**Table I.** Redox Potentials of Aromatic Hydrocarbons in DMA/TBABr[a]

|  | $-E°_1$, V | $-E°_2$, V | $-E°_3$, V | $-E°_4$, V |
|---|---|---|---|---|
| benzene | 3.35[b] | | | |
| naphthalene | 2.53 | | | |
| anthracene | 2.04 | 2.64 | | |
| phenanthrene | 2.49 | 3.13 | | |
| tetracene | 1.55 | 2.15 | | |
| azulene | 1.62 | 2.6[d] | | |
| fluoranthene[c] | 1.78 | 2.37 | | |
| 9-phenylanthracene | 1.99 | 2.55 | | |
| 9,10-diphenylanthracene | 1.98 | 2.50 | | |
| perylene | 1.70 | 2.29 | | |
| pyrene | 2.13 | 2.86 | | |
| triphenylene | 2.42 | 2.97 | | |
| bianthryl | 1.915 | 2.14 | 2.82 | 3.165 |
| biphenanthryl | 2.35 | 2.51 | 3.23[b] | |
| biphenyl | 2.68 | 3.18 | | |
| terphenyl | 2.40 | 2.70 | | |
| quaterphenyl | 2.28 | 2.455 | | |
| *trans*-stilbene | 2.26 | 2.72 | | |

[a] Cyclic voltammetry was performed at a Pt electrode ($\phi$ = 1 mm) with solution $10^{-3}$–$10^{-4}$ M in substrate. All redox potentials are determined from the average of the cathodic and anodic peak potentials and are expressed in V vs Ag/AgCl (calibration with $[Cp_2Co]^+$/ $[Cp_2Co]$). $T$ between −40 °C and −65 °C. [b] Cathodic peak potential measured at the rising portion of the background current. The redox potential is determined by digital simulation[14] after subtraction of the background voltammogram. [c] In MA/TBMAI. [d] Irreversible.

finally—the most important aspect—the cathodic limits are shifted to extremely negative potentials, e.g., −3.3 V vs Ag/AgCl for MA and −3.4 V for DMA. By using Pt electrodes, both solvents exhibit a significant low background current density with 2.5 $\mu$A/cm$^2$ (100 mV s$^{-1}$), which facilitates measurements at low substrate concentrations too.

The extraordinary qualities of MA and especially DMA in electrochemistry is documented in voltammetric reduction experiments at several simple aromatic hydrocarbons. In most cases—the only exceptions were benzene, naphthalene, and azulene—dianions were generated fully reversible in the time scale of slow sweep cyclic voltammetry. For benzene and naphthalene only a monoanion formation was observed, while for azulene the reduction to the dianion was chemically irreversible. Bianthryl and biphenanthryl could be reduced to their respective tetra- and trianions. The extremely negative redox potentials for the $X^-/X^{2-}$ ($X^{2-}/X^{3-}$) couples of phenanthrene (Figure 1), triphenylene, pyrene, biphenyl, terphenyl, and biphenanthryl in the presence of tetrabutylammonium bromide as supporting electrolyte were measured for the first time. The redox potential for the reduction of benzene, which has already been published by Heinze and Mortensen,[12] was confirmed. The reduction potentials measured in this study are summarized in Table I.

It should be emphasized that redox potential measurements with tetrabutylammonium salts may differ significantly from those with alkali salts, especially then when higher reduction states are studied. The reason is that alkali counterions shift redox potentials to more positive values due to ion-pairing effects. Furthermore, in most solvents with highly basic di- or multianions tetrabutylammonium cations undergo Hofmann eliminations, which produce protonated followup products. We can only speculate why Hofmann elimination does not occur in these amine solvents. A possible reason is that highly charged anions are well-stabilized, like solvated electrons which have long life-times in liquid ammonia, MA, and DMA. On the other hand, MA and DMA have better donor properties than solvents usually used for reduction experiments, such as THF, HMPA, DMF, and ACN. Thus, a plausible explanation is that the tetraalkylammonium ions are stabilized by the amine solvents.

The experimental technique for the preparation and the use of MA and DMA is simple and resembles, in principle, that

(12) Mortensen, J.; Heinze, J. *Angew. Chem.* 1984, *96*, 64–65; *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 84–85.

reported for liquid ammonia.[9,10] The gas (Messer–Griessheim, 99%) is condensed into a flask containing activated alumina and then refluxed for 1 h to remove all protic impurities. Afterwards it is condensed under vacuum into an electrochemical cell,[13] which allows low-temperature electrochemistry. In order to avoid IR drop problems, small electrodes, e.g., discs with a diameter of less than 1 mm, should be used.

(13) Kiesele, H. *Anal. Chem.* 1981, *53*, 1952–1954.

(14) Heinze, J.; Störzbach, M.; Mortensen, J. *J. Electroanal. Chem.* 1984, *165*, 61–64.

## A Parity Restriction on Dynamic Gearing Immobilizes the Rotors in Tris(9-triptycyl)germanium Chloride and Tris(9-triptycyl)cyclopropenium Perchlorate

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The 9-triptycyl (Tp) groups in molecules of the type $Tp_2X$ (X = $CH_2$, etc.) undergo virtually unhindered disrotatory cogwheeling in the manner of securely meshed and almost frictionless mechanical bevel gears.[1] Activation energies for this internal motion amount to at most a few kcal mol$^{-1}$.[2] However, when $N$ meshed gears are arranged in a closed cyclic array, disrotation is possible only if $N$ is even;[3] if $N$ is odd the gears are rigidly locked in place. We now report that the three Tp rotors in each of the title compounds, $Tp_3GeCl$ (1) and $Tp_3C_3^+ClO_4^-$ (2), are immobilized by this parity restriction on dynamic gearing. To our knowledge, the operation of this mechanical selection rule at the molecular level is without precedent.

Reaction of $GeCl_4$ with TpLi yielded 1,[4] whose $^{13}C$ and $^1H$ NMR spectra[5] are consistent only with a chiral ($C_3$) conformation in which the three equivalent Tp groups are statically geared.[6] At elevated temperatures there is some line broadening but no evidence of coalescence up to 120 °C (decalin-$d_{18}$). The lower limit for site exchange and enantiomerization is therefore ca. 20 kcal mol$^{-1}$. The $^1H$ and $^{13}C$ NMR signal patterns of $Tp_3SnCl$ are similar to those of 1.[7] $Tp_3MX$ compounds of this type exemplify a novel species of molecular propeller[8] in which each

(1) Iwamura, H.; Mislow, K. *Acc. Chem. Res.* 1988, *21*, 175 and references therein.

(2) Conrotation corresponds to gear slippage and requires significantly higher activation energies (e.g., $E_a$ = 33 kcal mol$^{-1}$ for X = $CH_2$).[1]

(3) Iroff, L. D. *J. Comput. Chem.* 1980, *1*, 76.

(4) All new compounds were fully characterized by elemental and spectral analyses.

(5) $^{13}C\{^1H\}$ NMR (62.9 MHz, CDCl$_3$, ambient temperature) $\delta$ 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)). $^1H$ NMR (250 MHz, CDCl$_3$, ambient temperature) $\delta$ 9.51 (ddd), 7.43 (ddd), 7.06 (two overlapping ddd's); 8.08 (d), 7.21 (dd), 6.62 (ddd), 5.68 (ddd); 7.77 (d), 7.33 (dd), 6.80 (ddd), 5.90 (ddd) (three sets of four aromatic proton resonances, one for each of the three nonequivalent benzene rings, assigned by NOE difference and COSY experiments—in each set the most downfield proton is the one closest to C(9)); 5.27 (s, H(10)).

(6) Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* 1980, *20*, 65.

(7) A previous report on the synthesis of this compound contains no information on the NMR spectra nor does it address the issues discussed in this paper. See: Ranson, R. J.; Roberts, R. M. G. *J. Organomet. Chem.* 1976, *107*, 295.

(8) Mislow, K. *Acc. Chem. Res.* 1976, *9*, 26 and references therein.
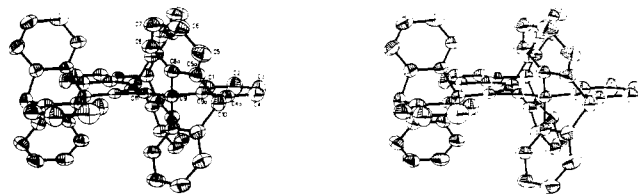
**Figure 1.** Stereoview of the X-ray structure of the cation in tris(9-triptycyl)cyclopropenium perchlorate (**2**) with thermal motion ellipsoids (50% probability) and atom labels. Hydrogen atoms are suppressed for clarity.

of the three blades is replaced by a three-toothed gear and in which structural rigidity is induced by the odd number of interlocked rotors.[9]

The axes of the Tp gears in Tp$_3$MX are coextensive with the C(9)–M bonds to form a pyramidal array with M at the apex. In **2** the three bevel gear axes are coplanar, and their extensions intersect at the center of the molecule. This compound was readily prepared from bis(9-anthryl)cyclopropenone:[10] addition of benzyne gave bis(9-triptycyl)cyclopropenone,[4] and addition of TpLi to the latter followed by reaction with HClO$_4$ afforded **2**.[4] The number of signals and their relative intensities in the $^{13}$C and $^1$H NMR spectra[11] are consistent only with a statically geared triskelion ($C_{3h}$) conformation which is also adopted by the molecule in the solid state (Figure 1).[12] There is no evidence of signal broadening up to 80 °C (acetonitrile), and the lower limit for site exchange is therefore ca. 17 kcal mol$^{-1}$.

In sum, torsional motion of the three Tp rotors in **1** and **2** is frozen because *uncorrelated as well as correlated rotation is mechanically disallowed in a closed cyclic array consisting of an odd number of securely meshed gears.* Further studies of these and related compounds are in progress.

**Supplementary Material Available:** Tables of atomic coordinates, bond lengths and bond angles with standard deviations, and anisotropic thermal parameters for **2** (5 pages); table of observed and calculated structure factors for **2** (7 pages). Ordering information is given on any current masthead page.

(9) Molecules of the type (Me$_3$C)$_3$MX also have $C_3$ ground-state symmetry, but the three *tert*-butyl groups are not securely gear-meshed, and enantiomerization takes place at very low temperatures on the NMR time scale by processes that involve conrotatory motion of two or all three of the *tert*-butyl groups. See: Hounshell, W. D.; Iroff, L. D.; Wroczynski, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 5212. Wroczynski, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1979**, *101*, 3980.

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

(11) $^{13}$C{$^1$H} NMR (125.8 MHz, CD$_3$CN, ambient temperature) δ 188.75 (cyclopropenium carbon C(11)), 146.28, 137.44 (aromatic carbons C(4a) and C(9a)), 145.37, 140.62 (aromatic carbons C(5a) and C(8a)), 128.18, 126.06, 124.50, 123.76 (aromatic carbons C(1)–C(4)), 129.47, 127.06, 126.90, 122.97 (aromatic carbons C(5)–C(8)), 62.01 (C(9)), 53.56 (C(10)). $^1$H NMR (500 MHz, CD$_3$CN, ambient temperature) δ 7.84 (dd, 2 H, H(5)), 7.54 (dd, 1 H, H(4)), 7.29 (ddd, 2 H, H(6)), 7.23 (dd, 2 H, H(8)), 6.93 (ddd, 2 H, H(7)), 6.89 (ddd, 1 H, H(3)), 6.82 (dd, 1 H, H(1)), 6.01 (s, 1 H, H(10)), 5.90 (ddd, 1 H, H(2)). Resonance assignments by NOE difference and COSY experiments.

(12) Crystals of **2** are hexagonal, space group *P*6$_3$/*m* (No. 176), with *a* = *b* = 15.145 (5) Å, *c* = 13.617 (4) Å, *V* = 2704 (1) Å$^3$, and $d_{calcd}$ = 1.32 g cm$^{-1}$ for *Z* = 2 (C$_{63}$H$_{39}$ClO$_4$, *M* = 895.5). Intensity data were measured on a Nicolet R3m diffractometer with 3° < 2θ < 114° with graphite monochromated Cu Kα radiation at room temperature. Of 1281 unique reflections, 1148 were considered to be observed [|$F_o$| > 3σ($F_o$)] after applying Lorentz and polarization corrections. Three additional reflections (010, 002, and 004) were omitted because $F_o$ ≪ $F_{calcd}$ for these reflections, presumably due to extinction. The structure was solved in *P*6$_3$ with the SHELXTL direct methods software and was refined in *P*6$_3$/*m*. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included at standard positions (C–H, 0.96 Å; C–C–H 120° or 109.5°) and refined isotropically with a riding model. Refinement with 130 least-squares parameters converged at *R* = 0.056 and $R_w$ = 0.059. The unit cell contains two molecules with crystallographic $C_{3h}$ ($\bar{6}$) 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.

## 2-Phosphino- and 2-Phosphinylbenzenethiols: New Ligand Types

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Compounds containing both thiol and phosphino or phosphinyl groups should be particularly useful as bidentate or polydentate ligands. A few examples of such compounds and their metal complexes are known,[1] but general syntheses are not available. It has been recently reported[2] that 2- and 2,6-substituted thiophenols such as **1** and **2**[3] (eq 1) and related 3- and 3,6-substituted



(1)
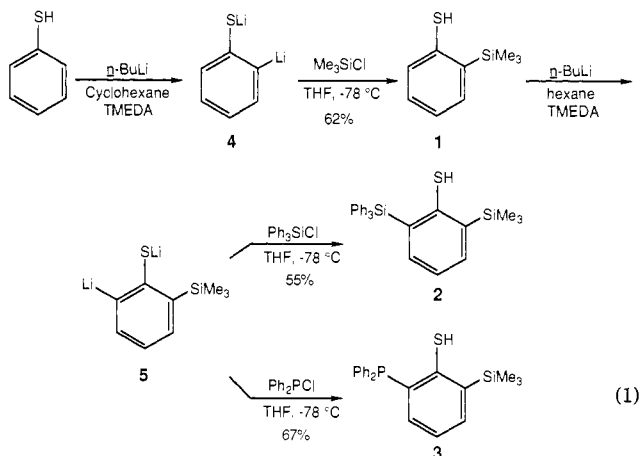
pyridinethiols[4] can be readily prepared from the parent compounds by ortho lithiation–electrophilic substitution procedures, and that these substituted thiols form a variety of novel transition-metal complexes.[4,5] We find that such methods can also be used to make 2-phosphino- and 2-phosphinylbenzenethiols (e.g., **3**), previously unknown types of mixed phosphorus–sulfur compounds.[1b] We report the application of this useful procedure to the preparation of interesting new classes of polydentate ligands containing phosphorus, sulfur, and in some cases silicon as well as a novel heterocyclic system.

(1) (a) 2-Phosphinoethanethiol derivatives represent a related, known ligand type: Blower, P. J.; Dilworth, J. R.; Leigh, G. J.; Neaves, B. D.; Normanton, F. B.; Hutchinson, J.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1985**, 2647. Jurkschat, K.; Uhlig, W.; Mügge, C.; Tzschach, A.; Schmidt, B.; Dräger, M. *Z. Anorg. Allg. Chem.* **1988**, *556*, 161. White, G. S.; Stephan, D. W. *Organometallics* **1988**, *7*, 903. (b) A brief report of a multistep synthesis of 2-phosphinobenzenethiol (*o*-HSC$_6$H$_4$PH$_2$) has appeared: Issleib, K.; Vollmer, R. *Z. Chem.* **1978**, *18*, 451. We thank Professor T. B. Rauchfuss for calling this reference to our attention.

(2) (a) Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658. (b) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654. (c) Smith, K.; Lindsay, C. M.; Pritchard, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 665.

(3) (Trimethylsilyl)benzenethiol$^{2a,c}$ (**1**) was treated with *n*-BuLi (2 equiv) and TMEDA (*N*,*N*,*N'*,*N'*-tetramethylethylenediamine; 1 equiv) in hexane for 24 h, and the solid was filtered off under argon and dissolved in THF cooled to −78 °C. Chlorotriphenylsilane (0.38 equiv) in THF was added, and the mixture was worked up as previously described.$^{2a}$ Chromatography gave **2** as a colorless solid (55%; based on Ph$_3$SiCl): mp 141–143 °C; $^1$H NMR δ 7.8–7.0 (m, 18 H), 3.58 (s, 1 H, SH), 0.46 (s, 9 H); $^{13}$C NMR δ 145.1, 142.7, 140.1, 137.1, 136.3, 134.4, 134.2, 129.5, 128.0, 125.1, 0.2. Anal. (C, H).

(4) Block, E.; Gernon, M.; Kang, H.; Zubieta, J. *Angew. Chem., Int. Edn. Engl.* **1988**, *27*, 1342.

(5) (a) Block, E.; Aslam, M. *Tetrahedron* **1988**, *44*, 281. (b) Block, E.; Gernon, M.; Kang, H.; Liu, S.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1988**, 1031. (c) Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta* **1989**, *156*, 27. (d) Block, E.; Gernon, M.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chem.* **1989**, in press. (e) Giolando, D. M.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 1636. (f) For a related approach to *o*-diphenylphosphinophenol and its coordination compounds, see: Rauchfuss, T. B. *Inorg. Chem.* **1977**, *16*, 2966.