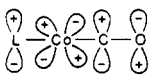
can be attributed to the extra electron. To account for the lability of the 19-electron complex, we propose there is a delocalization of the odd electron into an orbital that is Co-CO antibonding (π^*);[27] occupation of these orbitals will weaken the Co-CO bond and labilize the complex toward CO dissociation. The ESR spectrum of the $Co(^{13}CO)_3L_2$ complex is consistent with this hypothesis. Spectra a and b of Figure 2 show the ESR spectra of the $Co(^{13}CO)_3L_2$ and $Co(CO)_3L_2$ complexes, run under identical conditions. The spectra are nearly identical, but note the line broadening in the $Co(^{13}CO)_3L_2$ spectrum. As tested by varying the conditions, this line broadening was not caused by the instrument, the concentration of the compound, or the presence of oxygen, and therefore it must reflect a slight electronic coupling to the ^{13}C atoms. Note that only a slight weakening of the Co-CO bond is required for labilization. Although exact numbers are not available, the 24 kcal/mol enthalpy for the Co-CO bond from $\Delta H^{\ddagger}$ is probably about 5 to 10 kcal/mol less than typical Co-CO bond energies of 18-electron complexes.[28] A 5 to 10 kcal/mol decrease in activation energy corresponds to an increase in the rate constant for dissociation of about 10^4-10^8.[29] Thus, the delocalization of the 19th electron and the concomitant decrease in the Co-CO bond energy (as reflected in $\Delta H^{\ddagger}$) give the $Co(CO)_3L_2$ complex its substitutional lability.

The conclusion above can be extended to other 19-electron complexes. Note that in type I complexes[9] [e.g., $Fe(CO)_5^-$] there is a greater likelihood that the extra electron will occupy a metal-ligand antibonding orbital because low-energy π^* ligand orbitals are not available [as in $Co(CO)_3L_2$ and other type III complexes]. Thus, the M-L bond will be significantly weakened in these complexes and fast dissociative processes are predicted and apparently observed.[30] The point is that if the $Co(CO)_3L_2$ complex, especially chosen because it might undergo associatively activated substitution, reacts dissociatively, then certainly other 19-electron complexes are also going to react dissociatively.

Acknowledgment. This work was supported by the National Science Foundation. The Sloan Foundation is acknowledged for a fellowship to D.R.T. Drs. P. Krusic, W. Kaim, and P. Rieger are thanked for helpful discussions.

Supplementary Material Available: A description and tables giving the details of crystallographic data collection, bond distances and angles, intra- and intermolecular distances and angles, positional parameters, and thermal parameters for $Co(CO)_2L_2PPh_3$, a plot of $-\ln [(A_t - A_\infty)/(A_0 - A_\infty)]$ vs time for the reaction of $Co(CO)_3L_2$ with PPh_3, a plot of $-\ln (k/T)$ vs T^{-1} for the reaction of $Co(CO)_3L_2$ with PPh_3, and a sketch of the double-valve reaction cell used for the kinetics studies (22 pages); listings of calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

(27) The molecular orbital containing the odd electron would be primarily an L_2 π^* orbital mixed with an antibonding combination of a Co d orbital and a CO (π^*) orbital:



The Co/CO portion of this MO is the antibonding combination of the Co and CO (π^*) orbitals used in "back-bonding."

(28) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71-110.

(29) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 211.

(30) Examples of reactions in which the dissociative behavior of 19-electron complexes can be inferred are found in: (a) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879-886. (b) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1976**, 749-752. (c) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817-819. (d) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.

A Study of Asymmetric Induction during the Addition of Enolate Nucleophiles, Having Sulfoximine Chiral Auxiliaries, to Diene-Molybdenum and Dienyliron Complexes

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Contribution from the Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and University of Toledo, Toledo, Ohio 43606. *Received May 31, 1988*

Abstract: Asymmetric induction as high as 90% ee was obtained during the reaction of enolates, derived from optically pure sulfoximinyl esters of type **16**, with the cycloheptadiene-$Mo(CO)_2Cp$ cation. Lower, but still significant asymmetric induction was observed during the reaction of these enolates with cyclohexadiene-$Mo(CO)_2Cp$, cycloheptadienyl-$Fe(CO)_2P(OPh)_3$, and cyclohexadienyl-$Fe(CO)_3$ complexes. It was established that enolates derived from the (-)-(*R*)-sulfoximine preferentially add to the *pro-R* terminus of the diene and dienyl complexes, by determination of absolute stereochemistry of derived alcohols using Mosher's method and by X-ray crystal structure determination of a major adduct **33** from reaction with cyclohexadiene-$Mo(CO)_2Cp$ hexafluorophosphate. Desulfonylation of the sulfoximine ester adducts gave enantiomerically enriched monoester derivatives **21-24**, which could, in some cases, be further functionalized by hydride abstraction and second nucleophile addition. An attempt is made in this paper to rationalize the observed stereoselectivity on the basis of Seebach's topological rule for somewhat related Michael additions of enamines to nitroolefins.

The control of stereochemistry during carbon-carbon bond formation is one of the central issues in contemporary organic synthesis.[2] The definition of relative stereochemistry during the attachment of substituents to six- and seven-membered rings, with a transition-metal moiety as a stereodirecting template, is currently being studied in our laboratory and has led to new methodology for the construction of subunits of potential value in natural products synthesis.[3] For example, the cyclohexadiene-Mo-

(1) (a) Case Western Reserve University. (b) University of Toledo.

(2) Morrison, J. D. *Asymmetric Synthesis*; Academic: Orlando, FL, 1983-1985; Vol. 1-5.

(3) (a) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. (b) Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276. (c) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060. Pearson, A. J.; Ray, T. *Tetrahedron* **1985**, *41*, 5765.

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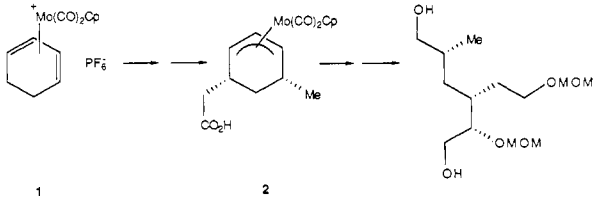
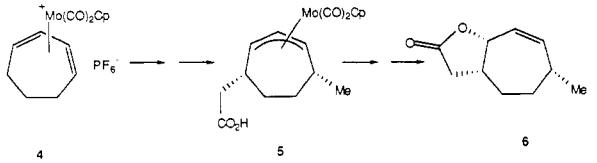
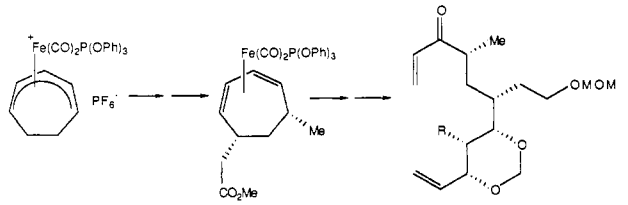
$(CO)_2Cp$ complex **1** has been converted,[3a] via **2**, to the acyclic molecule **3**; cycloheptadiene-$Mo(CO)_2Cp$ **4** can be converted[3b]



1 2 3

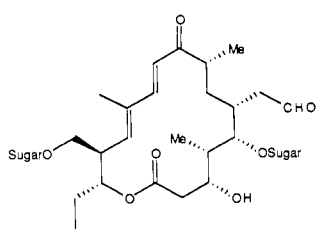


4 5 6



7 8 9 (a) R = Me (b) R = OMe

to **5** and then to **6**; the cycloheptadienyliron complex **7** is readily converted,[3c] via **8**, to the acyclic molecule **9**. Compounds **3** and **9** are of particular interest, since they have relative stereochemistry appropriate for the construction of the right-hand half of macrolide antibiotics such as tylosin (**10**)[4] and carbomycin B (**11**).[5]



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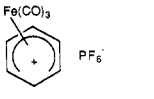

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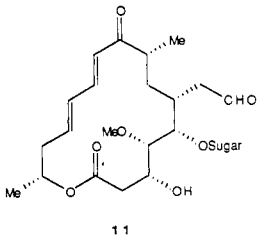

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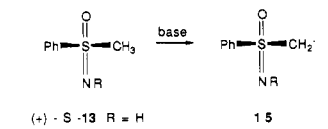
However, a major shortcoming of this chemistry stems from the fact that the starting complexes **1**, **4**, and **7** all have a plane of symmetry, so that intermediates **2**, **5**, and **8** are produced in racemic form. This would lead to problems of diastereomer formation during the attachment of a left-hand subunit of **10** or **11**, in addition to a loss of half of the material as biologically inactive product. While it could be argued that chiral modifications of **1**, **4**, or **7**, formed by introducing chiral ligands onto the metal, might allow asymmetric induction during nucleophile addition,[6] there were compelling reasons for the study of an alternative strategy involving reaction of the prochiral complexes with chiral nucleophiles.

An earlier observation[3a] that reactions of complex **1** or **4** with unsymmetrical enolate nucleophiles, such as that derived from methyl phenylsulfonylacetate, occurred with pronounced diastereoselectivity prompted us to examine similar reactions with enolates bearing chiral auxiliaries. We hoped that this diastereoselectivity would allow stereochemical information to be transmitted from the chiral auxiliary to the newly formed asymmetric center. The most appropriate choice for our preliminary experiments appeared to be the sulfoximines recently developed by Johnson,[7,8] since these are clearly related to the phenylsulfonyl derivatives. This paper reports the asymmetric induction achieved by using such nucleophiles with complexes **1**, **4**, **7**, and **12** and attempts to rationalize the results on the basis of an X-ray crystallographic study of the major stereoisomer formed in one of these reactions.[9]

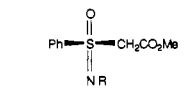
Results

Optical resolution of *S*-methyl-*S*-phenylsulfoximine **13** using (+)-10-camphorsulfonic acid has been described by Johnson,[7] allowing efficient preparation of the (+)-(*S*)-sulfoximine. The



(+) - S -13 R = H 15

14 R = Ts, Me, TBDMS, DMTS



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mother liquors from this resolution are reduced in volume and treated with base to liberate enriched (−)-(*R*)-sulfoximine, and the resolution is repeated on this material with (−)-10-camphorsulfonic acid to give optically pure (−)-(*R*)-sulfoximine. For brevity, the absolute stereochemistry of the (+)-(*S*) derivative is indicated in structure **13**. N-Substitution is readily achieved to give a range of derivatives **14**. While these compounds can be deprotonated with a variety of bases to give carbanion nucleophiles **15**, these species were found problematic in reaction with **1**, **4**, and **12**, giving multiple products. Consequently, each N-substituted sulfoximine **14** was converted to the corresponding ester derivative **16**. The enolate anions from these are equivalent to the sulfonyl derivatives used earlier[3] and react satisfactorily with diene-$Mo(CO)_2Cp$ and dienyl-$Fe(CO)_2L$ complexes. Examination of the ^1H NMR spectra of the crude products **17–20** from these reactions showed the expected mixtures of diastereomers, usually with one of them predominating. Since no information regarding asymmetric induction could be deduced from this data, each adduct was desulfonylated, using sodium– or aluminum–mercury amalgam to give monoester derivatives **21–24**. Some of the *N*-silyl-protected compounds were quite resistant to direct desulfonylation, and a two-step sequence [(1) Bu_4NF; (2) Na–Hg or Al–Hg] was necessary to effect this conversion.

(4) A recent review of macrolide synthesis gives an excellent coverage of the literature in this area: Paterson, I.; Mansuri, M. M. *Tetrahedron* **1985**, *41*, 3569.

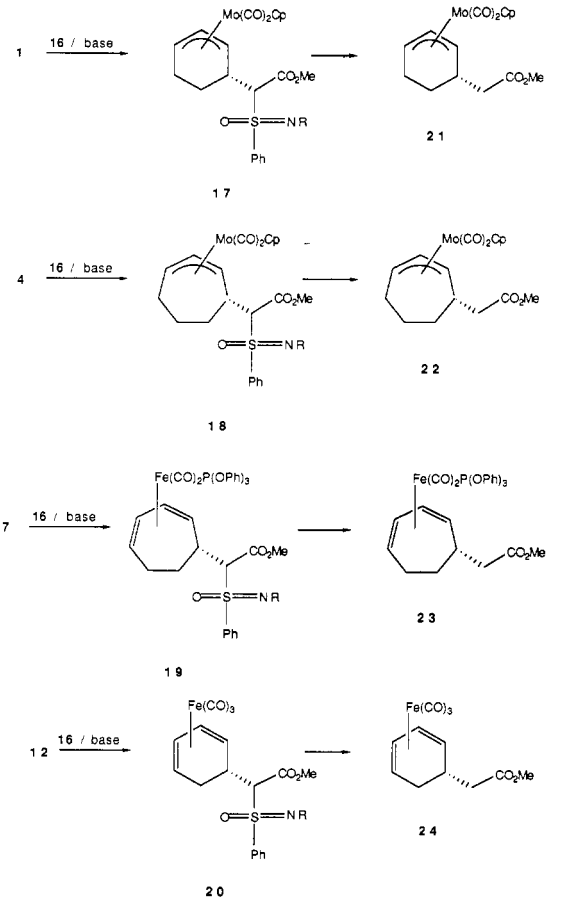
(5) For previous synthetic work, see: Tatsuta, K.; Amemiya, Y.; Maniwa, S.; Kinoshita, M. *Tetrahedron Lett.* **1980**, *21*, 2837.

(6) Chiral phosphine ligands have been used in conjunction with π-allylpalladium complexes to achieve asymmetric allylation: Trost, B. M.; Dietsche, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 8200. Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649. Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143. Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191. Hayashi, T.; Yamamoto, A.; Ito, Y. *Chem. Lett.* **1987**, 177. Yamamoto, K.; Tsuji, J. *Tetrahedron Lett.* **1982**, *23*, 3089. Bosnich, B.; Mackenzie, P. B. *Pure Appl. Chem.* **1982**, *54*, 189.

(7) (a) Johnson, C. R. *Aldrichimica Acta* **1985**, *18*, 3. (b) *Acc. Chem. Res.* **1973**, *6*, 341. (c) Johnson, C. R.; Stark, C. J., Jr. *J. Org. Chem.* **1982**, *47*, 1196. (d) Johnson, C. R.; Haake, M.; Schroeck, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 6544. (e) Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc.* **1973**, *95*, 7418. (f) Johnson, C. R.; Schroeck, C. W.; Shanklin, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 7424. (g) Johnson, C. R.; Kirchhoff, R. A.; Reischer, R. J.; Katekar, G. F. *J. Am. Chem. Soc.* **1973**, *95*, 4287.

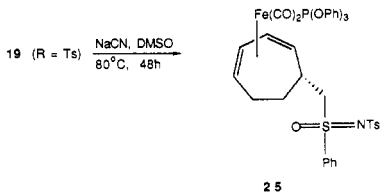
(8) There is some inconsistency in the reporting of absolute stereochemistry of **13** in ref 7b and 7c, but the correct stereochemistry is shown here. The stereochemistry of (−)-sulfoximinyl esters given in ref 9b is incorrect.

(9) Preliminary communications: (a) Pearson, A. J.; Yoon, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1467. (b) Pearson, A. J.; Blystone, S. L.; Roden, B. A. *Tetrahedron Lett.* **1987**, *28*, 2459.



The monoester derivatives **21–24** showed optical activity. In order to assess the degree of asymmetric induction, the product from each reaction was submitted to ^{1}H NMR study at 200 MHz in the presence of the chiral lanthanide shift reagent (+)-tris-[(heptafluorobutyryl)camphorato]europium(III) [Eu(hfbc)$_3$]. For compounds **21**, **23**, and **24** the ester methyl singlet was shifted to lower field and split into two peaks, separated by ca. 0.03 ppm, while for compound **22** the Cp singlet was shifted downfield and split into two peaks, separated by ca. 0.02 ppm. The results of these investigations are summarized in Table I, in which the enantiomeric excess (ee) is estimated from peak areas of the split resonances. As a cross-check, it was observed that opposite enantiomers of sulfoximine derivative **16** gave opposite enantiomers of **21–24**.

The estimates of enantiomeric excess obtained for reactions of complex **7** were confirmed by decarboxylation of the initial crude adduct **19** (R = Ts) to give the sulfoximine derivative **25**, which



was obtained as a mixture of two diastereomers. These showed different chemical shifts for the toluenesulfonyl methyl group (δ 2.46 and 2.43), which allowed estimates of diastereomeric excess, summarized in Table II. Similar decarboxylations could not be performed on the π-allyl-Mo(CO)$_2$Cp complexes, owing to their instability under these reaction conditions.

Some general features of this reaction emerge from an inspection of Table I. The reactions of dienyliron complexes show very little dependence on the nature of the sulfoximine N-substituent, but the enantiomeric excesses are quite sensitive to the method of generation of the enolate (solvent, countercation, etc.). On the other hand, reactions of the diene–molybdenum complexes

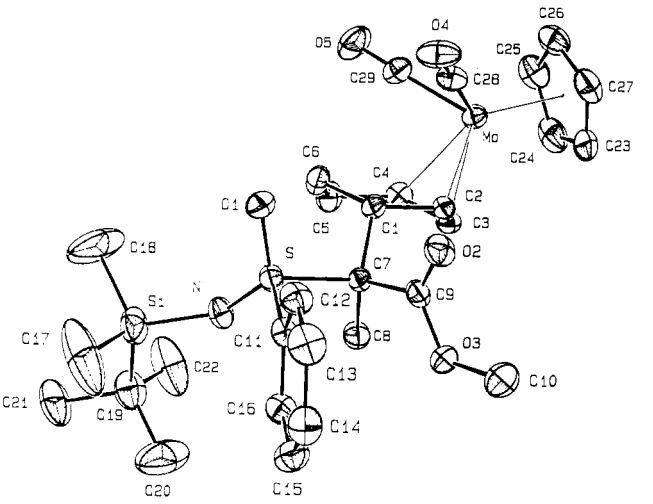
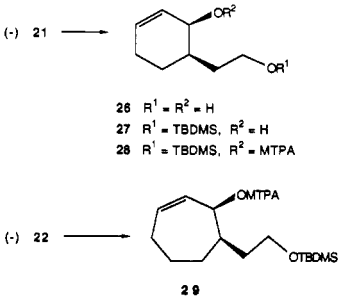


Figure 1. Drawing of a single molecule of complex **33** showing 30% probability ellipsoids.

show a marked dependence on sulfoximine N-substituent and a somewhat less well-defined dependence on enolate countercation. While in most cases the use of lithium enolates gave rather low enantiomeric excess, the corresponding sodium and potassium enolates gave quite similar ee's, in all cases higher than those observed for the lithium enolates.[10] The asymmetric inductions observed for reactions of complexes **1** and **4** (Table I, entries 9 and 17) are quite respectable and synthetically useful, while those for complexes **7** and **12** are less useful.

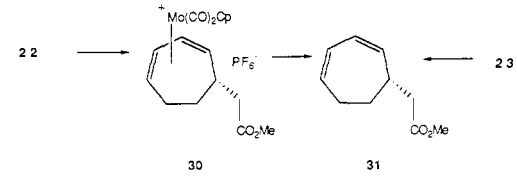
The absolute stereochemistry of monoester derivatives **21** and **22** was determined as follows. Conversion of **21** to the diol **26** was accomplished with the previously described method,[3a] and



monosilylation of **26** gave **27**, which was treated with (+)-α-(trifluoromethyl)phenylacetyl chloride to give the MTPA ester **28**. Similarly, ester **22** was converted to the mono MTPA ester **29**. Comparison of ^{1}H NMR spectra of **28** and **29** obtained from racemic monoesters **21** and **22** with those obtained from optically enriched materials, by using Mosher's method,[11] indicated that the (+)-enantiomers of **21** and **22** each have (*S*) stereochemistry, as indicated in the structures. In these experiments it was found that NMR changes according to Mosher's rule-of-thumb occurred for the vinyl proton H2 and the CH_2O(TBDMS) triplet. Signals for protons closer to the MTPA ester group were obscured by ring methylene group resonances. Since the stereochemical relationship between sulfur and the newly formed asymmetric center has also been confirmed by X-ray crystallography (see later), NMR studies were not pursued further. The absolute stereochemistry of the diene–Fe(CO)$_2$L complexes was derived by correlation with the molybdenum systems, as follows. Hydride abstraction, using triphenylmethyl hexafluorophosphate, from optically enriched (+)-**22** gave diene complex **30** (86% yield), demetalation of which, using Me$_3$NO, gave the cycloheptadiene derivative **31** (79% yield).

(10) Lithium enolates were not examined in ref 9b. The results given for sodium and potassium enolates in that paper were inaccurate. Those experiments were repeated several times, and the results presented in this paper are internally consistent and reproducible.

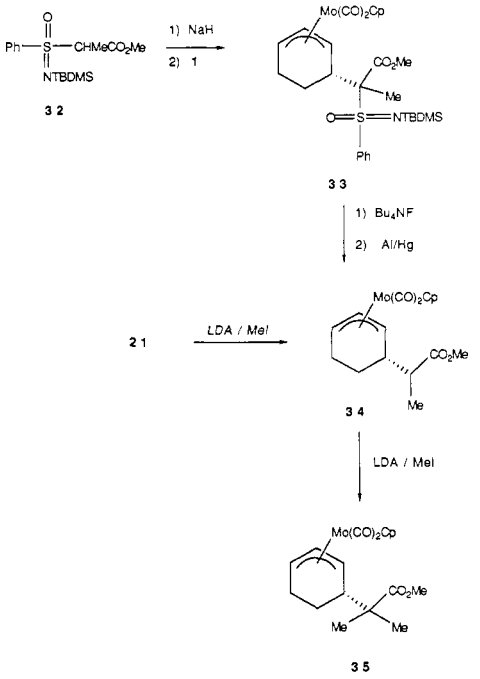
(11) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.



30 31

The same cycloheptadiene was produced by demetalation of (+)-**23**, and both samples were found to be dextrarotatory. On this basis, the absolute stereochemistry shown in structures **23** and **24** is assigned to the *dextrarotatory* enantiomer. This also confirms that use of sulfoximine ester enolates **16** with both diene-$Mo(CO)_2Cp$ and dienyl-$Fe(CO)_2L$ complexes leads to asymmetric induction in the same sense.

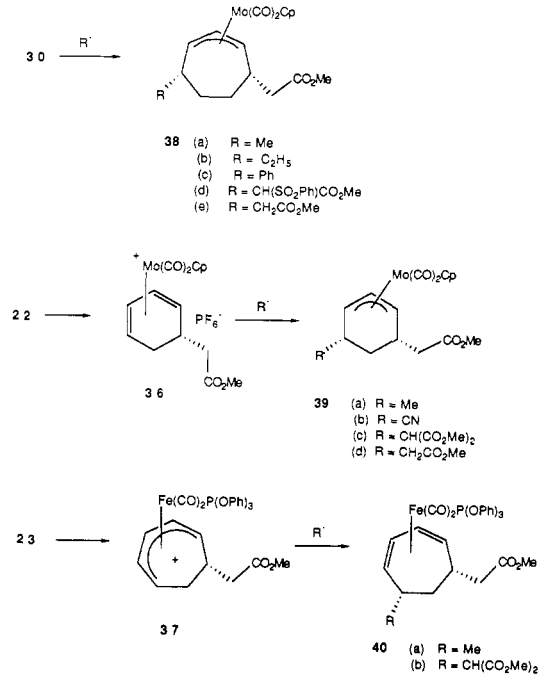
During the addition of sulfoximinyl ester enolates to these organometallic complexes, two new asymmetric centers are established. In order to try and understand the observed relay of stereochemical information from sulfur to the newly formed center on the ring, it is desirable to know the stereochemical relationship between all three stereocenters in the major diastereomers of **17–20** resulting from this reaction. Since **17–20** have epimerizable centers, we studied the reaction between complex **1** and the sulfoximine derivative **32**. This reaction gave a mixture of dia-



stereomers **33** in the approximate ratio 15:4:1:1, and the major isomer was obtained pure by fractional crystallization from dichloromethane–hexane followed by crystallization from carbon tetrachloride–hexane. The X-ray crystal structure of this compound was determined and is illustrated in Figure 1, showing the preferred (*SSS*, *RRR*) stereochemical relationship between sulfur and the two newly formed chiral centers. (In fact, racemic **32** was used for the X-ray study, but *relative* stereochemistry observed is independent of whether optically pure or racemic material is employed.)

Next, it was established that the enantiomeric form of **33** produced in this latter reaction is the same as that formed during the reaction between **1** and the unsubstituted sulfoximines **16**. Desulfonylation of the mixture of diastereomers **33** obtained from (+)-(*S*)-sulfoximine **32** gave a 2:1 mixture of diastereomers **34** having + optical rotation (see the Experimental Section). Methylation of monoester **21** (LDA, CH_3I) gave an identical 2:1 mixture of diastereomers, and the complex obtained via (*R*)-sulfoximine derivatives showed – optical rotation, while samples obtained from (*S*)-sulfoximines gave + rotation. (Presumably, this is the equilibrium (thermodynamic) ratio of epimers.) Since the same mixture of epimers at the CHMe center is used, we conclude that an identical stereochemical relationship between sulfur and the ring chiral centers is established for both methylated and nonmethylated sulfoximinyl ester derivatives. Conversion of **34** to **35** (LDA, MeI) allowed an estimate of the enantiomeric excess (52%) produced during the reaction between **1** and **32**. This is somewhat lower than that obtained from the corresponding nonmethylated sulfoximine (Table I, entry 5).

In order to assess whether this methodology is of value for the asymmetric formation of two or more centers of asymmetry in six- and seven-membered rings, we have studied the further functionalization of monoester derivatives **21–23**. Hydride abstraction to give electrophilic diene complexes **30** and **36** or dienyl



complex **37**, proceeded in good yield. Reactions of these complexes with a variety of nucleophiles, to give π-allyl complexes **38** and **39** or diene complexes **40**, were studied, and the results are summarized in Table III. In all cases the products were isomerically pure, though in a few examples disappointing yields were obtained. It may be noted that previous studies have centered on hydride abstraction from simpler complexes having no side-chain functionality.[3] These results demonstrate that the introduction of ester substituents does not prevent the sequence of hydride abstraction–nucleophile addition from being carried out, so that optically active compounds with defined relative stereochemistry are accessible.

Discussion

The methodology described above provides a new approach to the formation of one or more asymmetric centers, in reasonably high enantiomeric excess, on six- or seven-membered rings. The relative stereochemistry between two centers is established by the directing effect of the organometallic moiety, while the absolute stereochemistry is controlled by the sulfoximine group used as a chiral auxiliary. Coupled with our previously established methods for demetalation of the product π-allyl and diene complexes,[3] this chemistry can provide access to organic intermediates of potential synthetic value.

We now turn our attention to a discussion of the chiral recognition phenomenon outlined in the Results. NMR studies established that the use of sulfoximine having (*R*) stereochemistry at sulfur leads to the formation of (*R*)-monoester derivatives such as **21**, and this is now confirmed by the X-ray crystal structure determination of compound **33** (major diastereomer; Figure 1). During this reaction there is a preference for the formation of **33** having *RRR* (or *SSS*) stereochemical relationship at the three asymmetric centers. Table I also gives results of a fairly extensive investigation of the effects of changing the countercation associated

Table I. Asymmetric Induction Observed during the Addition of Sulfoximinyl Ester Enolates to Complexes **1**, **4**, **7**, and **12**, Measured as Enantiomeric Excess for Product Complexes **21–24**

entry	starting complex	substituent (R)[a] on **16** (ent)	enolate countercation	monoester product (yield, %)[b]	$[\alpha]_D$	% ee[c]
1	**1**	Ts (+)	Li	**21** (79)	+7.0	9
2	**1**	Ts (+)	Na	**21** (77)	+9.5	12–14
3	**1**	Ts (+)	K	**21** (79)	+10.1	16
4	**1**	Me (+)	Na	**21** (45)	+15.4	35
5	**1**	TBDMS (+)	Li	**21** (75)	+16	49
6	**1**	TBDMS (+)	Na	**21** (75)	+39	75
7	**1**	TBDMS (+)	K	**21** (80)	+38	78
8	**1**	DMTS (−)	Li	**21** (77)	−29	55
9	**1**	DMTS (−)	Na	**21** (83)	−38	75
10	**1**	DMTS (−)	K	**21** (80)	−43	80
11	**4**	Ts (+)	Li	**22** (67)	+11	13
12	**4**	Ts (+)	Na	**22** (75)	+7	11
13	**4**	Ts (+)	K	**22** (70)	+28	49
14	**4**	TBDMS (+)	Li	**22** (75)	+30	50
15	**4**	TBDMS (+)	Na	**22** (77)	+51	86
16	**4**	TBDMS (+)	K	**22** (80)	+49	84
17	**4**	DMTS (−)	Li	**22** (78)	−42	70
18	**4**	DMTS (−)	Na	**22** (83)	−56	89
19	**4**	DMTS (−)	K	**22** (80)	−53	85
20	**7**	Ts (+)	Li	**23** (70)	+2.6	20
21	**7**	Ts (+)	Na	**23** (73)	+5.6	25–30
22	**7**	Ts (+)	K	**23** (71)	+8.3	35–40
23	**7**	Ts (+)	Na(18-c-6)[d]	**23** (75)	+9.6	50
24	**7**	Ts (−)	Na(18-c-6)[d]	**23** (73)	−9.9	50
25	**7**	Ts (+)	K(DME)[e]	**23** (75)	+9.8	50
26	**7**	TBDMS (+)	Li	**23** (67)	nd	20
27	**7**	TBDMS (+)	Na	**23** (72)	nd	25
28	**7**	TBDMS (+)	K	**23** (62)	nd	35
29	**7**	TBDMS (+)	K(DME)[e]	**23** (65)	nd	50
30	**12**	Ts (+)	Li	**24** (72)	+3.2	20
31	**12**	Ts (+)	Na	**24** (78)	+3.0	18
32	**12**	Ts (+)	K	**24** (81)	+3.9	25
33	**12**	Ts (+)	K(DME)[d]	**24** (79)	+5.5	30

[a] Ts = 4-toluenesulfonyl-, TBMS = *tert*-butyldimethylsilyl-, DMTS = dimethylthexylsilyl-. All reactions run in THF unless otherwise stated. [b] Overall yield after desulfonylation. [c] Determined by 200-MHz ^{1}H NMR as outlined in text. Precision of measurement of the order ±5% of value quoted. [d] Run in presence of 18-crown-6 ether. [e] Run in 1,2-dimethoxyethane solvent.

Table II. Diastereomeric Excesses Obtained for Complex **25**

entry	enolate countercation for nucleophile addn[a]	% de for **25**[b]
1	Li	20
2	Na	30
3	K	40

[a] All enolate addition reactions were carried out in THF at 0 °C. [b] Estimated from 200-MHz ^{1}H NMR. Correspond to entries 20–22 of Table I.

Table III. Addition of Nucleophiles to Complexes **30**, **36**, and **37**

entry	complexes	nucleophile (R^-)	product	yield %
1	**30**	Me_2CuLi	**38a**	85
2	**30**	$Et_2CuMgBr$	**38b**	80
3	**30**	Ph_2CuLi	**38c**	85
4	**30**	$NaCH(CO_2Me)_2$	**38d**	87
5	**36**	$Me_2Cu(CN)Li_2$	**39a**	35
6	**36**	NaCN	**39b**	24
7	**36**	$NaCH(CO_2Me)_2$	**39c**	47
8	**36**	$NaCH(SO_2Ph)CO_2Me$	**39d**[a]	80[a]
9	**37**	Me_2CuLi	**40a**	91
10	**37**	$NaCH(CO_2Me)_2$	**40b**	95

[a] Overall yield after desulfonylation of initial adduct with Na–Hg.

with the enolate, undertaken with the hope of establishing whether the chiral recognition is maximized when the enolate is strongly associated with the gegenion. Apparently, the reverse is true; i.e., maximum effect is observed with noncoordinated enolate (compare Na or K enolates with Li, and see the effect of 18-crown-6), although very little difference was observed for reaction of Na or K enolates with the diene–molybdenum systems.

An explanation of this stereoselectivity is complicated by the fact that an open transition state must be involved; i.e., a model

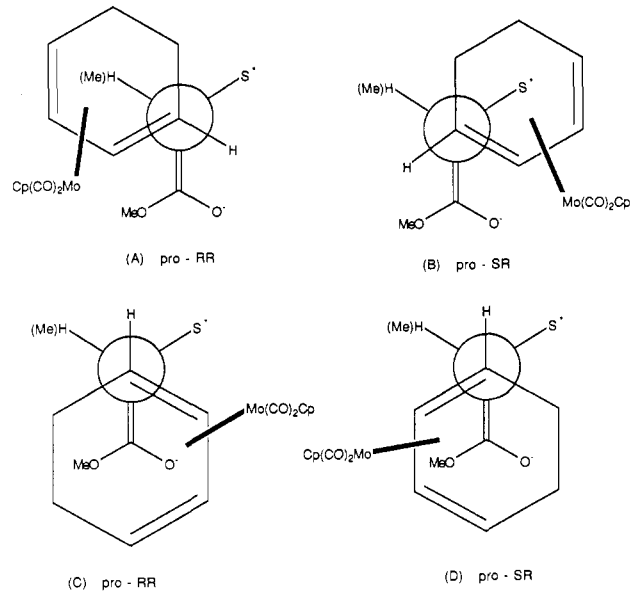


Figure 2. Possible transition states for addition of enolates to diene–molybdenum complexes, assuming synclinal arrangement of C–C double bonds (fractional structures only).

such as the Zimmerman–Traxler model[12] for aldol reactions cannot be utilized here. Using an open transition-state model, we can explain the diastereoselectivity observed between the carbon centers in the formation of complex **33**, by assuming a gauche (synclinal)

(12) Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920.

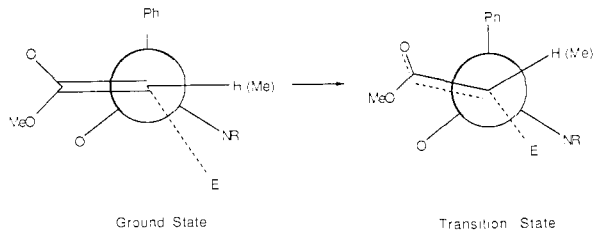


Figure 3. Conformation of (*R*)-sulfoximine-stabilized ester enolate, leading to preferred transition state for electrophile addition.

arrangement of C–C double bonds of enolate and the diene–$Mo(CO)_2Cp$ system, as proposed by Seebach for the Michael addition of enamines to nitroolefins.[13] This model is presented in Figure 2 for the diastereomeric transition states.

From Figure 2 it is apparent that both *pro-SR* transition-states (B) and (D) involve quite severe steric (gauche) interactions; one of the *pro-RR* transition states (C) is similarly destabilized, while transition state (A), also *pro-RR*, appears to involve fewer destabilizing interactions. It is noteworthy that the conformation shown for transition-state (A) is analogous to that adopted in the product **33** as shown in the X-ray structure (Figure 1).

The effect of the chiral sulfoximine group in controlling the absolute stereochemistry of the reaction results from a preferred stereochemical relationship in the transition state between sulfur and the enolate stereogenic center. The X-ray structure in Figure 1 indicates that the preferred arrangement is *R,R* (or *S,S*), which is the result of addition of electrophile to the *re* face of the enolate for the (*R*)-sulfoximine derivative. Unfortunately, the conformational preference for these enolates is not well understood,[14] and what follows is our attempt to rationalize the above observations. Molecular orbital calculations[15] and crystallographic studies[16] for sulfonyl α-carbanions indicate that the preferred conformation for enolates derived from **16** is that shown in the Newman projection given in Figure 3.

As indicated in Figure 3, in order to give the observed *R,R* stereochemical relationship in the product, the electrophile approaches the enolate along a vector that is approximately anti to the phenyl substituent. The transition state corresponding to this mode of attack probably has a structure indicated in Figure 3, and this is consistent with the product conformation revealed by the crystallographic study presented above, in which the torsional angle C11–S–C7–C1 is 139.3°. This places the large phenyl- and cyclohexenyl-$Mo(CO)_2Cp$ groups far apart, the deviation from perfect anti periplanarity being due to a *gauche*-butane interaction between NTBDMS and the organomolybdenum residue. Such an arrangement for the transition state would clearly be the lowest energy, and therefore the preferred one. Consequently, the model presented in Figure 3 is consistent with this being the lowest energy pathway. We also assume that a bulkier N-substituent favors the conformation for the enolate shown in Figure 3, where the ester residue is placed at greatest distance from the NR group, and this would explain the higher selectivity observed with, e.g., NTBDMS compared with NMe (Table I).

The effect of metal countercations is rationalized as follows. Presumably Na^+ and K^+ are less strongly coordinated than Li^+, and the latter can be chelated by the sulfoximinyl enolate. Johnson[7] has suggested that such enolates chelate via the nitrogen although such X-ray crystallographic studies as are available on sulfonyl-stabilized carbanions[16] do not preclude the possibility of chelation via oxygen. In either case, chelation would be expected to decrease stereoselectivity. As shown in Figure 4, chelation via oxygen would probably rotate the sulfur so as to move the NR group into a position that more closely eclipses the trajectory of the incoming electrophile, thereby increasing the degree of addition syn to the phenyl substituent, while chelation via nitrogen would completely invert the stereochemical result. In the latter case, the degree of stereoselectivity is dependent upon the exact nature of the equilibrium between chelated and nonchelated forms of the enolate. A more complete resolution of this situation requires a detailed crystallographic study of the enolates and has not been undertaken at this time.

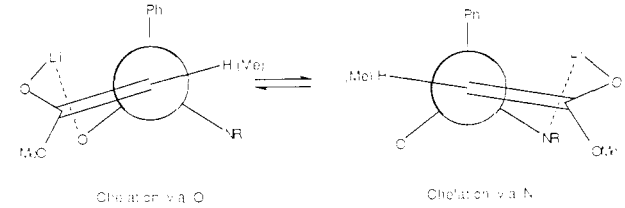


Figure 4. Possible conformational effects of chelation of Li^+ by sulfoximine-stabilized enolate.

Conclusions

From these results, it appears that practical asymmetric carbon–carbon bond formation will be attainable by using diene–molybdenum or dienyliron cations in conjunction with chiral enolate nucleophiles. While the sulfoximine derivatives described in this paper give good results in some cases, they are far from ideal. Furthermore, removal of the chiral sulfur auxiliary results in its complete destruction. Given these shortcomings, it is clear that studies should be directed to the use of recoverable and better understood chiral auxiliaries, and this will form the basis of future work in our laboratory. The results presented herein, and the rationalization given for the observed stereoselectivity, should be of value in guiding further studies in this area.

Experimental Section

General Procedures. Infrared spectra were recorded with a Perkin-Elmer 1420 instrument, and optical rotations were recorded on a Perkin-Elmer 141 polarimeter at room temperature. More recently, a new Perkin-Elmer 241 polarimeter was used, and values determined on both instruments are in reasonable agreement. NMR spectra were recorded in deuteriochloroform solution unless otherwise stated, by a Varian XL 200 instrument, and mass spectra were obtained in-house on a Kratos MS25A instrument or by the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE, an NSF regional facility. Molecular ions are given for ^{96}Mo for molybdenum complexes. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. All reactions were performed under inert atmosphere (dry, O_2-free nitrogen or argon) unless otherwise noted. Solvents were purified by distillation as follows: THF and benzene from Na–benzophenone; ether from $LiAlH_4$; dichloromethane and acetonitrile from CaH_2.

Preparation of N-Substituted *S*-Methyl-*S*-phenylsulfoximines 14. Literature procedures[7] were used for the preparation of the *N*-tosyl [**14**, R = Ts, $[\alpha]_D = +146°$ (*c* = 1.0), acetone] and *N*-methyl [**14**, R = Me, $[\alpha]_D = +184°$ (*c* = 1.7), acetone] derivatives. The *N*-silyl-substituted compounds were prepared according to a published procedure for *N*-(trimethylsilyl) derivatives, as follows. To a 10% solution of optically pure **13** in dry pyridine at 0 °C was added 1.1–1.2 equiv of the appropriate trialkylsilyl chloride. The resulting solution was stirred at room temperature overnight, quenched with excess water, and extracted in the usual way with dichloromethane. The combined organic extracts were washed with water and dried ($MgSO_4$), and solvent was removed in vacuo. The crude product was distilled under reduced pressure to give pure N-substituted sulfoximine.

***S*-Methyl-*S*-phenyl-*N*-(*tert*-butyldimethylsilyl)sulfoximine.** (+)-*S*-Methyl-*S*-phenylsulfoximine **13** (0.85 g) and *tert*-butyldimethylsilyl chloride (0.99 g) gave 1.4 g (94%) of **14** (R = TBDMS) as a colorless oil after distillation; bp 91–93 °C (0.6 mmHg). IR (CCl_4): ν_{max} 3070, 1319, 1296, 1160, 690 cm^{-1}. ^1H NMR: δ 7.80 (2 H, m), 7.50 (3 H, m), 2.93 (3 H, s), 0.87 (9 H, s), 0.11 (6 H, s). $[\alpha]_D = +83.9°$ (*c* = 1.1; acetone). Anal. Calcd for $C_{13}H_{23}NOSSi$: C, 57.9; H, 8.6; N, 5.2. Found: C, 57.78; H, 8.31, N, 5.41.

(13) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413. For a consideration of this type of transition state during enolate addition to alkene–Fp complexes, see: Chang, T. C. T.; Coolbaugh, T. S.; Foxman, B. M.; Rosenblum, M.; Simms, N.; Stockman, C. *Organometallics* **1987**, *6*, 2394.

(14) Hwang, K.-J.; Logusch, E. W.; Brannigan, L. H.; Thompson, M. R. *J. Org. Chem.* **1987**, *52*, 3435.

(15) Wolfe, S.; Stolow, A.; LaJohn, L. A. *Tetrahedron Lett.* **1983**, *24*, 4071 and references cited therein.

(16) Grossert, J. S.; Hoyle, J.; Cameron, T. S.; Roe, S. P.; Vincent, B. R. *Can. J. Chem.* **1987**, *65*, 1407.

S-Methyl-S-phenyl-N-(dimethylthexylsilyl)sulfoximine. (−)-S-Methyl-S-phenylsulfoximine (1.01 g) and dimethylthexylsilyl chloride (1.18 g) gave 1.52 g (79%) of **14** (R = DMTS). IR (CCl_4): ν_{max} 2960, 1317, 1291, 1247, 1156, 675 cm^{-1}. ^1H NMR: δ 7.95 (2 H, m), 7.52 (3 H, m), 2.98 (3 H, s), 0.91 (12 H, m, thexyl), 0.12 and 0.08 (each 3 H, s). $[\alpha]_D$ = −68.8° (c = 1.35; acetone). Anal. Calcd for $C_{15}H_{27}NOSSi$: C, 60.55; H, 9.15; N, 4.7. Found: C, 60.70; H, 8.92; N, 4.99.

Preparation of Sulfoximinyl Esters 16. The carbomethoxy group can be attached by either of the two methods described below, the method of choice being that of Hwang[17] (Method A).

Method A. To a stirred solution of 24 mmol of tetramethylpiperidine in 10 mL of THF at 0 °C was slowly added, via syringe, a solution of 20 mmol of *n*-butyllithium in hexane. The solution was stirred for 10 min at 0 °C and cooled to −78 °C, and a solution of the appropriate sulfoximine **14** (10 mmol) in 5 mL of THF was added dropwise. After stirring for 0.5 h, 24 mmol of methyl chloroformate was added dropwise. Stirring was continued for 1 h, the cooling bath was removed, and additional stirring was maintained for 10 min. The still cold reaction mixture was quenched with 1 mL of saturated aqueous ammonium chloride, and the product was isolated in the usual way by extraction with ethyl acetate, followed by vacuum distillation or crystallization.

Method B. A 60% dispersion of sodium hydride in mineral oil (6.7 mmol of NaH) was washed three times in a closed reaction vessel with ca. 2 mL of dry pentane. Tetrahydrofuran (25 mL) and dimethyl carbonate (5 mL) were added, and the stirred mixture was heated to reflux temperature while a solution of the appropriate sulfoximine **14** (2.6 mmol) in a minimum amount of THF was added dropwise. The mixture was boiled under reflux overnight, cooled in ice, and carefully quenched with 2:1 MeOH–AcOH (4 mL). The solution was added to excess water and the product extracted with ether. The combined ether layers were washed with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated to give the crude ester, which was purified by vacuum distillation or crystallization.

S-(2-Methoxy-2-oxoethyl)-S-phenyl-N-(p-tolylsulfonyl)sulfoximine (16; R = Ts). When method B was used, the (+)-N-tosylsulfoximine **14** (R = Ts, 0.80 g) gave **16** (R = Ts, 0.84 g, 88%) as a white crystalline solid, mp 93–96 °C (EtOH). IR: ν_{max} 2950, 2940, 1780, 1440, 1280, 1090, 1050 cm^{-1}. ^1H NMR: δ 8.02 (2 H, d, J = 7.7 Hz), 7.88 (2 H, dd, J = 8.3, 4.9 Hz), 7.57–7.73 (1 H, m), 7.62 (2 H, d, J = 7.7 Hz), 7.27 (2 H, m), 4.70 (2 H, ABq, J = 14.5 Hz), 3.66 (3 H, s), 2.40 (3 H, s). $[\alpha]_D$ = +81° (c = 1.7; acetone). Anal. Calcd for $C_{16}H_{17}O_5S_2N$: C, 52.30; H, 4.66. Found: C, 52.60; H, 4.73.

S-(2-Methoxy-2-oxoethyl)-S-phenyl-N-methylsulfoximine (16; R = Me). Using method B (+)-**14** (R = Me) gave (+)-**16** (R = Me) as a colorless oil in 71% yield. IR (CCl_4): ν_{max} 1759, 1683, 1439, 1265 cm^{-1}. ^1H NMR: δ 7.98 (2 H, m), 7.65 (3 H, m), 4.64 and 4.56 (1 H each, ABq, J = 14.4 Hz), 3.74 (3 H, s), 3.66 (3 H, s). $[\alpha]_D$ = +8.8° (c = 1.25; acetone). Anal. Calcd for $C_{10}H_{13}O_3NS$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.71; H, 6.19; N, 5.56.

S-(2-Methoxy-2-oxoethyl)-S-phenyl-N-(tert-butyldimethylsilyl)sulfoximine (16; R = TBDMS). When method A was used, the (+)-N-TBDMS sulfoximine **14** (R = TBDMS) (2.00 g) gave **16** (R = TBDMS, 1.35 g, 55%) as a pale yellow oil, bp 125–127 °C (0.6 mmHg). IR (CCl_4): ν_{max} 3070, 1700, 1330, 1305, 1278, 1062, 694 cm^{-1}. ^1H NMR: δ 7.90 (2 H, m), 7.55 (3 H, m), 4.05 and 3.99 (1 H each, ABq, J = 7.0 Hz), 3.65 (3 H, s), 0.92 (9 H, s), 0.11 (3 H, s), 0.09 (3 H, s). $[\alpha]_D$ = +49.1° (c = 0.96; acetone). Anal. Calcd for $C_{15}H_{25}NO_3SSi$: C, 55.01; H, 7.69; N, 4.28. Found: C, 55.14; H, 7.84; N, 4.39.

S-(2-Methoxy-2-oxoethyl)-S-phenyl-N-(dimethylthexylsilyl)sulfoximine (16; R = DMTS). When method A was used, the (−)-N-DMTS sulfoximine **14** (R = DMTS) (1.46 g) gave **16** (R = DMTS, 1.34 g, 77%) as a pale yellow oil, bp 145–147 °C (0.2 mmHg). Ir (CCl_4): ν_{max} 2959, 1748, 1326, 1302, 1274, 1156, 791 cm^{-1}. ^1H NMR: δ 7.93 (2 H, m), 7.55 (3 H, m), 4.04 and 4.00 (1 H each, ABq, J = 13.1 Hz), 3.65 (3 H, s), 1.71 (1 H, m), 0.91 (12 H), 0.17 (3 H, s), 0.13 (3 H, s). $[\alpha]_D$ = −44.3° (c = 1.0; acetone). Anal. Calcd for $C_{17}H_{29}NO_3SSi$; C, 57.43; H, 8.22; N, 3.94. Found: C, 57.68; H, 8.37; N, 4.14.

S-(1-Methyl-2-methoxy-2-oxoethyl)-S-phenyl-N-(tert-butyldimethylsilyl)sulfoximine (32). Both racemic and optically pure compound was prepared as follows. To a stirred suspension of 60% sodium hydride dispersion in mineral oil (2.8 mmol) in THF (15 mL) was added the ester **16** (R = TBDMS, 2.8 mmHg) in THF (5 mL). The mixture was stirred for 10–15 min, and methyl iodide (0.34 mL, 5.4 mmol) was added. Stirring was continued at room temperature for 2 h, the mixture was poured into excess water, and the product was extracted in the usual way with ethyl acetate. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated, and the residue was chromatographed on a short column of silica gel, by using 40% ethyl acetate in hexane to yield **32** (0.85 g, 92%). Further purification of small batches was effected by preparative layer chromatography prior to use. IR (CCl_4): ν_{max} 2963, 2865, 1748, 1327, 1304, 1255, 1157 cm^{-1}. ^1H NMR (showed two diastereomers): δ 7.84 (2 H, m), 7.50 (3 H, m), 3.90 (1 H, q, J = 7.1 Hz), 3.64 and 3.59 (3 H, 2s), 1.46 and 1.38 (3 H, 2d, J = 7.1 Hz), 0.90 and 0.88 (9 H, 2s), 0.067, 0.062 (3 H, 2s), 0.038 and 0.016 (3 H, 2s). $[\alpha]_D$ = +66° (c = 1.0; acetone). Anal. Calcd for $C_{16}H_{27}NO_3SSi$: C, 52.27; H, 7.97; N, 4.10. Found: C, 52.51; H, 8.17; N, 4.14.

Addition of Sulfoximinyl Ester Enolates to Organometallic Complexes. General Procedure. The procedure is described for the sodium enolates. That used for lithium and potassium enolates was identical except that LDA and potassium *tert*-butoxide, respectively, were used as base. To a stirred suspension of sodium hydride (60% dispersion in mineral oil; 1.02 mmol of NaH) in tetrahydrofuran (5 mL) under argon was added the desired sulfoximine ester **16** or **32** (1.0 mmol) in tetrahydrofuran (5 mL). The solution was stirred until hydrogen evolution had ceased and cooled to ca. −20 °C. The powdered diene–molybdenum or dienyliron complex (0.95 mmol) was added in one portion, and the mixture was stirred until dissolution of the complex was complete (usually 10–30 min), after which it was poured into an excess of water and the product was extracted in the usual way with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated to give crude product. The NMR spectra of these compounds usually showed a complicated mixture of diastereomers, the ratio of which depends on the stereoselectivity of addition. In order to avoid fractionation of diastereomers, and therefore false values of selectivity, the crude material was converted to monoester adduct **18**, **19**, **23**, or **24**, as outlined below. Spectral data is included here for some representative adducts, which were purified chromatographically.

17 (R = Ts) was obtained in 65% yield after purification. IR (CCl_4): ν_{max} 1948, 1873, 1334, 1158, 1092, 1065 cm^{-1}. Partial NMR data at 200 MHz: δ 5.31, 5.15 and 5.22 (Cp, s), 3.66, 3.62 and 3.40 (CO_2Me), 2.40 (3 H, s, tosyl Me). Anal. Calcd for $C_{29}H_{29}MoNO_7S_2$: C, 52.49; H, 4.40. Found: C, 54.94; H, 4.74.

17 (R = TBDMS) was obtained in 85% yield after purification. IR (CCl_4): ν_{max} 1964, 1888, 1756, 1339, 1312, 1174, 1163, 1138, 1096 cm^{-1}. Partial NMR data: δ 5.34, 5.27, 5.25, 5.13 (Cp, s), 3.9, 3.85, 3.8, 3.7 (CO_2Me), 0.92 and 0.89 (*t*-Bu), 0.06, 0.01 ($SiMe_2$). Anal. Calcd for $C_{28}H_{37}MoNO_5SSi$: C, 53.92; H, 5.98. Found: C, 54.33; H, 6.24.

Complex 33 was obtained as a mixture of four diastereomers (15:4:1:1) in 87% yield. Recrystallization from methylene chloride–hexane followed by a final crystallization from carbon tetrachloride–hexane afforded a pure sample of the major stereoisomer (racemic). ^1H NMR: δ 7.8–7.4 (5 H, m), 5.26 (5 H, s), 4.29 (1 H, t, J = 7 Hz), 3.80 (1 H, d, br, J = 7 Hz), 3.68 (3 H, s), 2.86 (1 H, d, br, J = 7 Hz), 2.24 (1 H, d, br, J = 4 Hz), 1.9 (1 H, m), 1.64 (1 H, m), 1.76 (3 H, s), 0.9 (9 H, s), 0.36 (2 H, m), 0.0 (6 H, s). That this material was indeed the major diastereomer was established by direct comparison of NMR spectra of pure compound and the mixture.

Deprotection of Silyl-Substituted Adducts. General Procedure. In general, direct desulfonylation of *N*-silyl-protected sulfoximines gave low yields of monoesters. Prior desilylation led to better overall yields. To the crude sulfoximinyl ester adduct obtained from the above procedure in THF (25 mL) under argon at 0 °C was added a 1 M solution of tetra-*n*-butylammonium fluoride in THF (2.85 mmol). The reaction mixture was stirred for 0.5 h and quenched with excess water, and the product was extracted in the usual way with ethyl acetate. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated. Generally, the crude mixture of diastereomers was used directly in the desulfonylation step to avoid any fractionation on purification. Representative spectral data is given for complex **17** (R = H): IR (CCl_4): ν_{max} 1941 (br), 1950, 1872, 1742, 1240, 1105 cm^{-1}. Partial NMR: δ 5.31, 5.28 (Cp), 3.79, 3.74 (CO_2Me).

Desulfonylation of Sulfoximine Adducts. General Procedure. Desulfonylation can be effected with either sodium–mercury or aluminum–mercury amalgam. As a general rule, Al–Hg is the reagent of choice since overreduction (of the metal carbonyl moiety) is kept to a minimum. Careful monitoring of each reaction by TLC (25% ethyl acetate in hexane, on silica gel) is essential.

Using Na–Hg. The crude addition product, e.g., **17** (0.226 mmol), was dissolved in methanol (3.75 mL) and THF (1 mL) under argon and cooled to 0 °C, Na_2HPO_4 (0.193 g) was added, and the stirred mixture was treated with small portions of ca. 2% Na–Hg amalgam until the reaction was shown to be complete by TLC. Aqueous $NaHCO_3$ was then added and stirring was continued for 0.5 h. The product was extracted in the usual way with ether and purified by either preparative TLC or column chromatography (60–230-mesh silica gel) using 25% ethyl acetate in hexane to give the monoester **21** as a yellow crystalline solid, spectroscopically identical to the corresponding racemic monoester previously reported.[3]

(17) Hwang, K.-J. *J. Org. Chem.* **1986**, *51*, 99.

Using Al–Hg. The sulfoximine adduct, e.g. **17** (0.40 mmol), was stirred under argon at room temperature in a mixture of methanol (18 mL) and THF (4 mL) while Na_2HPO_4 buffer (0.33 g) was added. The Al–Hg amalgam was freshly prepared by adding aluminum foil (0.105 g, 3.9 mmol) in small portions, with swirling, to a 2% aqueous mercuric chloride solution. Swirling was continued for ca. 30 s, the aqueous phase was decanted, and the amalgam was washed by decantation with methanol and then ether and added to the reaction flask. The mixture was stirred until TLC examination indicated the reaction to be complete (generally 1–5 h, with slow disintegration of the aluminum foil). The solution was filtered through Celite to remove aluminum residues, water was added, and the product was extracted with ether. The combined extracts were dried ($MgSO_4$) and evaporated, and the monoester product was purified as above. Overall yields of monoester are quoted in Table I.

Dicarbonyl(η^5-cyclopentadienyl)[methyl 2-(2–4-η-cyclohex-2-enyl)-propanoate]molybdenum (34). Method A from Complex 33. A sample of complex **33** obtained from (+)-**32** (of ca. 90% ee) was desilylated as above and desulfonylated using Al–Hg amalgam as described above to give optically active complex **34** as a 2:1 mixture of epimers (0.087 g, 58% yield) after purification by preparative TLC (silica gel, 25% ethyl acetate in hexane). IR (CCl_4): ν_{max} 1952, 1875, 1742 cm^{-1}. ^1H NMR: δ 5.30 (5 H, s, Cp, major epimer), 5.29 (5 H, s, Cp, minor epimer), 4.24 (m, H-3 both epimers), 3.74 (m, 4-H both epimers), 3.72 (3 H, s, CO_2Me, minor), 3.66 (3 H, s, CO_2Me, major), 3.58 (1 H, d, J = 7.4 Hz, H-2, major), 3.43 (1 H, d, J = 7.1 Hz, H-2, minor), 2.46 (m, $CHCO_2Me$ both), 1.98 (m), 1.59 (m), 1.29 (3 H, d, J = 6.9 Hz, Me, major), 1.19 (3 H, d, J = 6.9 Hz, Me, minor), 0.97 (1 H, m, *endo*-H-6, minor), 0.79 (1 H, m, *endo*-H-6, major), 0.55 (*exo*-H-6, both). $[\alpha]_D$ = +39° (c = 1.1; acetone; corrected for optical purity of **32** and corresponding to ca. 55% ee for the formation of **33**). Anal. Calcd for $C_{17}H_{20}MoO_4$: C, 53.13; H, 5.25. Found: C, 53.02; H, 5.68.

Method B by Methylation of Complex 21 (16% ee from Table I, entry 3). To a stirred solution of diisopropylamine (0.024 mL, 0.17 mmol) in THF (5 mL) at 0 °C under argon atmosphere was added, via syringe, a solution of *n*-butyllithium (2.5 M in hexane, 0.071 mL). After the mixture was stirred for 15 min, a solution of (+)-**18** (0.0312 g, 0.0843 mmol) in THF (5 mL) was added, and stirring was continued for 15 min, after which time methyl iodide (52 μL) was added. The mixture was allowed to warm to room temperature, stirred overnight, and poured into water. Extraction with ether in the usual way followed by aqueous wash, drying ($MgSO_4$), and evaporation of extracts afforded crude complex (+)-**34**. Purification as in method A gave an identical mixture of epimers with + optical rotation. Use of (−)-**18** gave (−)-**34**.

Dicarbonyl(η^5-cyclopentadienyl)[methyl 2-(2–4-η-cyclohex-2-enyl)-2-methyl propanoate]molybdenum (35). To a stirred solution of diisopropylamine (0.036 mL, 0.255 mmol) in THF (5 mL) at 0 °C under argon atmosphere was added a solution of *n*-butyllithium in hexane (0.10 mL, 2.5 M). After stirring 15 min, a solution of complex **34** (0.0490 g, 0.1275 mmol), prepared by method A above, in THF (5 mL) was added via syringe, and stirring was continued for 15 min. Methyl iodide (0.080 mL, 1.3 mmol) was added, the reaction mixture was allowed to warm to room temperature, and stirring was continued overnight. The mixture was poured into excess water, and the product was extracted with ether as described above. Purification by preparative TLC (silica gel, 25% ethyl acetate in hexane) afforded complex **35** (0.0422 g, 83%) as a yellow crystalline solid, mp 106–108 °C. IR (CCl_4): ν_{max} 1949, 1873, 1744 cm^{-1}. ^1H NMR: δ 5.27 (5 H, s), 4.33 (1 H, t, J = 7.2 Hz, H-3), 3.72 (1 H, d, J = 7.2 Hz, H-2), 2.11 (1 H, d, J = 6.9 Hz, H-1), 1.94 (1 H, m, *endo*-H-5), 1.60 (1 H, m, *3exo*-H-5), 1.22 (6 H, s), 0.87 (1 H, dd, br, J = 51.1, 6.8 Hz, *endo*-H-6), 0.48 (1 H, m, *exo*-H-6). The enantiomeric excess was shown to be 52% ee (corrected for optical purity of **32**) by NMR in the presence of Eu(hfbc)$_3$. $[\alpha]_D$ = +71° (c = 0.74; acetone). Anal. Calcd for $C_{18}H_{22}MoO_4$: C, 54.28; H, 5.57. Found: C, 54.85; H, 5.84.

Determination of Enantiomeric Excess. General Procedure. The monoester complex **18** was dissolved in 0.25 mL of benzene-d_6 (all other complexes in $CDCl_3$) in a 5-mm bore NMR tube. A solution of the shift reagent (+)-tris(heptafluorobutyryl)camphorato europium [Eu(hfbc)$_3$] of approximately twice the molar concentration of the organometallic complex was made in benzene-d_6 ($CDCl_3$ for other complexes). Care should be exercised in choosing the amount of complex so that not more than 10–20 mg of the shift reagent is used (generally only 3–8 mg of complex is necessary). The solution of shift reagent was added in small portions (ca. 0.5 cm as measured in the NMR tube), the mixture was shaken well, and a spectrum was obtained after each addition to follow the splitting of the CO_2Me singlet, accompanied by a downfield shift (for complex **19** no splitting of the CO_2Me peak occurred, but the Cp singlet showed the analogous splitting). The enantiomeric content of each sample was determined from integrated intensities of the split peaks, usually by the "cut-and-weigh" method after appropriate expansion of the spectrum. In a few runs complete separation of peaks was not obtained, and the values were estimated from the overlapping peaks. In all cases cited in this paper the (+)-enantiomer gave the higher field peak in the presence of the shift reagent.

Table IV. Experimental Details for Crystal Structure Determination

A. Crystal Data

$C_{29}H_{39}MoSiNO_5S$
FW = 637.73, $F(000)$ = 1328
cryst dimens 0.24 × 0.20 × 0.04 mm
peak width at half-height 0.15°
Mo Kα radiatn (λ = 0.71073 Å)
temp 21 ± 1°
monoclinic space gp $P2_1/n$
a = 16.398 (4), b = 8.369 (1), c = 22.239 (5) Å
β = 90.78 (2)°
V = 3051.8 Å^3
Z = 4, ρ = 1.39 g/cm^3
μ = 5.6 cm^{-1}

B. Intensity Measurements

instrument	Enraf-Nonius CAD4 diffractometer
monochromator	graphite crystal, incident beam
attenuator	Zr foil, factor 19.5
take-off angle, deg	2.8
detector aperture	2.2–2.3-mm horizontal 4.0-mm vertical
crystal-detector dist, cm	21
scan type	ω–2θ
scan rate, deg/min	1–7 (in ω)
scan width, deg	0.7 + 0.340 tan θ
max 2θ, deg	52.0
no. of reflcns measd	6651 total, 6421 unique
corrections	Lorentz–polarization linear decay (0.922–1.048 on I) reflection averaging (agreement on I = 2.0%) empirical absorption (0.93–1.00 on I)

C. Structure Solution and Refinement

solution	Patterson method
hydrogen atoms	refined as riding atoms
refinement	full-matrix least squares
minimization function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares wts	$4F_o^2/\sigma^2(F_o^2)$
anomalous dispersion	all non-hydrogen atoms
reflctns included	3650 with $F_o^2 > 3.0\sigma(F_o^2)$
param refined	343
unweighted agreement factor	0.043
weighted agreement factor	0.053
factor including unobs data	0.043
esd of obs of unit weight	1.47
convergence, largest shift	0.01σ
high peak in final diff map, e/Å^3	0.69 (7)
low peak in final diff map, e/Å^3	−0.62 (5)
computer hardware	VAX11/750
computer software	SDP/VAX (Enraf-Nonius & B. A. Frenz & Associates, Inc.)

Determination of Absolute Stereochemistry of 21 and 19. Hydrolysis of ester **21** to the corresponding carboxylic acid ($[\alpha]_D$ = −46°; c = 0.8; acetone), lactonization, and conversion to diol **26** ($[\alpha]_D$ = −192° (c = 0.23), acetone) were carried out on both a racemic and (−)-enriched sample (ca. 78% ee) according to previously published procedures.[3a] Monoprotection of **26** to give **27** was accomplished by treating **26** (0.016 g, 0.113 mmol) in dichloromethane (3 mL) with triethylamine (0.017 mL), *tert*-butyldimethylsilyl chloride (0.019 g, 0.12 mmol), and 4-(dimethylamino)pyridine (0.0006 g, 0.005 mmol). After stirring at room temperature overnight, the solution was added to water, and the product was extracted with dichloromethane, dried ($MgSO_4$), and evaporated. The crude product was purified by HPLC (silica gel, 15% ethyl acetate in hexane) to give pure **27** (0.0175 g, 64%). IR (CCl_4): ν_{max} 35000, 2925, 2860, 1253, 1212 cm^{-1}. ^1H NMR: δ 5.87 (2 H, m, vinyl), 4.12 (1 H, br, $CHOH$), 3.74 (2 H, m, CH_2OSi), 2.78 (1 H, d, J = 5.4 Hz, OH, exchangeable D_2O), 2.06–1.42 (7 H, m), 0.91 (9 H, s), 0.08 (6 H, s). Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.00. Found: C, 65.51; H, 11.03.

The (+)-α-(trifluoromethyl)phenylacetic (MTPA) ester **28** was pre-

Table V. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
Mo	0.23610 (2)	0.60895 (5)	0.63002 (2)	3.246 (7)	C11	0.3661 (3)	0.0393 (5)	0.3932 (2)	3.25 (9)
S	0.27788 (7)	0.0929 (1)	0.43550 (5)	3.26 (2)	C12	0.4291 (3)	−0.0433 (6)	0.4203 (2)	4.3 (1)
Si	0.1345 (1)	−0.0435 (2)	0.36705 (8)	6.10 (4)	C13	0.4963 (3)	−0.0852 (6)	0.3874 (3)	5.1 (1)
O1	0.2848 (2)	0.0042 (4)	0.4910 (1)	4.11 (7)	C14	0.5006 (3)	−0.0439 (6)	0.3281 (2)	4.7 (1)
O2	0.4321 (2)	0.2895 (4)	0.4907 (1)	4.43 (8)	C15	0.4370 (3)	0.0378 (6)	0.3010 (2)	4.7 (1)
O3	0.4070 (2)	0.4234 (4)	0.4057 (1)	4.61 (8)	C16	0.3695 (3)	0.0792 (5)	0.3330 (2)	3.9 (1)
O4	0.3344 (2)	0.3013 (4)	0.6563 (2)	5.88 (9)	C17	0.1879 (6)	−0.2146 (8)	0.3316 (4)	15.2 (3)
O5	0.0890 (2)	0.4125 (5)	0.6742 (2)	6.7 (1)	C18	0.0646 (5)	−0.115 (1)	0.4260 (4)	20.1 (3)
N	0.2037 (2)	0.0865 (5)	0.3971 (2)	4.03 (9)	C19	0.0737 (4)	0.0664 (7)	0.3105 (3)	6.0 (2)
Cl	0.2654 (3)	0.3363 (5)	0.5207 (2)	2.95 (9)	C20	0.1334 (5)	0.125 (1)	0.2621 (3)	11.4 (3)
C2	0.2843 (3)	0.5098 (5)	0.5378 (2)	2.99 (9)	C21	0.0074 (4)	−0.0430 (8)	0.2821 (3)	8.0 (2)
C3	0.2253 (3)	0.6306 (5)	0.5319 (2)	3.5 (1)	C22	0.0327 (4)	0.2092 (8)	0.3391 (4)	10.8 (2)
C4	0.1444 (3)	0.5884 (6)	0.5469 (2)	3.9 (1)	C23	0.3066 (4)	0.8559 (7)	0.6328 (3)	5.9 (1)
C5	0.1128 (3)	0.4264 (6)	0.5283 (2)	4.4 (1)	C24	0.2242 (4)	0.8900 (6)	0.6419 (3)	6.1 (1)
C6	0.1760 (3)	0.2919 (5)	0.5341 (2)	3.9 (1)	C25	0.2010 (4)	0.8171 (7)	0.6950 (3)	5.6 (1)
C7	0.2929 (3)	0.3102 (5)	0.4549 (2)	2.97 (9)	C26	0.2689 (4)	0.7380 (6)	0.7190 (2)	5.2 (1)
C8	0.2466 (3)	0.4133 (5)	0.4089 (2)	4.0 (1)	C27	0.3348 (3)	0.7648 (7)	0.6799 (2)	5.4 (1)
C9	0.3855 (3)	0.3374 (5)	0.4535 (2)	3.36 (9)	C28	0.2968 (3)	0.4152 (6)	0.6462 (2)	4.1 (1)
C10	0.4942 (3)	0.4495 (8)	0.4006 (3)	7.0 (2)	C29	0.1442 (3)	0.4834 (6)	0.6568 (2)	4.3 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

pared as follows.[18] In a flame-dried vial under nitrogen atmosphere was placed, consecutively, dry pyridine (300 μL) and compound **27** (0.0146 g, 0.061 mmol). After the mixture was stirred at room temperature overnight, 4 drops of water were added and the product was extracted with ether. The extracts were washed with dilute hydrochloric acid, water and aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated to give **28** (0.022 g, 76%), which was not purified in order to avoid diastereomer separation. This procedure was carried out with material derived from both racemic and (−)-enriched monoester **21**. The ^1H NMR spectrum of this compound in benzene-d_6 at 400 MHz showed the following features: racemate-derived **28** showed two triplets, at δ 3.74 and 3.60, respectively, corresponding to the CH_2O(TBDMS) methylene, and two overlapping multiplets, centered at δ 5.67 and 5.72, respectively, corresponding to the vinyl proton adjacent to the O(MTPA) group; **28** derived from (−)-**21** showed substantial loss of the triplet at δ 3.60 and the multiplet centered at δ 5.72. On this basis, when Mosher's rule-of-thumb is used,[11] the absolute stereochemistry of **28** derived from (−)-**21** is (1*S*,6*R*). When identical methods were used, samples of "racemic" and (−)-enriched **29** were obtained. These compounds showed the following ^1H NMR features at 400 MHz (in acetone-d_6): CH_2O(TBDMS) triplets at δ 3.71 and 3.62; vinyl dd at δ 5.82 and 5.70; **29** derived from (−)-enriched **30** showed loss of δ 3.62 and 5.82 signals.

Hydride Abstraction Reactions. General Procedure. The monoester complex **21** (0.3032 g, 0.82 mmol) was dissolved in dry dichloromethane under argon, cooled to 0 °C, and treated with triphenylmethyl hexafluorophosphate (0.3343 g, 0.86 mmol). After it was stirred at 0 °C for 2 h, the solution was transferred via cannula to a Schlenk funnel prepared with a bed of Celite. The reaction mixture was filtered through the Celite, using a slight positive pressure of argon, directly into ether. Removal of ether from the insoluble product was effected by evaporation under reduced pressure, and the residue was washed by decantation with ether to give diene complex **36** (0.3754 g, 0.73 mmol, 89%) as a greenish yellow powder. The complex **30** was prepared analogously, using a reaction time of 1 h at 0 °C (86% yield) while dienyl complex **37** was prepared in 75% yield using refluxing dichloromethane as solvent and a reaction time of 2 h. Spectroscopic data is given as follows:

36. IR (CH_3CN): ν_{max} 2062, 2022, 1965, 1737, 848 cm^{-1}. ^1H NMR (acetone-d_6): δ 6.08 (2 H, m), 6.03 (5 H, s), 4.76 (2 H, m), 3.60 (3 H, s), 2.73 (1 H, m), 2.48–2.37 (4 H, m). Anal. Calcd for $C_{16}H_{17}F_6MoO_4P$: C, 37.3; H, 3.33. Found: C, 37.66; H, 3.23.

30. IR (CH_3CN): ν_{max} 2010, 1960, 1730, 850 cm^{-1}. NMR (CD_3CN): δ 5.84 (2 H, m), 5.76 (5 H, s), 4.84 (1 H, m), 4.58 (1 H, m), 3.68 (3 H, s), 2.64 (1 H, m), 2.38 (2 H, m), 1.32 (4 H, m). Anal. Calcd for $C_{17}H_{19}F_6MoO_4P$: C, 38.6; H, 3.62. Found: C, 38.7; H, 3.6.

37. IR (CH_3CN): ν_{max} 2080, 2040, 1750 cm^{-1}. NMR (CD_3CN): δ 7.8–7.2 (15 H, m), 6.05 (1 H, t, *J* = 5.9 Hz), 5.9 (1 H, m), 5.7 (1 H, t, br, *J* = 6 Hz), 5.55 (1 H, t, *J* = 20 Hz), 4.7 (2 H, m), 4.5 (1 H, m), 3.62 (3 H, s), 3.52 (1 H, m), 1.7 (1 H, m), 0.9 (1 H, m). $[\alpha]_D$ = +1.2 (*c* = 0.011; acetone; corresponds to 40% ee). Anal. Calcd for $C_{30}H_{28}F_6FeO_7P_2$: C, 49.2; H, 3.85. Found: C, 49.67; H, 3.99.

Methyl Cyclohepta-2,5-dienylacetate (31). From Complex (+)-23: Collins reagent was prepared according to the literature procedure.[19] The iron complex (+)-**23** and Collins reagent (20 equiv) mixture was stirred at room temperature in dry dichloromethane for 2 days. After this time infrared spectroscopy of an aliquot showed disappearance of the metal carbonyl bands, the mixture was decanted into ether, and the residues were washed by decantation with ether. The combined organic extracts were washed with water, dried ($MgSO_4$), evaporated, and purified by preparative TLC to give (+)-**31** in 76% yield as a colorless oil, spectroscopically identical with the previously prepared racemic material.[3] $[\alpha]_D$ = +20° (*c* = 0.011; acetone; corresponds to 40% ee).

From Complex (+)-30: The diene–$Mo(CO)_2Cp$ complex (+)-**30** (0.10 g, 0.19 mmol) was dissolved in acetonitrile (10 mL), and the stirred solution was cooled to 0 °C. Trimethylamine *N* oxide (0.043 g, 0.57 mmol) was added in one portion. After 30 min the reaction mixture was poured into water (100 mL), and the product was extracted with ether (3 × 25 mL). The combined extracts were washed with brine (2 × 20 mL), dried ($MgSO_4$), and evaporated, and the product was purified as above; yield 35 mg (79%). $[\alpha]_D$ = +37° (*c* = 1.0; acetone).

Decarboxylation of Complex 19. The sulfoximinyl ester derivative (+)-**19** (0.88 g, 1 mmol) was stirred under nitrogen in dimethyl sulfoxide (10 mL, deoxygenated) containing water (3–4 drops) and sodium cyanide (0.25 g, 5 mmol) at 80 °C (reflux condenser) for 48 h. The mixture was then cooled and poured into ice cold water (100 mL), the aqueous mixture was saturated with NaCl, and the organic products were extracted with ether (3 × 10 mL). The combined extracts were washed with water (5 × 10 mL), dried ($MgSO_4$), and evaporated to give the product. Since no separation of diastereomers occurred on chromatography, the product was purified by preparative TLC on silica gel (20% ethyl acetate in hexane) to give **25** (0.62 g, 75%), mp 64–66 °C. The ratio of diastereomers was determined from integrated intensity of Ar–Me singlets at δ 2.46 and 2.43 in the 200-MHz ^1H NMR spectrum. IR ($CHCl_3$): ν_{max} 2000, 1950, 1600, 1490, 1190, 1150 cm^{-1}. NMR ($CDCl_3$): δ 8.03–7.21 (24 H, m, aromatic), 4.68–4.52 (2 H, m), 3.58 and 3.44 (2dd, *J* = 14, 5.9 Hz, one of CH_2S, diastereomers), 3.22 and 3.18 (2dd, *J* = 14, 5.9 Hz, one of CH_2S, diastereomers), 2.92–2.74 (1 H, m), 2.46 and 2.43 (2s, CH_3), 2.39–2.33 (1 H, m), 1.90–1.76 (2 H, m), 1.54–1.47 (1 H, m), 1.34 (1 H, m, *endo*-H-7), 0.97 (1 H, qd, J_{gem} = 12.1 Hz, J_{vic} = 4.3 Hz, *exo*-H-7). Anal. Calcd for $C_{41}H_{38}O_8FeNPS_2$: C, 59.78; H, 4.65. Found: C, 59.96; H, 4.63.

Nucleophile Additions to Complexes 30, 36, and 37. Addition of Dimethylcopperlithium. The general procedure is described for complex **30**, others being similar. Cuprous iodide (0.044 g, 0.23 mmol) was stirred in ether (5 mL) at 0 °C while a solution of methyllithium in ether (1.4 M), sufficient to just dissolve the yellow precipitate of methyl copper initially formed, was added dropwise via syringe. Complex **30** (0.10 g, 0.19 mmol) was added in one portion, and the reaction mixture was stirred for 30 min, then poured into saturated aqueous ammonium chloride (20 mL), and stirred for 15 min. The product was extracted with ether (2 × 20 mL), and the combined extracts were washed with water, dried ($MgSO_4$), and evaporated to give crude product, which was purified

(18) See: ref 11 and Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(19) Collins, J. L.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, 3363.

Table VI. Bond Distances (Å)[a]

Mo–C2	2.359 (4)	C1–C2	1.532 (6)
Mo–C3	2.195 (4)	C1–C6	1.546 (6)
Mo–C4	2.373 (5)	C1–C7	1.553 (6)
Mo–C23	2.368 (6)	C2–C3	1.404 (6)
Mo–C24	2.375 (5)	C3–C4	1.418 (7)
Mo–C25	2.340 (6)	C4–C5	1.507 (7)
Mo–C26	2.312 (5)	C5–C6	1.534 (7)
Mo–C27	2.345 (5)	C7–C8	1.532 (6)
Mo–C28	1.934 (5)	C11–C12	1.376 (7)
Mo–C29	1.937 (5)	C11–C16	1.382 (6)
S–O1	1.443 (3)	C12–C13	1.376 (7)
S–N	1.478 (4)	C13–C14	1.367 (8)
S–C7	1.884 (4)	C14–C15	1.379 (7)
S–C11	1.794 (5)	C15–C16	1.369 (7)
Si–N	1.702 (4)	C19–C20	1.54 (1)
C7–C9	1.536 (6)	C19–C21	1.550 (9)
Si–C18	1.852 (9)	C19–C22	1.515 (9)
Si–C19	1.840 (6)	C23–C24	1.400 (9)
O2–C9	1.189 (5)	C23–C27	1.371 (8)
O3–C9	1.335 (5)	C24–C25	1.386 (8)
O3–C10	1.453 (6)	C25–C26	1.396 (8)
O4–C28	1.156 (6)	C26–C27	1.414 (8)
O5–C29	1.154 (6)	Si–C17	1.859 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

by preparative TLC to give pure **38a** (64 mg, 85%). This compound, **39a**, and **40a** were identical with those previously reported.[3] The reactions of **30** with $Et_2CuMgBr$ and Ph_2CuLi were carried out in analogous manner. Spectroscopic data for the products are given here.

39b. IR ($CHCl_3$): ν_{max} 1940, 1850, 1730 cm^{-1}. NMR ($CDCl_3$): δ 5.25 (5 H, s), 3.92 (1 H, d, J = 8.8 Hz), 3.82 (1 H, d, J = 8.8 Hz), 3.69 (3 H, s), 3.62 (1 H, t, J = 8.8 Hz), 2.62 (2 H, m), 2.52 (2 H, two overlapping d, J = 6.5 Hz and J = 7.7 Hz, CH_2CO_2Me), 1.5 (4 H, m), 0.96 (3 H, t, J = 7.3 Hz). HRMS calcd for $C_{19}H_{24}MoO_4$: M = 412.0740. Found: M = 412.0708.

38c. IR ($CHCl_3$): ν_{max} 1950, 1840, 1730 cm^{-1}. NMR ($CDCl_3$): δ 7.3 (5 H, m), 5.25 (5 H, s), 4.1 (1 H, d, J = 8.5 Hz), 3.95 (1 H, d, J = 8.5 Hz), 3.74 (3 H, s), 3.5 (1 H, t, J = 8.5 Hz), 2.8 (1 H, m), 2.62 (2 H, m), 1.9 (1 H, m), 1.2 (4 H, m). HRMS calcd for $C_{23}H_{24}MoO_4$: M^+ = 460.1733. Found: M^+ = 460.1802.

Addition of Dimethyl Malonate. To a stirred suspension of sodium hydride (6 mg, 0.23 mmol, from 60% dispersion in mineral oil) in THF (10 mL) at 0 °C was added a solution of dimethyl malonate (31 mg, 0.23 mmol) in THF (0.5 mL). After 15 min the diene complex **30** (0.10 g, 0.19 mmol) was added, and the mixture was stirred until no insoluble complex remained (ca. 15 min) and then poured into water (100 mL). The mixture was extracted with ether (2 × 20 mL), and the combined extracts were washed with water, dried ($MgSO_4$), and evaporated. Preparative TLC on silica gel (40% ethyl acetate in hexane) afforded pure complex **38d** as a yellow oil (85 mg, 87%). IR ($CHCl_3$): ν_{max} 1940, 1860, 1730 cm^{-1}. NMR ($CDCl_3$): δ 5.12 (5 H, s), 3.8 (2 H, m), 3.65 (3 H, s), 3.63 (3 H, s), 3.60 (3 H, s), 3.5 (1 H, t, J = 8.5 Hz), 2.8 (1 H, m), 2.5 (1 H, m), 2.35 (2 H, m), 1.5 (4 H, m). HRMS calcd for $C_{22}H_{26}MoO_8$: M^+ = 514.0666. Found: M^+ = 514.0680.

39c (mp 158–159 °C). IR (CCl_4): ν_{max} 1955, 1880, 1742 cm^{-1}. NMR ($CDCl_3$): δ 5.27 (5 H, s), 4.16 (1 H, t, J = 7.1 Hz), 3.76 (3 H, s), 3.66 (3 H, s), 3.65 (3 H, s), 3.6 (2 H, m), 3.38 (1 H, d, J = 11.1 Hz), 2.55 (1 H, m), 2.48 (2 H, d, J = 7.3 Hz), 2.26 (1 H, m), 0.91 (1 H, dt, J = 15.2, 6.9 Hz), 0.07 (1 H, d, br, J = 15.2 Hz). Anal. Calcd for $C_{21}H_{24}MoO_8$: C, 50.41; H, 4.83. Found: C, 50.32; H, 4.61.

Addition of Cyanide. Complex **36** (0.050 g, 0.097 mmol) was stirred in acetonitrile (2 mL) at room temperature while a solution of sodium cyanide (0.005 g) in water (0.2 mL) was added. After it was stirred for 15 min, the reaction mixture was poured into water (20 mL), and the product was extracted with ethyl acetate (3 × 5 mL). The combined extracts were washed with water, dried ($MgSO_4$), and evaporated, and the crude product was purified by preparative TLC (25% ethyl acetate in hexane) to give **39b** (0.0092 g, 24%) as a yellow oil. IR (CCl_4): ν_{max} 2235, 1953, 1880, 1741 cm^{-1}. NMR ($CDCl_3$): δ 5.24 (5 H, s), 4.32 (1 H, t, J = 6.9 Hz), 3.82 (1 H, d, br, J = 6.9 Hz), 3.70 (3 H, s), 3.67 (1 H, d, br, J = 6.9 Hz), 2.77 (2 H, d, J = 7.2 Hz), 2.76 (1 H, m), 2.41 (1 H, m), 1.29 (1 H, d, br, J = 14.6 Hz), 0.91 (1 H, dt, J = 14.6, 6.9 Hz). Anal. Calcd for $C_{17}H_{17}MoNO_4$: C, 51.66; H, 4.33; N, 3.54. Found: C, 51.90; H, 4.68; N, 2.98.

Addition of Methyl Phenylsulfonylacetate and Desulfonylation. General Procedure. This is described for complex **38e**. To a stirred suspension of sodium hydride (6 mg, 0.23 mmol) in THF (3 mL) at 0 °C was added, via syringe, a solution of methyl phenylsulfonylacetate (49 mg, 0.23 mmol) in THF (0.5 mL). After 15 min, diene complex **30** (0.100 g, 0.19 mmol) was added. Completion of the reaction was indicated by dissolution of **30** (ca. 15 min), and the mixture was poured into water (100 mL) and extracted with ether (3 × 10 mL). The combined extracts were washed with water and dried ($MgSO_4$), and the solvent was evaporated to give the crude adduct as a mixture of diastereomers. This was desulfonylated as follows. The complex (100 mg) was stirred in MeOH–THF (4:1, 10 mL) while Na_2HPO_4 (95 mg, 0.67 mmol) was added. This mixture was treated with 2% sodium–mercury amalgam in small portions added at 10-min intervals until TLC examination showed complete conversion to product. The mixture was poured into cold dilute hydrochloric acid, and the product was extracted with ether as above. The crude diester was purified by preparative TLC (silica gel, 40% ethyl acetate in hexane). Spectral data for all products was as follows. Yields are given in Table III.

38e. IR (CCl_4): ν_{max} 1940, 1850, 1720 cm^{-1}. NMR ($CDCl_3$): δ 5.26 (5 H, s), 3.88 (2 H, m), 3.69 (6 H, s), 3.66 (1 H, t, J = 8.0 Hz), 2.64

Table VII. Bond Angles (deg)[a]

C2–Mo–C3	35.7 (2)	C28–Mo–C29	83.6 (2)
C2–Mo–C4	60.9 (2)	O1–S–N	122.0 (2)
C2–Mo–C23	99.2 (2)	O1–S–C7	107.0 (2)
C2–Mo–C24	118.3 (2)	O1–S–C11	105.4 (2)
C2–Mo–C25	152.5 (2)	N–S–C7	105.7 (2)
C2–Mo–C26	146.3 (2)	N–S–C11	110.5 (2)
C2–Mo–C27	111.7 (2)	C14–C15–C16	120.7 (5)
C2–Mo–C28	71.9 (2)	C11–C16–C15	119.1 (4)
C2–Mo–C29	110.4 (2)	Si–C19–C20	107.1 (4)
C3–Mo–C4	35.9 (2)	Si–C19–C21	110.7 (4)
C3–Mo–C23	89.2 (2)	Si–C19–C22	110.3 (5)
C3–Mo–C24	91.3 2)	C20–C19–C21	110.6 (5)
C3–Mo–C25	122.4 (2)	C20–C19–C22	109.3 (6)
C3–Mo–C26	145.8 (2)	C21–C19–C22	108.9 (5)
C3–Mo–C27	118.0 (2)	Mo–C23–C24	73.1 (3)
C3–Mo–C28	106.7 (2)	Mo–C23–C27	72.2 (3)
C3–Mo–C29	107.4 (2)	C24–C23–C27	108.5 (5)
C4–Mo–C23	112.8 (2)	Mo–C24–C23	72.6 (3)
C4–Mo–C24	96.1 (2)	Mo–C24–C25	71.5 (3)
C4–Mo–C25	112.1 (2)	C7–S–C11	104.9 (2)
C4–Mo–C26	147.0 (2)	N–Si–C17	110.1 (3)
C4–Mo–C27	146.6 (2)	N–Si–C18	110.1 (3)
C4–Mo–C28	113.8 (2)	N–Si–C19	107.5 (2)
C4–Mo–C29	73.3 (2)	C17–Si–C18	110.6 (4)
C23–Mo–C24	34.3 (2)	C17–Si–C19	110.4 (4)
S–C7–C9	105.3 (3)	C18–Si–C19	108.1 (3)
C1–C7–C8	113.8 (4)	C9–O3–C10	114.5 (4)
C1–C7–C9	107.3 (3)	S–N–Si	142.1 (3)
C8–C7–C9	112.6 (4)	C2–C1–C6	111.7 (3)
O2–C9–O3	124.1 (4)	C2–C1–C7	107.8 (3)
O2–C9–C7	124.3 (4)	C6–C1–C7	115.9 (3)
O3–C9–C7	111.6 (4)	Mo–C2–C1	118.7 (3)
S–C11–C12	120.1 (4)	Mo–C2–C3	65.8 (2)
S–C11–C16	119.4 (3)	C1–C2–C3	121.5 (4)
C12–C11–C16	120.5 (4)	Mo–C3–C2	78.5 (2)
C11–C12–C13	119.8 (5)	Mo–C3–C4	78.9 (3)
C12–C13–C14	120.1 (5)	C2–C3–C4	116.4 (4)
C13–C14–C15	119.9 (5)	Mo–C4–C3	65.2 (2)
C23–Mo–C25	57.2 (2)	Mo–C4–C5	119.4 (3)
C23–Mo–C26	57.5 (2)	C3–C4–C5	118.6 (4)
C23–Mo–C27	33.8 (2)	C4–C5–C6	114.0 (4)
C23–Mo–C28	118.5 (2)	C1–C6–C5	116.7 (4)
C23–Mo–C29	147.9 (2)	S–C7–C1	108.2 (3)
C24–Mo–C25	34.2 (2)	S–C7–C8	109.2 (3)
C24–Mo–C26	57.4 (2)	C23–C24–C25	108.1 (5)
C24–Mo–C27	56.9 (2)	Mo–C25–C24	74.3 (3)
C24–Mo–C28	148.5 (2)	Mo–C25–C26	71.4 (3)
C24–Mo–C29	115.9 (2)	C24–C25–C26	107.9 (5)
C25–Mo–C26	34.9 (2)	Mo–C26–C25	73.6 (3)
C25–Mo–C27	57.9 (2)	Mo–C26–C27	73.6 (3)
C25–Mo–C28	129.8 (2)	C25–C26–C27	107.5 (5)
C25–Mo–C29	90.8 (2)	Mo–C27–C23	74.0 (3)
C26–Mo–C27	35.3 (2)	Mo–C27–C26	71.0 (3)
C26–Mo–C28	96.9 (2)	C23–C27–C26	107.9 (5)
C26–Mo–C29	99.4 (2)	Mo–C28–O4	178.6 (4)
C27–Mo–C28	91.6 (2)	Mo–C29–O5	177.8 (4)
C27–Mo–C29	133.7 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

(2 H, m), 2.5 (4 H, m), 1.0 (4 H, m). HRMS calcd for $C_{20}H_{24}MoO_6$: M^+ = 456.0621. Found: M^+ = 456.0620.

39d (mp 148-150 °C (dec)). IR (CCl_4): ν_{max} 1953, 1877, 1743 cm^{-1}. NMR ($CDCl_3$): δ 5.27 (5 H, s), 4.17 (1 H, t, J = 7 Hz), 3.68 (6 H, s), 3.57 (2 H, m), 2.51 (4 H, d, J = 7.6 Hz), 2.32 (2 H, t, br, J = 6.8 Hz), 0.92 (1 H, dt, J = 14.4, 6.7 Hz), 0.72 (1 H, d, br, J = 14.4 Hz). Anal. Calcd for $C_{19}H_{22}MoO_6$: C, 51.59; H, 5.01. Found: C, 51.63; H, 5.16.

Determination of X-ray Structure for Complex 33. A yellow elongated plate of $C_{29}H_{39}MoSiNO_5S$ having approximate dimensions of 0.24 × 0.20 × 0.04 mm was mounted on a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius diffractometer. The monoclinic cell parameters and calculated volume are as follows: a = 16.398 (4), b = 8.369 (1), c = 22.239 (5) Å; β = 90.78 (2)°; V = 3051.8 Å^3. For Z = 4 and FW = 637.73, the calculated density is 1.39 g/cm^3. The space group was determined to be $P2_1/n$ from systematic absences.

A total of 6651 reflections were measured of which 6421 were unique and not systematically absent. The data were corrected for decay (2.6%), absorption (μ = 5.6 cm^{-1}), and Lorentz and polarization. The structure was solved using Patterson and Fourier techniques. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least squares to a final R = 0.043. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w, is defined as $4F_o^2/\sigma^2(F_o)^2$. Scattering factors were taken from Cromer and Waber,[20] and anomalous dispersion coefficients, from Cromer.[21] All calculations were carried out on a VAX 11/750 computer with SDP/VAX.[22]

Details of data collection and structure solution are given in Table IV, final atomic parameters in Table V, and derived bond lengths and angles in Tables VI and VII. A perspective view of complex **33** is presented in Figure 1.

A complete report of the structure determination, tables of anisotropic temperature factors, and lists of observed and calculated structure factors are available as supplementary material.

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Supplementary Material Available: Structural report for the X-ray structure determination of complex **33**, giving a description of experimental procedures, data collection, data reduction, and structure solution and refinement, tables of general temperature factor expressions and torsional angles, and a drawing of complex **33** (7 pages); listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Boron–Phosphorus Analogues of Benzene and Cyclobutadiene. Synthesis and Characterization of the Boraphosphabenzenes $(RBPR')_3$ (R = Mes, Ph; R′ = Ph, Mes, C_6H_{11}, *t*-Bu) and the Diphosphadiboretane $(ThexylBPMes)_2$

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Abstract: The synthesis and characterization of a range of boraphosphabenzenes having the formulas $(MesBPPh)_3$ (**1**), $(MesBPC_6H_{11})_3$ (**2**), $(MesBPMes)_3$ (**3**), $(MesBP\text{-}t\text{-}Bu)_3$ (**4**), and $(PhBPMes)_3$ (**5**) and a diphosphadiboretane of formula $(ThexylBPMes)_2 \cdot {}^2/_3Et_2O$ (**6**) are described (Mes = 2,4,6-$Me_3C_6H_2$, Thexyl = $(CH_3)_2CH((CH_3)_2C)$. The complete X-ray crystal structures of **1** and **6** are also reported and discussed in conjunction with the structure of **2**, which has appeared in a preliminary report. The main features of the structures of **1** and **2** are (i) the $B_3P_3C_6$ cores are planar, (ii) the B–P bonds are all equal, and (iii) the B–P bonds are short, averaging 1.84 Å. The four-membered-ring compound **6** has a planar B_2P_2 core with planar boron but pyramidal phosphorus centers. All the BP bonds are equal but they are significantly longer (ca. 1.9 Å) than those seen in **1** and **2**. Compounds **1–5** are the first examples of boraphosphabenzenes, the boron–phosphorus analogues of borazine and benzene. Compound **6** is the first structurally characterized diphosphadiboretane with no π-donor substituents (other than phosphorus) on boron. Both the X-ray structural and ^{11}B, ^{31}P, and ^1H NMR data for **1–5** support highly delocalized bonding and indicate considerable aromatic character. On the other hand, the nonplanar nature of the phosphorus centers in the cyclobutadiene-like **6**, the lengthened B–P bonds, and the very different ^{11}B and ^{31}P NMR observed chemical shifts support a bonding picture with considerably less delocalization. In effect, the π-bonding in **6** may be considered antiaromatic. This further supports the aromatic characteristics suggested for compounds **1–5**. Crystal data for **1** and **6** with Mo Kα radiation (λ = 0.71069 Å) at 130 K: (**1**) $a = b$ = 22.738 (8) Å, c = 13.729 (3) Å, trigonal, space group $R\bar{3}$, Z = 6, R = 0.047; (**6**) $a = b$ = 31.046 (11) Å, c = 9.829 (2) Å, trigonal, space group $R\bar{3}$, Z = 9, R = 0.108. A table of ^{11}B and ^{31}P NMR data for compounds **1–6** is provided and discussed in the context of the most closely related known boron–phosphorus compounds. In addition, incomplete X-ray crystal structures of compounds **3–5** together with explanatory notes are provided in the Supplementary Material. Crystal data for **3**, **4**, and **5** with Mo Kα radiation at 130 K: (**3**) a = 18.020 (4) Å, b = 12.161 (3) Å, c = 28.245 (8) Å, β = 93.53 (2)°, monoclinic, space group $P2_1/c$; (**4**) 26.072 (7) Å, β = 21.645 (5) Å, c = 16.991 (5) Å, β = 113.90 (2)°, monoclinic, space group $C2/c$; (**5**) $a = b$ = 22.810 (5) Å, c = 13.694 (8) Å, trigonal, space group $P\bar{3}$.

Borazine, $(HBNH)_3$, the boron–nitrogen analogue of benzene, was first reported in 1926 by Stock and Pohland.[2] In the intervening years both borazine and related molecules have attracted considerable interest, mainly due to their isoelectronic relationship

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