergo the transition. In sharp contrast, racemic and enantiomeric films, spread from solution in the absence of the bulk phase, demonstrate only scant differences in their packing arrangements as reflected by surface pressure vs area isotherms taken in the same temperature range. Surface shear viscosities indicate that both spread films may be characterized as fluid. Taken together with previous results, these data indicate that short-range forces govern enantiomeric discrimination in fluid monolayer films and that the mechanism of detectable chiral molecular recognition between enantiomers lies in the transition to a tightly packed, crystalline surface state.

It is well-known that stereoselective interactions between enantiomeric pairs form a special subset of molecular recognition that is based entirely on molecular symmetry properties.[1] There is apparently no general pattern governing the preference of a given molecule for heterochiral ($R$,$S$) or homochiral ($R$,$R$ or $S$,$S$) interactions. Extremely short-range forces ($r^{-6}$–$r^{-12}$) differentiate the interactions between enantiomers, so that one might reasonably expect the greatest degree of stereorecognition to occur in very tightly packed, condensed states. This implies that any difference

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