

For the synthesis of allylic amines, compound **2** was treated with 1 equiv of triflic acid at $-78\text{ }^{\circ}\text{C}$ to afford **3** (see Scheme I). A solution of lithium anilide was then added at room temperature, followed by an alkyne, and the solution was heated to $80\text{ }^{\circ}\text{C}$ for several hours. During this time **4** lost methane to give imine complex/zirconaaziridine **5**, which was trapped in situ by the alkyne to give metallapyrroline **6**. We expected that the steric constraints of the EBTHI ligand would force the imine complex **5** to exist only as the trans diastereomer, as shown in Scheme I. Insertion of an alkyne was then expected to proceed with retention of configuration at the imine carbon atom,¹⁴ generating diastereomerically pure metallacycle **6**. Indeed, in most cases, the metallapyrroline **6** appeared to be diastereomerically and regioisomerically pure by ^1H NMR. Hydrolysis of **6** (aqueous HCl/ether), followed by chromatographic purification, afforded the allylic amine **7** in moderate to good yield. When (*S,S*)-**2** was used as the starting material, **7** was obtained with ee's $>90\%$ to $\sim 99\%$ (except for **7e**; see below).¹⁵ Thus, for 100:1 diastereoselectivity at $80\text{ }^{\circ}\text{C}$, we compute either $\Delta\Delta G^{\ddagger}$ or $\Delta\Delta G^{\circ} \geq 3.2$ kcal/mol for formation of the two diastereomers of **5**.

The method tolerates a wide variety of structures in both the alkyne and the amine, as shown in Table I, including substrates with oxygen functionalities. Also, 1-(trimethylsilyl)alkynes and 1-phenylalkynes react in a highly regioselective manner. Unfortunately, terminal alkynes do not insert, giving instead the alkynyl(amido)zirconium species, in contrast to their reaction with imine complexes of unsubstituted zirconocene.^{3,16} To our surprise, imine complex **5e** ($\text{Ar} = \text{R}_1 = \text{Ph}$) does not couple alkynes diastereoselectively, and allylic amine **7e** is obtained with a low ee.¹⁷ However, **5e** does couple diastereoselectively to propionaldehyde and 1-hexene, and good ee's were obtained for the resulting organic compounds. We note that the metallacyclic precursors to compounds **8** and **9** contain two new stereogenic centers that have been formed with excellent absolute stereoselectivity.

An X-ray crystallographic study of one of the racemic metallacycles, **6b** ($\text{Ar} = \text{Ph}$; $\text{R}_1 = n\text{-Bu}$; $\text{R}_2 = \text{R}_3 = \text{CH}_3$), allowed us to assign the absolute stereochemistry of the enantiomerically pure amines.¹⁸ The allylic carbon atom possessed *RS* configuration with respect to the ligand's *RS,RS* configuration. Thus, the enantiomerically pure allylic amines derived from (*S,S*)-**2** have the *S* absolute configuration, as drawn in Scheme I.

These results demonstrate the feasibility of using **1** and its derivatives as starting materials for asymmetric organic synthesis. The availability of enantiomerically pure **1**, the ability to functionalize unactivated substrates, and the very high ee's obtained for the allylic amines at $80\text{ }^{\circ}\text{C}$ make this an ideal system for further study. We are working to develop several other highly enantioselective, catalytic reactions based on the EBTHI ligand system.

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Supplementary Material Available: Detailed experimental procedures for the resolution of **1** and the synthesis and characterization of **6b**, **7a-i**, **8**, and **9**, experimental details for the crystallographic analysis of **6b**, an ORTEP diagram for **6b**, and lists of atom positions, thermal parameters, and bond lengths and angles for **6b** (26 pages). Ordering information is given on any current masthead page.

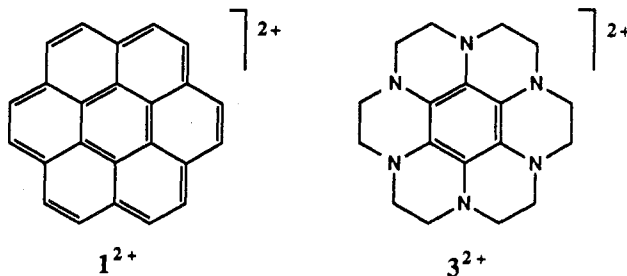
Coronene Dication: A Thermally Accessible Triplet[†]

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We find that the reaction of coronene (**1**) with strong oxidants yields the ESR spectrum of a thermally accessible triplet associated with the dipositive ion **1**²⁺. The triplet arises, by Hund's rule, from the 2-fold degeneracy of the HOMOs of the 6-fold-symmetric framework. The species is surprisingly stable at ambient temperature, decomposing above $50\text{--}70\text{ }^{\circ}\text{C}$. **1**²⁺ and the previously reported coronene dianion¹ **1**²⁻ provide a pair of aromatic dions to test if the MO-pairing relationships for alternate hydrocarbons² can be extended to their triplet states. Dications of benzene derivatives of 3-fold or higher symmetry³ have also been of recent interest as potential components of molecular ferromagnetic materials.⁴

As an unsubstituted aromatic dication, **1**²⁺ may be compared with the substituted cases reported previously. The hexachlorobenzene dipositive ion (**2**²⁺) is a ground-state triplet.⁵ No evidence for a thermally excited singlet state was found. The species was produced by reaction of **2** with Cl_2/SbF_5 to produce the radical cation; irradiation at $4\text{--}100\text{ K}$ yielded the dication. The latter did not survive softening of the SbF_5 matrix at about 180 K . The elegant synthesis of a derivative of hexaaminobenzene by Breslow et al., and its oxidation to a dication (**3**²⁺) exhibiting a triplet ESR



spectrum, provided a system stable at ambient temperature.⁶ A

[†] Contribution No. 5706.

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(12) Mp $92\text{--}135\text{ }^{\circ}\text{C}$ (*rac*-**2**:¹³ mp $148\text{--}162\text{ }^{\circ}\text{C}$). The ee was determined by treatment with excess (*R*)-(-)-*O*-acetylmandelic acid in C_6D_6 . Only one of the two possible diastereomers could be detected by ^1H NMR. See the supplementary material for details of the resolution procedure.

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(15) Ee's of **7** were in most cases determined by comparison of the ^1H NMR spectra of the racemates with those of the enantioenriched compounds, upon addition of $\text{Eu}(\text{hfc})_3$.

(16) Coordination of a second ligand, which is not possible for (EBTHI)Zr-imine complexes but occurs for Cp_2Zr -imine complexes, has been shown to alter the insertion reactivity of at least one other complex of zirconocene. Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441.

(17) (a) The ee of the metallacycle **6e** (as observed by ^1H NMR) is dependent on the reaction conditions, ranging from ca. 50% down to ca. 0%. (b) In contrast to *N*-phenylbenzylamine and dibenzylamine, *N*-(trimethylsilyl)benzylamine does couple diastereoselectively to 2-butyne, as observed by ^1H NMR.

(18) Full details are given in the supplementary material.

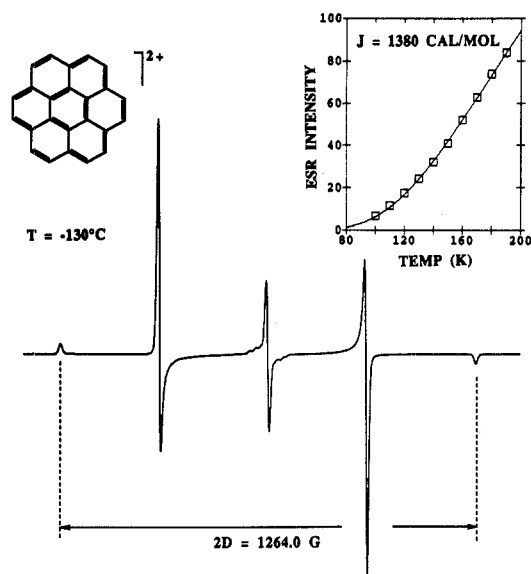


Figure 1. ESR spectrum of the coronene dication at $-130\text{ }^{\circ}\text{C}$ in frozen $\text{SbF}_5/\text{SO}_2\text{ClF}$ and temperature dependence of the intensity of the half-field line ($\Delta M = \pm 2$).

detailed examination of crystalline salts of 3^{2+} by Miller et al.⁷ showed that these solids possess thermally accessible triplets. In frozen solutions, however, small amounts (~ 0.1 – 10%) of 3^{2+} with a triplet ground state are found together with a majority of singlet ground state 3^{2+} and the associated thermally accessible triplets, the amounts varying with the solvent, the counteranion, and the thermal history of the sample.⁸ Recently, Martin et al. made the intriguing observation that the dication of hexaiodobenzene is a ground-state singlet with no evidence for a nearby triplet.⁹ The authors suggest that the positive holes reside in the equatorial belt of nonbonding σ orbitals forming a closed-shell dication.

The highest yields of 1^{2+} were obtained by SbF_5 in SO_2ClF (1:1 v/v) reacting, presumably by eq 1, with solid coronene at room temperature with vigorous stirring.¹⁰ The reaction is complete



within minutes and produces an almost black suspension. Examination by ESR takes place when the suspension is frozen or after removal of volatiles under high vacuum. Of the reagents used (e.g., XeF_2 , NOSbF_6 , BF_3 in SO_2ClF , SO_2 , and AsF_3 as solvents), only neat SbF_5 (low yield), $\text{SbF}_5/\text{CoF}_3$, and SbF_5/Cl_2 (slow reaction) produced the triplet ESR spectrum. $\text{SbF}_5/\text{SO}_2\text{ClF}$ was used previously to generate dications from polycyclic aromatic hydrocarbons for NMR studies.¹¹ Recently, the closely related AsF_5 and other oxidants were used to oxidize coronene to paramagnetic powders of high electrical conductivity: magnetic susceptibility measurements indicated the presence of paramagnetic species.¹²

The intense ESR spectrum displayed by a freshly prepared frozen suspension of oxidized **1** (Figure 1) is characteristic of

randomly oriented triplets with at least 3-fold symmetry ($E = 0$).¹³ The parameter D of the zero-field splitting tensor (defining the dipole–dipole interaction of the two unpaired electrons) is $D = 632\text{ G}$ (0.0591 cm^{-1}), while the components of the axially symmetric g tensor are $g_{zz} = 2.0006$ and $g_{xy} = 2.0017$.¹⁴ The latter are appropriate for an unsubstituted hydrocarbon: e.g., the triplet C_5H_5^+ has $g_{xy} = 2.0023$,¹⁵ while for 2^{2+} , g_{xy} is significantly shifted to 2.0192.⁴ The central feature in Figure 1 has $g = 2.0027$ and almost certainly arises from 1^{++} ($g = 2.00256^{20c}$).¹⁶ The triplet spectrum is associated with small particles since it can be observed even in fluid environments where tumbling of individual molecules would average out the spin–spin interaction. The resonance of 1^{++} grows with time and also on removal of the volatiles: otherwise, the spectrum of the solid residue is identical with that of the frozen reaction mixture.¹⁷

The intensity of the triplet spectrum of the solid residue increases with temperature (Figure 1), indicating that the triplet is not a ground state.¹⁸ A nonlinear least-squares fit to the Bleaney–Bowers equation¹⁹ (eq 2) yields $\Delta E = 1.4\text{ kcal/mol}$ as the energy gap separating the singlet and triplet states.

$$I \propto 1/[\exp(\Delta E/kT) + 3]T \quad (2)$$

The D and ΔE parameters of 1^{2+} (632 G, 1.4 kcal/mol) are close to those found for the triplet coronene dianion 1^{2-} (580 G, ca. 2.3 kcal/mol above the ground singlet¹). This similarity may be regarded as a manifestation of the MO-pairing relationships,² observed in alternate π systems, arising from the energy symmetry of bonding and antibonding π molecular orbitals in the parent coronene.²⁰ The agreement is particularly notable since, apart from the theoretical limitations of such pairing relationships, the effects of changes in bond lengths, counterions, and different solvents may well introduce additional complications.

We may regard 1^{2+} as closer to an ideal π system than the benzene dication, which has not yet been observed. Using MINDO/3 calculations for the latter, Dewar and Holloway predicted significant distortions of both singlet and triplet states from planar regular hexagons.²¹ A more drastic structural change occurs with the dication of hexamethylbenzene,²² which rearranges to a pentagonal pyramid in a singlet state. Coronene, with a larger number of occupied π orbitals above the highest σ orbital, remains planar on removal of two electrons.²³ Computations with Dr. D. A. Dixon are underway in a more thorough examination of symmetric aromatic dications.

Acknowledgment. We thank Drs. J. S. Miller, D. L. Thorn, and F. N. Tebbe for interesting discussions and S. A. Hill and F. W. Barney for technical assistance.

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(16) The three shoulders on each side of this signal, spreading over ca. 150 G, may be associated with aggregates of higher spin multiplicity with very small D 's.

(17) The growth of 1^{++} is presumably caused by the conproportionation reaction: $1 + 1^{2+} \rightarrow 2\,1^{++}$ in the presence of sparingly soluble unreacted **1**.

(18) Microwave power was reduced to a minimum to prevent saturation.

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