

0.0025 ± 0.0003 for AntiCl and SynCl, respectively. By comparison, the quantum efficiencies for loss of ExoCl and EndoCl are 0.66 ± 0.001 and 0.0079 ± 0.0005, respectively.⁴

It is evident from these results that neither of the 7-chloro epimers show the theoretical and spectral characteristics associated with the relatively photoactive ExoCl, and that they are indeed both comparable in reactivity to EndoCl. Perhaps of even more significance is the fact that

the relative reactivity of the respective isomer pairs has markedly diminished from $\phi_{\text{dis}}(\text{ExoCl})/\phi_{\text{dis}}(\text{EndoCl}) = 8.7$ to $\phi_{\text{dis}}(\text{AntiCl})/\phi_{\text{dis}}(\text{SynCl}) = 2.8$. All of these observations are consistent with our proposal⁴ that, for these compounds, C-Cl photolytic cleavage derives from π^*/σ^* mixing in their lowest unoccupied molecular orbitals, and therefore delocalized excitation in their electronic excited states.³

Use of Metal Carbonyl Complexes To Achieve High Enantioselectivity in the Asymmetric Allylboration of Unsaturated Aldehydes

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Summary: The enantioselectivity of the asymmetric allylborations of aromatic and propargylic aldehydes is significantly enhanced by using metal carbonyl derivatives 4 and 8 as substrates.

Transition metal carbonyl complexes of unsaturated organic substrates have found numerous applications in organic synthesis.¹ For example, arene-chromium tricarbonyl complexes, among others, are highly activated toward nucleophilic attack; transition metal stabilized benzylic, allylic, and propargylic cations have found widespread application in stereocontrolled nucleophilic substitution reactions,^{1b,2} and metal carbonyl units have been used as bulky substituents on *chiral substrates* enabling the diastereoselectivity of C-C bond forming reactions at adjacent positions to be enhanced.^{1a,3} The electronic and/or steric influence of the metal on the unsaturated organic ligand is of course central to the success of these and many other applications. *We report herein a new and extremely useful effect of metal carbonyl complexes, specifically the ability of such complexes to enhance the enantioselectivity of the asymmetric allylboration of unsaturated (aryl and propargylic) aldehydes.* The reactions we report are unique in that they are among the first examples⁴ in which metal carbonyl ligands of *achiral substrates* lead to an enhancement of the enantiofacial selectivity of a chiral reagent. This is in

contrast to the vast majority of previously reported examples in which it is the diastereoface selectivity of the *metal carbonyl containing chiral substrates* that is enhanced.¹⁻³

Previous studies from our laboratories have established that the asymmetric allylboration of aromatic aldehydes (e.g., benzaldehyde) proceed with only moderate enantioselectivity (55-72% ee for reactions with 1-3 in THF).⁵ We thus decided to explore the use of the benzaldehyde chromium tricarbonyl complex 4 as a surrogate for C₆-H₅CHO.⁶ In the event, we were delighted to find that the asymmetric allylboration of 4 with (*R,R*)-1 (toluene, -78 °C, 4-Å sieves) followed by oxidative decomplexation (*hν*, O₂, CH₃CN) provided (*S*)-5 in greater than 90% yield and 83% ee.^{7a} The (*E*)-crotylboration of 4 with (*R,R*)-2 was even more selective, providing 6 with an ee of 92% (98:2 anti:syn; 90% yield).^{7b} It is noteworthy that the sense of asymmetric induction is the same with or without the Cr(CO)₃ unit;⁸ this substituent has simply led to an increase in the energy difference ($\Delta\Delta G^\ddagger$) between the favored (leading to the indicated enantiomers of 5 and 6) and disfavored transition states.

Encouraged by these results, we examined the asymmetric allylboration of 2-decynal-dicobalt hexacarbonyl complex 8.^{9,10} This substrate was chosen for study since

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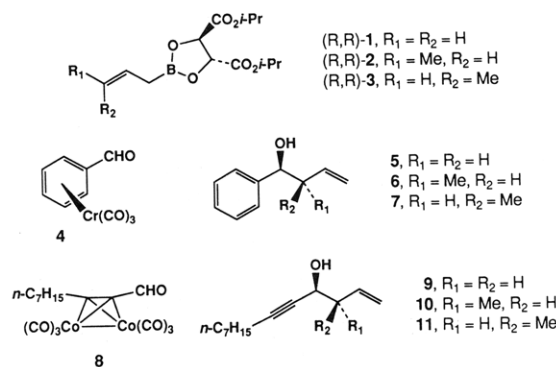
(6) For previous examples of diastereoselective reactions of allylmetal compounds with metal carbonyl complexes of unsaturated aldehydes: (a) Uemura, M.; Minami, T.; Isobe, K.; Kobayashi, T.; Hayashi, Y. *Tetrahedron Lett.* 1986, 27, 967. (b) Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* 1989, 30, 309. (c) Nunn, K.; Mosset, P.; Grée, R.; Saalfrank, R. W. *Angew. Chem., Int. Ed. Engl.* 1989, 27, 1188.

(7) (a) The reactions of benzaldehyde and 1-3 are more selective in THF than in toluene, while those of benzaldehyde-Cr(CO)₃ (4) display the highest selectivity in toluene. (b) The reaction of (*Z*)-crotylboronate 3 and 4 in toluene (-78 °C) provides 7 with 41% ee, while the reaction of 3 and PhCHO proceeds in only 25% ee under the same conditions. Thus, even though the enantioselectivity of the (*Z*)-crotylboration is enhanced (in toluene) by using 4 as a surrogate for PhCHO, the % ee does not exceed that obtained in the reaction of 3 and PhCHO in THF (55% ee). Reasons for the aberrant behavior of 3 compared to 1 or 2 with 4 as a substrate are unclear at present.

(8) The relative and absolute stereochemistries of 5-7 have been rigorously established: (a) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.*, submitted. (b) Roush, W. R.; Ando, K.; Powers, D. B.; Halterman, R. L.; Palkowitz, A. D. *J. Am. Chem. Soc.*, submitted.

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the enantioselectivity of the allyl- and crotylboration of α,β -unsaturated aldehydes is poor (62–74% ee for (*E*)-decenal and 1-3),⁵ and the masked acetylene unit of 8 can be viewed as a synthetic equivalent of both *E* and *Z* olefins in the reaction products. 2-Decynal, too, is a poor allylboration substrate: the reactions with 1–3 under standard conditions provide 9–11 with enantiomeric excesses of only 72%, 72%, and 58%, respectively. *It is thus significant that the reactions of 8 with (R,R)-1, (R,R)-2, and (R,R)-3 (toluene, -78 °C, 4-Å sieves) followed by oxidative decomplexation (Fe(NO₃)₃, EtOH, 23 °C) provide 9¹⁰ (92% ee), 10¹⁰ (96% ee; 97:3 anti to syn), and 11¹⁰ (86% ee; 97:3 syn to anti) in 85–95% yield. Here again, the absolute stereochemical outcome is the same with both 2-decynal and the dicobalt hexacarbonyl complex 8.¹¹*

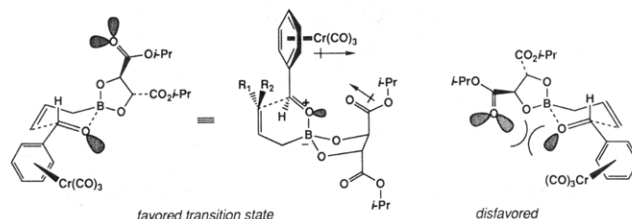


These examples clearly demonstrate that the enantioselectivity of the asymmetric allylboration of aryl and propargylic aldehydes may be significantly improved by using appropriate metal carbonyl derivatives. The origin of this effect, however, cannot be explained by invoking previously established principles of metal carbonyl chemistry.¹⁻³ For example, while the Cr(CO)₃ unit of 4 is well known to have a significant inductive effect, comparable to a *p*-NO₂ substituent,^{1c} this electronic effect is not responsible for the increased enantioselectivity: the allyl-

(10) Satisfactory ¹H NMR, IR, mass spectra, and C, H analytical data were obtained for this compound.

(11) The relative and absolute stereostructures of 9–11 have been assigned by hydrogenation of each to the corresponding tridecanols that have been correlated with materials prepared by the Sharpless asymmetric epoxidation reactions (ref 8a,b).

boration of *p*-nitrobenzaldehyde with 1 proceeds with the same enantioselectivity as PhCHO.¹² The increased enantioselectivity also does not appear to be due to a steric effect, since the bulky metal carbonyl units can be positioned away from the allyl group in both the favored and disfavored transition states as indicated below for the reaction of 4. Moreover, in the asymmetric allylboration of hindered substrates (e.g., pivalaldehyde) with 2 and 3, enantioselectivity in fact decreases relative to less sterically demanding substrates.⁵ Rather, we speculate that the stereochemically preferred transition state is stabilized by a favorable dipole–dipole interaction between the tartrate ester and the metal carbonyl unit as indicated in the three-dimensional structure presented below for 4.^{1c,13} Such interactions are possible only in the favored transition state.



In summary, we have shown that the enantioselectivity of the asymmetric allylboration of certain unsaturated aldehydes is significantly improved by using metal carbonyl derivatives as substrates. These results are also of considerable interest since the reaction products are chiral organometallic complexes that are potential substrates for a range of stereoselective transition metal mediated organic reactions, a line of investigation that we are actively pursuing.

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Enantiospecific Synthesis of an Aziridinobenzoazocinone, an Advanced Intermediate Containing the Core Nucleus of FR900482 and FK973

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Summary: A route to the enantiospecific synthesis of the aziridinobenzoazocinone ketone 14, containing the core nucleus of FR900482 and FK973, has been developed. It consists of coupling the two key intermediates, sulfonamide 7 and methyl (2*S*,3*S*)-2,3-aziridino-4-hydroxybutyrate 12, prepared from vinylglycine, followed by cyclization to the azocinone 14.

In 1987 the isolation was reported of a potent anti-neoplastic agent from cultures of *Streptomyces sandaensis*

No. 6897; it was designated FR900482, 1.¹⁻³ This unique compound exists in two diastereomeric forms, A and B, due to the hydroxylamine hemiketal functionality. The A form is favored in neutral and acidic media possibly due

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