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Communications to the Editor

Auxiliary-Directed, Asymmetric Complexation and Metal-Promoted Higher-Order Cycloaddition in the Cycloheptatriene Series

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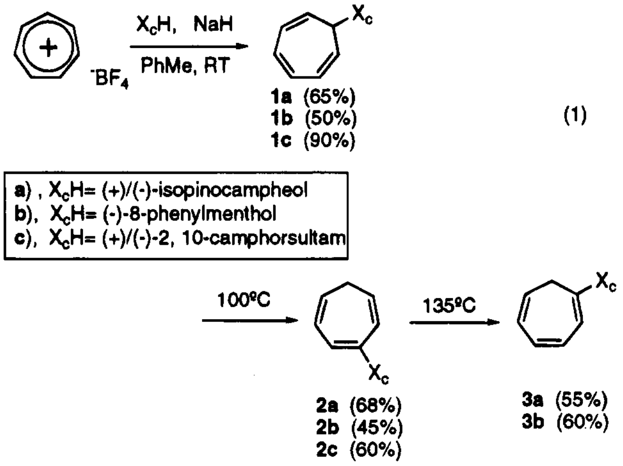
Transition metal-mediated higher-order cycloaddition reactions have recently emerged as powerful methods for the construction of structurally elaborate polycyclic systems with attendant high levels of diastereoselection.[1] We now report that these transformations can deliver optically active cycloadducts from diastereomerically enriched tricarbonyl(cycloheptatriene)-chromium(0) complexes that can be conveniently prepared with very good to excellent selectivity by chiral auxiliary-directed complexation.

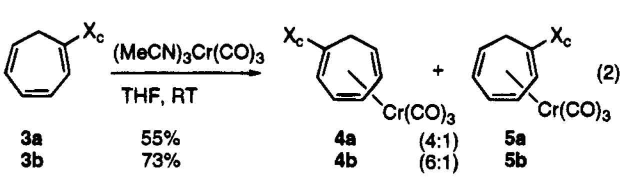
Access to chiral, nonracemic metal π-complexes in related arene–chromium, ferrocene, and iron–diene systems is difficult and has most frequently been accomplished by employing various resolution techniques,[2] by diastereoselective deprotonation of complexes containing chiral side chains,[3] or by nucleophilic substitution on complexes possessing chiral auxiliaries.[4] A potentially more direct entry into diastereomerically enriched complexes would involve face-selective complexation of an auxiliary-substituted π-system. This strategy, however, has met with only limited success in a number of instances.[3c,5] Useful approaches have employed specialized, rigid auxiliaries[6] or heteroatom delivery[7] for controlling π-face selectivity during complexation. Recently, Pearson[8] and Alexakis[9] have reported auxiliary systems that promise some generality for the production of chiral, nonracemic iron–diene and arene–chromium complexes, respectively.

The requisite substituted cycloheptatriene ligands used in the current study were prepared using known procedures[10] employing readily available auxiliaries. Both the 1- and 3-isomers were examined in the isopinocampheol (**a**) and 8-phenylmenthol (**b**) series; however, only the 3-substituted cycloheptatriene ligand could be accessed in the camphorsultam (**c**) series. The corresponding 2-substituted systems are more difficult to assemble via this addition–isomerization protocol, and complexation results with these systems will be reported at a later time.

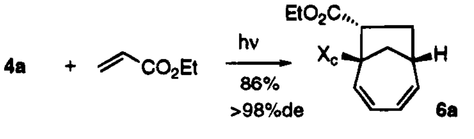


(1)

Isomerically homogeneous trienes **3a**[11] (from (+)-isopinocampheol) and **3b**[11] (from (−)-8-phenylmenthol) were treated with excess $(MeCN)_3Cr(CO)_3$ to afford diastereomeric mixtures of complexes **4a**[11]/**5a**[11] and **4b**[11]/**5b**,[11] respectively (eq 2). The major product (**4a,b**) in each case was isolated by recrystallization (hexanes) and the absolute configuration established by X-ray analysis or by correlation with a complex of known stereogenicity. Photochemically initiated $[6\pi + 2\pi]$ cycloaddition of **4a** with ethyl acrylate afforded **6a**[11] in 86% yield (>98% de (^{1}H NMR)), suggesting that the face-integrity of the metal–triene complex remained intact throughout the cycloaddition event.[12]



(2)



(3)

Remarkably, ambient temperature complexation of triene **2c** (from (+)-camphorsultam) with $(MeCN)_3Cr(CO)_3$ provided diastereomerically homogeneous complex **4c**[11] (>98% de) in good chemical yield. None of the alternative complex could be detected in the crude reaction mixture by ^{1}H NMR (500

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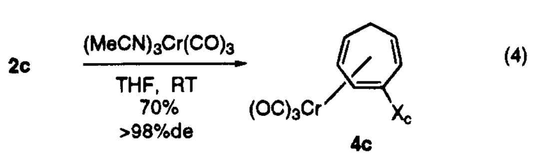
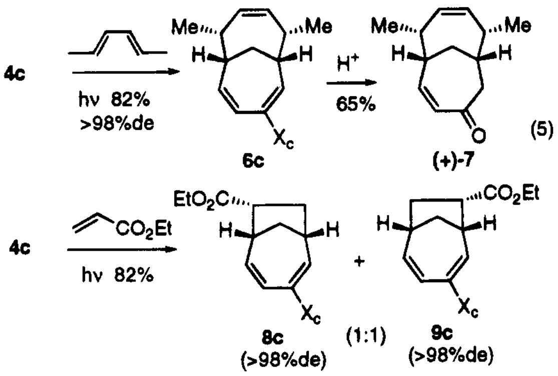
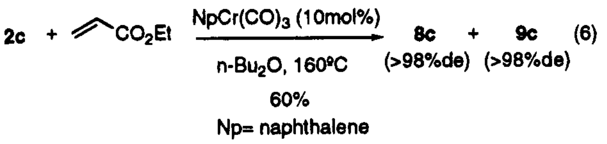


MHz). Photocycloaddition of this material with excess 2,4-hexadiene afforded adduct **6c** (82% yield, >98% de, X-ray). The auxiliary could be recovered by mild hydrolysis to the enantiomerically pure enone (+)-**7** (>99:1). The stereochemical homogeneity of this product was ascertained by performing a chiral europium shift reagent study and comparing the results with those obtained from racemic **7** prepared from the corresponding 3-methoxy-substituted complex. A [6π + 2π] cycloaddition with complex **4c** gave a 1:1 mixture of regioisomeric adducts **8c** and **9c** upon photolysis in the presence of ethyl acrylate; however, each of these compounds was produced in virtually diastereomerically pure from (>98% de, assayed as above).





It is noteworthy that efforts to produce quantities of the complex diastereomeric to **4c** via thermal equilibration[9] afforded only quantitative recovery of the unchanged starting complex. This observation suggested that a thermal, catalytic version of the cycloaddition process[13] could be performed directly on the metal-free camphorsultam-substituted triene substrate and that this reaction would afford chiral, nonracemic products. *Indeed, heating a mixture of* ***2c*** *with excess ethyl acrylate in the presence of a substoichiometric quantity of tricarbonyl(naphthalene)-chromium(0)*[14] *(10 mol %) afforded a mixture of adducts* ***8c*** *and* ***9c****, in which each regioisomer was produced in essentially diastereomerically pure form (>98% de).* In contrast, triene **2a** (X_c = (+)-isopinocampheol) afforded a mixture of adducts in which each regioisomer was produced without any detectable diastereoface selection under similar conditions.

The remarkably high levels of face selection exhibited by the camphorsultam-derived triene system are difficult to rationalize at the present time. It is tempting to suggest the involvement a heteroatom-mediated delivery mechanism[7] (via intervention of a sulfonamide oxygen); however, models are not particularly supportive of this explanation. Further work will be required to clarify this issue.[15]

In conclusion, the feasibility of diastereoface-selective complexation of substituted cycloheptatrienes has been demonstrated, and the asymmetry of the resultant complexes can be translated into [6π + 4π] and [6π + 2π] cycloadducts with complete integrity.

Acknowledgment. The authors thank the National Institutes of Health (GM-30771) for their support of this research.

Supporting Information Available: Experimental procedures and complete spectroscopic data for compounds **4a–c**, **6a,c**, **8c**, and **9c**; details of the X-ray crystal structure determination, diagrams, and selected bond lengths and angles for **4a** and **6c** (31 pages); observed and calculated structure factors for **4a** and **6c** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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