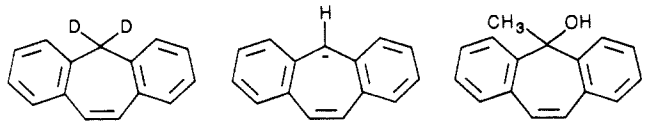
vinylic regions (δ 7-7.4) of the ^{1}H NMR spectrum remain essentially unchanged, indicating no observable deuterium incorporation into other positions of the compound. The ^{13}C NMR spectrum (^{1}H decoupled) shows carbon 5 of **1** at δ 41.6 and the same carbon of **4** at δ 41.26, as a 1:1:1 triplet ($J_{C-H} \approx 20$ Hz). Again, no changes are observed in the other carbon signals, indicating that deuterium incorporation is exclusively at the 5-position of **1**. Extended photolysis of **1** does result in formation of ≈5-10% yield of α,α'-dideuteriosuberene (**5**), as indicated by mass spectrometry.



5 **6** **7**

Although a radical mechanism resulting in incorporation of deuterium from solvent D_2O is unlikely, we have ruled this out by showing that deuterium is not incorporated when **1** is photolyzed in pure CD_3CN. Additionally, when pure **5**[6] is photolyzed in H_2O/CH_3CN, facile formation of **4** and subsequently **1** is observed, as shown by both ^{1}H and ^{13}C NMR. Again no exchange is observed when **5** is photolyzed in pure CH_3CN.

Photolysis of **2** and **3** under similar conditions as described above for **1** resulted in no observable deuterium incorporation in recovered substrates, consistent with the absence of a simple radical mechanism, since such a mechanism should not show such a drastic selectivity in reactivity. In the ground state, **2** undergoes deuterium incorporation at the 9-position with a half-life of about 10 h in refluxing D_2O/CH_3CN (pD ≈ 12), unlike **1** and **3**, which do not undergo exchange under these and more forcing conditions. These observations are consistent with their known ground-state pK_a's, with fluorene (**2**) being the most acidic (p$K_a \approx 23$)[1] and **1** and **3** much less acidic (p$K_a \geq 32$).[1,7] The observed facile photoexchange of **1** suggests that it becomes vastly more acidic kinetically than **2** and **3** in the excited state, implying that there is inherent stability associated with an $8\pi(4n)$ conjugated cyclic carbanion in S_1.

Steady-state fluorescence studies show that water is a very efficient quencher of S_1 of **1** but not the corresponding singlet states of **2** and **3**. For example, on going from pure CH_3CN to 80% H_2O/CH_3CN, the fluorescence quantum yield of **1** decreases by over an order of magnitude. Furthermore, the fluorescence lifetime of **1** also decreases, from 4.6 ns (pure CH_3CN) to 0.13 ns (80% H_2O/CH_3CN). On the other hand, the lifetime of **2** stays unchanged at ca. 6 ns in the different solvents. *It is therefore reasonable to assume that water is acting as the deprotonating base for photoexcited* **1**, *resulting in formation of transient suberenyl carbanion* **6**. Consistent with this proposal are the observations that neither the fluorescence intensity or fluorescence lifetime of **7** are changed significantly on going from pure CH_3CN to aqueous CH_3CN, since this suberene derivative has no benzylic protons. These results rule out a lifetime effect in explaining the observed reactivity differences in photoionization of the benzylic C-H bonds of **1-3**.

In summary, we have discovered a way to promote photochemical C-H bond heterolysis, viz., by choosing a compound which on ionization of the C-H bond gives formally a ground-state antiaromatic carbanion. This opens up a way for studying carbon acids in the excited state, a previously inaccessible area experimentally. In addition, the results of this and a previous study[3] suggest that $8\pi(4n)$ conjugated cyclic carbanions have aromatic[8] character in S_1.[9]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for an operating grant and a postgraduate scholarship to E.K. Additional support was provided by the University of Victoria. Single-photon fluorescence lifetime measurements and analyses were carried out at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Research Program of the Division of Research Resources of NIH (RR00886) and by the University of Texas at Austin.

Registry No. **1**, 256-81-5; **4**, 114185-93-2.

(6) A sample of pure **5** was made by $LiAlD_4/AlCl_3$ reduction of dibenzosuberenone in diethyl ether.

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(8) We use Breslow's[5b] working definition of aromaticity and antiaromaticity, based on relative stabilization or destabilization associated with cyclic π-systems, compared to reference compounds. As excited states are short-lived, it would not be fair, for example, to use an NMR criterion for aromaticity of excited states.

(9) We[10] have recently carried out Pariser-Parr-Pople π-SCF calculations of the above and related monocyclic systems which show that many ground-state antiaromatic systems become pseudoaromatic in the first excited singlet state, as indicated by more delocalized charge distributions in S_1. Jug and co-workers[11] have recently suggested such a possibility by using SINDO1 calculations on several monocyclic systems.

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π-Facial Selectivity: Heteroatom Directed Syn/Anti Stereoselection in Diels-Alder Cycloadditions of Plane-Nonsymmetric Cyclopentadienes†

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The synthetic utility of the Diels-Alder reaction is enhanced due to the regiospecificity and stereocontrol (endo/exo) engendered by favorable orbital interactions.[1] There is considerable current interest in the diastereoselectivity exerted by an adjacent heteroatom-substituted center on these cycloadditions, although the factors responsible for the observed facial stereoselection are still not fully understood.[2-4] It is clear that an allylic heteroatom can

† Dedicated to Professor Z. Valenta on the occasion of his 60th birthday.

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have a pronounced influence on the course of Diels–Alder reactions. Often the interpretation of the results is complicated by the necessity of determining the relative contribution and importance of various conformers in which the heteroatom is aligned "inside" as predicted by electronic factors or "outside" as favored on steric grounds. Cyclic dienes avoid this complication and examples that are plane-nonsymmetric afford insight into the "addition directing" influence of diverse functional groups as exemplified by the study of the pentamethylcyclopentadiene compounds **1–8** described below.

Woodward and co-workers[5] established that ethylene added syn[6] to 5-acetoxycyclopentadiene. Recent studies using other 5-acetoxy- and 5-hydroxycyclopentadiene systems revealed a similar bias,[7] as did pentachlorocyclopentadienes in which bond formation occurred preferentially at the sterically more hindered syn face.[8] In contrast, 5-bromo- and 5-iodocyclopentadiene reacted in an anti manner.[9] These observations have been rationalized, in part, by invoking the role played by the lone-pair electrons on the 5-substituent.[10,11] Secondary orbital interactions were considered responsible for the exclusive syn addition of triazolinediones to anhydride and imide bridged [4.4.3]propellane dienes.[12] Ether bridged dienes added anti, while most sulfur and sulfone systems reacted syn.[12] The electronically governed facial selectivity diminished with a methyl substituent and was primarily regulated by steric interactions in the case of **9** (Table I, entry k).[13] Similarly 9,10-dihydrofulvalene and related domino Diels–Alder reactions displayed varying degrees of facial control,[14] while in other carbocyclic systems such isodicyclopentadiene favorable σ/π interactions may control endo attack.[15] A recent study on conformationally locked (1*E*)-substituted-1,3-dienes found preferential addition anti to the allylic substituent (CH_3, OR, vinyl SO) indicating the syn preference observed in cyclopentadienes may not be general.[16] Prior to the present study no experimental evidence was available concerning the role of sulfur or nitrogen substituents on cycloadditions in a related series of cyclopentadienes, although a priori they might be expected to resemble their oxygen analogues.

The requisite cyclopentadienes, in which competing [1,5] sigmatropic rearrangements are degenerate, were synthesized from 1,2,3,4,5-pentamethylcyclopentadiene (Supplementary Material). The thiol **1** was prepared from dipentamethylcyclopentadiene sulfide[17] by sodium/ammonia reduction. Alkylation (*n*-BuLi, Me_2S_2), followed by oxidation, provided the sulfur compounds **2–4**, and the amine **8** was prepared as previously described.[18] The alcohol **5** was obtained via [2,3] sigmatropic rearrangement (22 °C) of the sulfoxide **3** in the presence of trimethylphosphite. Maleic anhydride or *N*-phenylmaleimide were employed as the dienophiles on the basis of their reactivity, their established endo selectivity, and their use in previous work, thus facilitating comparisons with earlier studies.

The results of the cycloadditions are summarized in Table I and establish the strong preference for syn addition exhibited by the oxygen and nitrogen substituents. *The striking reversal of facial selectivity encountered with the methyl–sulfur substituents is clearly of fundamental interest and potential synthetic utility*, as is the considerable difference in the relative cycloaddition rates. Separate samples of the anti thiomethyl adduct and its syn isomer were recovered unchanged from refluxing benzene (24 h) and confirmed the product distributions were kinetic. The structures and stereochemistries of the adducts were established by ^1H NMR solvent shifts, NOE measurements, chemical correlations, and from X-ray analysis of the hydroxy, oxymethyl, and sulfoxide adducts.

The unexpected results for the sulfur series are at variance with current literature explanations for the oxygen examples.[19] In the case of the sulfoxide **3** and the sulfone **4** the large size of these groups will cause the dienophile to approach the sterically less encumbered methyl face (anti). However, the reduced reactivity and altered facial selectivity of the thiomethyl derivative **2** compared to the methyl ether **6** indicates there is a significant electronic difference in these systems in spite of the fact that the steric bulk is not identical. (*A* values[20] and *n* values[21] indicate thiomethyl is approximately 8–17% larger than oxymethyl, but spatial requirements that include polarizability (MR, molar refractivity) imply a greater difference (>80%).)[22]

For C-5-oxygen substituted cyclopentadienes the preferential syn (contrasteric) approach has been rationalized by orbital mixing between the lone-pair electrons and the diene (HOMO),[10] alternatively Anh favors the beneficial interaction of the antisymmetric oxygen orbital with the dienophile (LUMO),[11] while an alternative explanation invokes a favorable σ/π interaction.[15] The Gleiter–Ginsburg rationalization involving secondary orbital interactions is not applicable to maleic anhydride.[12] On the basis of electrostatic interactions Kahn and Hehre concluded that electrophilic dienophiles should add preferentially to the more nucleophilic diene face syn to "a lone-pair-containing allylic substituent".[4] Clearly this simple electrostatic model cannot be extended in a straightforward manner to sulfur systems.

The cyclopentadienes may be a unique case since in an oxygen- and sulfur-bridged propellene, cycloaddition was anti to oxygen and syn to sulfur.[12,23] Photoelectron spectra and preliminary ab

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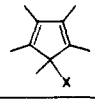
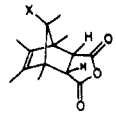
Table I. Stereoselection of Cycloadditions of C-5 Substituted Cyclopentadienes

				 addition ratio	
entry	compd	X	reaction time[a]	anti	syn
a	1	SH	3 h	4.5[b]	5.5[b]
b	2	SMe	27.5 h	9	1
c	2	SMe	46 h	11.5[b]	1[b]
d	3	SOMe	48 h	10	0
e	4	SO_2Me	9 days	10	0
f	5	OH	<30 s	0	10
g	6	OMe	<10 min	0	10
h	7	NHAc	3.5 h	0	10
i	7	NHAc	3.5 h	trace	10[b]
j	8	NH_2	3.5 h	0	10[b]
k	9	H	<30 s	2[13]	8[13]

[a] Approximate time for diene disappearance (TLC); reactions were run at 22 °C; yields in all cases were >90%; ratios were determined by integration of ^1H NMR spectra of the total reaction mixture. [b] *N*-phenylmaleimide adduct.

initio calculations[25] suggest that the electron density is decreased on the diene syn face and that the sulfur lone pair electrons interact more strongly with the diene (HOMO) than in the case of oxygen. This interaction must be disrupted prior to cycloaddition and favors the anti approach. The relative rates and stereoselection are also influenced by substituent orientation. The distal oxygen conformer is the most reactive and leads rapidly to adduct compared to the sulfur series in which both conformers have comparable energy. These factors—lone-pair interactions, conformational reactivity, and substituent electronegativity enhance anti cycloaddition in the sulfur series.

In conclusion, this study adds to our understanding of the facial preferences of addends in [4 + 2] cycloadditions of cyclopentadienes. Heteroatom-directed control of π-facial selectivity by variation of the substituent or through the judicious choice of mixed acetals (oxathiolane ketals) has considerable potential for the total synthesis of natural products. Approaches to multicyclic systems that utilize these features are under investigation.

Acknowledgment. We are grateful to Memorial University of Newfoundland and the Natural Sciences and Engineering Research Council of Canada for financial support of this research, to B. Gregory for high resolution mass spectra, to C. Jablonski for NOE and NMR measurements, to A. W. Hanson and M. J. Newlands for X-ray analysis, to R. W. Franck, P. G. McDougal, N. H. Werstiuk, R. A. Poirier, and D. J. Burnell for fruitful discussions, and to the referees for their constructive comments.

Supplementary Material Available: Synthetic schemes and brief reaction conditions for preparation of the dienes and adduct interconversions (2 pages). Ordering information is given on any current masthead page.

(23) Professor Franck has kindly informed us that acetylene dicarboxylates, tetracyanoethylene, and *N*-phenyltriazolinedione exhibit reversed facial selectivity in his acyclic dienes as also observed in an amino case by Kozikowski and co-workers[3] (also: Franck, R. W.; Tripathy, R.; Onan, K. D. *J. Am. Chem. Soc.* **1987**, in press and ref 16). Thus the thiomethyldiene **2** was treated with tetracyanoethylene. A single anti adduct was obtained whose structure was established by X-ray analysis. It seems likely that in acyclic cases more reactive dienophiles afford predominantly the anti (to the oxygen and nitrogen substituent) product as a consequence of the preferential trapping of a different rotamer ratio compared to maleic anhydride. This should allow a level of facial control by variation of the dienophile. In addition, recent evidence has indicated that cyanoethylene and triazolinediones react by an aziridinium imide (1,4-zwitterion) mechanism.[24]

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Molecular Recognition of Amino Acids: Two-Point Fixation of Amino Acids with Bifunctional Metalloporphyrin Receptors [1]

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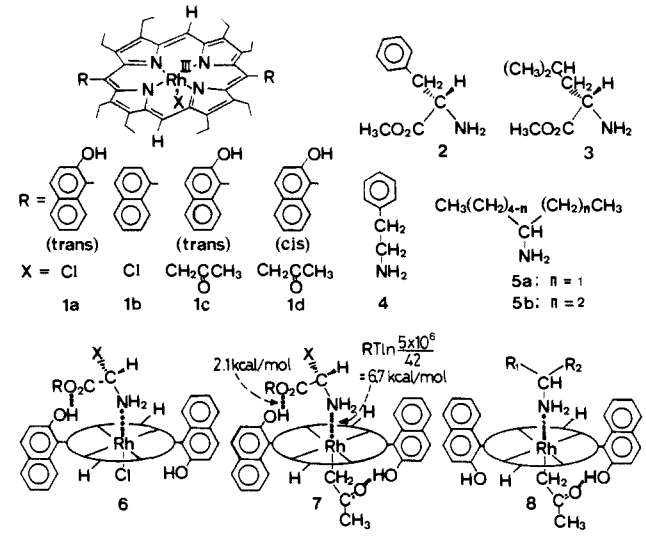
Amino acids can be solubilized in organic solvents in the form of ammonium or carboxylate ion upon formation of crown complexes[2] or hydrophobic salts.[3] The complexation of zwitterionic forms is generally weak,[4] but some elaborate receptor systems for these have been reported.[5,6] Nonionic *amino acids* ($H_2NCHRCO_2H$), on the other hand, seem to be a potential form in apolar organic solutions but have been receiving surprisingly little attention.[7] We report here the first successful two-point fixation of amino acids and amino esters in *nonionic forms* via simultaneous metal-coordination and hydrogen-bonding interactions with bifunctional metalloporphyrin receptors.



Chlororhodium(III) complexes of *trans*-5,15-bis(2-hydroxy-1-naphthyl- (**1a**) and 5,15-bis(1-naphthyl)octaethylporphyrin (**1b**)[8] form stable 1:1 rhodium–amine adducts, in a practically irreversible manner,[9] with L-phenylalanine methyl ester (**2**) and L-leucine methyl ester (**3**) as well as 2-phenylethylamine (**4**) and 3- (**5a**) or 4-aminoheptane (**5b**) as references in $CHCl_3$.[10] The

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