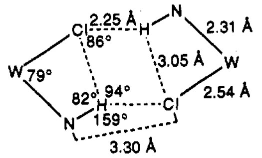
of the ligand (δ 5.092 (dd, $^3J_{HH}$ = 2.6 Hz, $^2J_{HH}$ = 13.8 Hz, 1 H), 4.438 (dd, $^3J_{HH}$ = 10.7 Hz, $^2J_{HH}$ = 13.8 Hz, 1 H). Addition of D_2O results in rapid exchange of the amine proton and loss of coupling to the benzylic hydrogens. The N-H stretch appears at 3255 cm^{-1} and the N-D stretch for the deuteriated material, prepared by exchange with excess D_2O in THF, occurs at 2422 cm^{-1}. Strong metal carbonyl bands observed at 2021, 1946, and 1905 cm^{-1} in CH_2Cl_2 are consistent with the tungsten(II) metallacycle formulation.[2,4]

Spectral properties of **5b** are similar,[8] and the regiochemistry of the product was confirmed by X-ray diffraction analysis of single crystals obtained from CH_2Cl_2/hexanes (Figure 1).[9] The seven-coordinate tungsten(II) metallacycle is formed by oxidative addition at the carbon-chlorine bond on the imine arm of the ligand. The geometry about tungsten can be approximated as a capped octahedron with the phenyl group as the cap.[2] The carbon-iodine bond remains intact. Direct ^{1}H NMR analysis of the crude reaction mixture failed to detect any other isomeric product. Thus the asymmetry of the ligand results in activation of the stronger C-Cl bond (95 kcal/mol) in the presence of a weaker C-I bond (64 kcal/mol).[10] This result implies that the unsaturated imine arm of the ligand is crucial in promoting oxidative addition to tungsten(0). Both steric (restricted rotation about the C=N bond) and electronic (conjugation of the C=N bond with the phenyl ring) factors appear to promote the oxidative addition process.

Structural studies of **5b** reveal that both intra- and intermolecular hydrogen bonding takes place between the chloride coordinated to tungsten (Cl(1)) and the proton of the amine group (H1n). Unfortunately, H1n could not be unambiguously located on the final electron density difference map and was placed in the calculated position. Intermolecular hydrogen bonds occur between pairs of molecules related by a center of inversion; metrical parameters are given below.



Both intramolecular N1···Cl (2.97 Å) and intermolecular N1···Cl (3.30 Å) are in the range expected for hydrogen bonding.[11] The close intramolecular N1···Cl interaction is in part a consequence of the acute N1-W-Cl angle of 79.3 (2)° in this seven-coordinate complex. The intermolecular N-H···Cl angle is much closer to 180° than the intramolecular case resulting in a significantly shorter H···Cl distance.[12] The importance of these intermolecular hydrogen bonds is seen in the solid state packing of this molecule. However, solution molecular weight measurements (Signer isothermal distillation)[13] on **5a** indicate that it is monomeric in dichloromethane. The observed ν_{NH}/ν_{ND} ratio of 1.34 is smaller than that expected (1.36) for molecules where hydrogen bonding is unimportant.[14]

The structural chemistry of this molecule provides a contrast to the behavior of a series of six-coordinate Rh(III) and Ir(III) amino halides in which intramolecular hydrogen bonding appears to be more important than intermolecular interactions.[15] Further exploration of ligand-based control of bond activation reactions and the role of hydrogen bonding in the chemistry of these materials is in progress.[16]

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Supplementary Material Available: Full crystallographic data for **5b** including tables of bond distances and angles and final positional and thermal parameters (16 pages); a listing of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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[8] Analytical data for **5b**: IR (CH_2Cl_2, cm^{-1}) 3226 (w, ν_{NH}), 2404 (w, ν_{ND}), 2020 (s), 1944 (s), 1906 (s) (ν_{CO}); nonaromatic ^{1}H NMR (acetone-d_6) δ 9.877 (s, 1 H, HC=N, $^3J_{WH}$ = 8.5 Hz), 6.304 (dd, ^3J = 10.7, 3.7 Hz, 1 H, NH), 5.027 (dd, ^2J = 13.4, ^3J = 3.7 Hz, 1 H, C*H*H′), 4.222 (dd, ^2J = 13.4, ^3J = 10.7 Hz, 1 H, CH*H′*). Anal. Calcd for $C_{23}H_{15}N_2Cl_2IO_3W$: C, 36.88; H, 2.02; N, 3.74. Found: C, 36.70; H, 2.06; C, 3.72.

[9] Crystal data for **5b**: $WICl_2O_3N_2C_{23}H_{15}$, red-orange, monoclinic, $P2_1/a$, a = 11.239 (4) Å, b = 15.533 (8) Å, c = 14.296 (4) Å, β = 106.60 (3)°; V = 2391.7 Å^3, Z = 4, Mo Kα. Of 4155 reflections collected at ambient temperature (Syntex P$\bar{1}$, $3° < 2\theta < 48°$) 3721 were unique of which 2386 had $I > 3\sigma(I)$ and were used in the solution and refinement (SDP PLUS Software). Final refinement included all non-hydrogen atoms as anisotropic and hydrogen atoms as idealized isotropic contributions. For 289 parameters, R = 0.039 and R_w = 0.043, GOF = 1.7, and highest peak in the final map of 1.1 e/Å^3 approximately 0.99 Å from W.

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Reversal of Stereochemical Path in Allylic Alkylations Promoted by Palladium and Molybdenum Complexes

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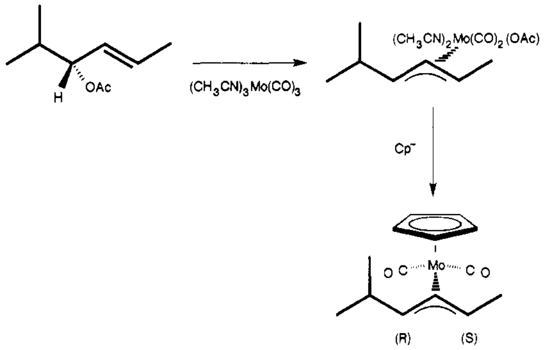
Summary: In allylic alkylations using palladium complexes, the oxidative addition of an allyl acetate to the metal usually occurs with inversion of configuration. The addition of (+)-(*R*)-(*E*)-4-acetoxy-5-methyl-2-hexene to $(CH_3CN)_3Mo(CO)_3$ has been shown to occur with retention of configuration. This leads to a reversal of the chirality at the stereogenic center formed in the addition of nucleophiles, such as malonate, when the products of palladium-catalyzed reactions are compared to those from stoichiometric reactions on molybdenum complexes. These results suggest that whereas net retention is a consequence of double inversion in the palladium-catalyzed reactions, net retention is a consequence of double retention in many molybdenum-catalyzed reactions of this type.

We have demonstrated the utility of cationic [CpMo(NO)(CO)(η^3-allyl)]$^+$ complexes in stoichiometric asymmetric synthesis that have provided a route to chiral allylically substituted olefins in high optical purity.[1] The stereochemical control in this system is due largely to the unsymmetrical electronic environment at the metal center. This system differs from palladium-catalyzed systems where asymmetric induction is primarily attributed to steric interactions between substrate and ligands.[2] Previously, resolution of the stereogenic center at molybdenum in the [CpMo(NO)(CO)(η^3-allyl)]$^+$ complexes was achieved by substituting the Cp$^-$ with a neomenthyl group.[3] In exploring an alternative approach to enantiomeric resolution by starting with an optically pure allyl acetate, we have determined that the initial oxidative addition of the chiral allyl acetate proceeds with retention, which contrasts with the generally accepted mode of inversion found for palladium complexes.

During catalytic palladium alkylation, an allyl acetate oxidatively adds to a palladium(0) complex to give a (π-allyl)palladium(II) complex. This undergoes nucleophilic attack to generate a palladium(0) π-olefin complex. The nucleophilic attack proceeds with either inversion or retention, depending on the nature of the nucleophile, while the initial oxidative addition has generally been conceded to proceed with inversion.[4] Hayashi[5] presented direct evidence for an oxidative addition mechanism involving inversion when he successfully isolated a cationic palladium(II) π-allyl complex generated by oxidative addition of a nonracemic chiral allyl acetate to a palladium(0) complex (81% stereoselectivity).

Relatively little work has been done to determine the stereochemistry of the oxidative addition step of an allyl acetate to a molybdenum(0) complex. In developing catalytic molybdenum systems for allylic alkylation, Trost[6] has used molybdenum(0) complexes to effect alkylation of allyl acetates with stabilized carbanion nucleophiles, e.g., sodiomalonate. He has concluded that the overall catalytic process proceeds with either a double-inversion or a double-retention mechanism to give products which have experienced a *net retention of configuration.* We now present evidence that the oxidative addition of an allyl acetate to a molybdenum(0) complex with a number of displaceable ligands proceeds with retention of stereochemistry.

During the preparation of CpMo(CO)$_2$(η^3-allyl) complexes, an allyl acetate oxidatively adds to (CH$_3$CN)$_3$Mo(CO)$_3$ to give a (π–allyl)molybdenum(II) complex. Addition of Cp$^-$ displaces the two remaining acetonitrile and the acetate ligands to give the desired complexes. A sample of the nonracemic methylisopropyl-π-allyl complex (+)-CpMo(CO)$_2$(5-methyl-2–4-η^3-hexenyl) (**1**) was prepared by oxidative addition of (+)-(*R*)-(*E*)-4-acetoxy-5-methyl-2-hexene (99% ee).[7-9] In order to determine the stereochemistry of the oxidative addition, we determined the absolute configuration of **1** by a single-crystal X-ray analysis.[10] As displacement of the other ligands would not affect the stereochemistry of the allylmolybdenum moiety, these results show that the 4-(*R*)-acetate oxidatively adds to (CH$_3$CN)$_3$Mo(CO)$_3$ with retention, followed by Cp$^-$ displacement to give 2(*S*),4(*R*)-**1**.



(+)-1

The stereoselectivity of the addition was determined by conversion of **1** to one diastereomer of CpMo(NO)(NCO)(5-methyl-2–4-η^3-hexenyl) (**2**) in which the diastereomeric ^{1}H NMR Cp singlets can be resolved by addition of the chiral shift reagent Eu(tfc)$_3$ in benzene-d_6. Use of 88% ee (*R*)-(*E*)-4-acetoxy-5-methyl-2-hexene yields a sample of complex (+)-**2** in 86% ee, which implies a 98% stereoselectivity in the oxidative addition.[11]

In order to promote nucleophilic attack on the η^3-allyl, we generated the cationic [CpMo(NO)(CO)(η^3-allyl)]$^+$ (**3**) by displacement of a carbonyl with NO$^+$. Nucleophilic attack on these coordinatively saturated complexes has been shown to occur on the β-face of the allyl (i.e., trans

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(7) The acetate **6** with $[\alpha]^{25}{}_{\mathrm{D}}$ +37.6° (*c* 4.71, CHCl$_3$) was prepared by acetylation (Ac$_2$O, pyridine) of (*R*)-(*E*)-4-hydroxy-5-methyl-2-hexene with $[\alpha]^{25}{}_{\mathrm{D}}$ −12.9° (*c* 4.75, CHCl$_3$). The nonracemic alcohol was prepared via a Sharpless kinetic resolution using L-(+)-diisopropyl tartrate.[8] The enantiometric purity of the alcohol and acetate was determined by using Eu(tfc)$_3$ in benzene-d_6.

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(9) (a) The assignment of absolute configuration of carbon-4 of *R* in compound (+)-**6** and the same carbon center C-3 in the (−)-alcohol is based on conversion to lactones of known absolute configuration.[9b] The formation of the (*R*)-alcohol is also expected from empirical rules for kinetic resolution using L-(+)-diisopropyl tartrate.[8] (b) Ziegler, F. E.; Kneisley, A.; Wester, R. T. *Tetrahedron Lett.* **1986**, *27*, 1221–1224.

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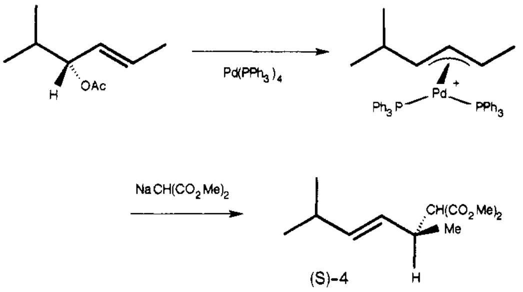
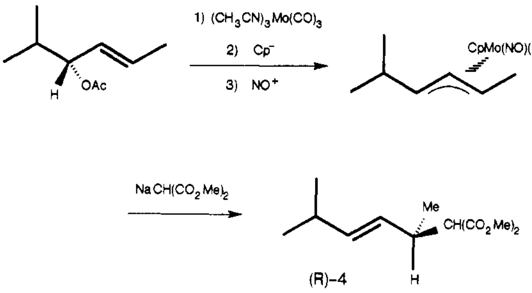
(11) In order to readily identify the resonances of the diastereomers and facilitate the ee determination using the chiral shift reagent Eu(tfc)$_3$, we chose to use a nonracemic sample of acetate with an ee lower than that which is obtainable via the Sharpless kinetic resolution.

to the metal), resulting in an inversion at the site of nucleophilic addition. Thus, a chiral allyl acetate should experience a net inversion of the stereochemistry relative to the chiral center during the stoichiometric molybdenum allyl alkylation.

To demonstrate this net-inversion mechanism, we prepared a sample of dimethyl [(*E*)-5-methyl-3-hexen-2-yl]malonate (4) by addition of sodiomalonate to **3**-BF_4,[12] followed by decomplexation of the η^2-olefin formed. The stereochemistry of the molybdenum-mediated allyl alkylation was compared to that of the palladium-catalyzed alkylation[14] where the overall process is known to proceed through a double-inversion mechanism for stabilized carbanions.[15] The relative configuration of the addition products was determined by using a chiral shift reagent and observing the separation of the diastereomeric methyl ester singlets. The experiment demonstrates that starting with the same enantiomer of a chiral allyl acetate, the stoichiometric molybdenum-mediated alkylation results in addition products that have the *opposite* configuration of those obtained through the palladium-catalyzed alkylation. This shows that indeed the alkylation products of the stoichiometric molybdenum system experience a net inversion of configuration of the stereochemistry of the starting allyl acetate. By virtue of the retention during the oxidative addition step of chiral allyl acetates, the stoichiometric molybdenum system provides a route to asymmetrically allylated products where inversion of the stereochemistry of the chiral center is desired.



A number of molybdenum and tungsten catalysts also promote allylic alkylation, and it appears that moderately high net retention is observed in the products. As $(MeCN)_3Mo(CO)_3$ is similar to many of the catalysts, particularly in regard to the feature that several readily displaceable ligands are present, the results above suggest that oxidative addition of allylic acetates may well occur with retention in the catalytic cycle. Thus, these results imply that whereas net retention is a consequence of double inversion with palladium catalysis, net retention may be a consequence of double retention in many of the molybdenum-catalyzed reactions reported thus far.



Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. 1, 114581-58-7; 2, 114581-59-8; (*S*)-**3**, 114672-91-2; (*R*)-**3**, 114581-61-2; (*R*)-4, 114581-62-3; (*S*)-**5**, 114581-63-4; Cp^-, 12127-83-2; (*R*),(*E*)-$(CH_3)_2CHCH(OH)CH{=}CHCH_3$, 92283-72-2; NO^+, 14452-93-8; $(CH_3CN)_2Mo(CO)_2(OAc)$(5-methyl-2-4-η^3-hexenyl), 114594-71-7; $NaCH(CO_2Me)_2$, 18424-76-5; (*R*),(*E*)-$(CH_3)_2CHCH(OAc)CH{=}CHCH_3$, 114613-28-4; $Mo(CO)_6$, 13939-06-5; L-(+)-diisopropyl tartrate, 2217-15-4.

Supplementary Material Available: Discussion of absolute configuration X-ray crystal structure determination of (+)-1 and tables of data parameters, atomic positions, bond lengths and angles, calculated hydrogen positions, thermal parameters, and Bijvoet pair intensity comparisons (10 pages); a listing of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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[12] Replacement of CO by NO^+ produces a new stereogenic center at Mo and, therefore, two diastereomers of **3**, [CpMo(NO)(CO)(5-methyl-2–4-η^3-hexenyl]$^+$, in a 48:52 ratio. The (*S*)-**3** diastereomer, which contains the 2(*S*),4(*R*)-(5-methyl-2–4-η^3-hexenyl) ligand, yields addition of nucleophiles exclusively to the methyl-substituted terminus of the allyl.[13] Addition of sodiomalonate to a diastereomeric mixture of **3**-BF_4 results in a mixture of regioisomers, where the nucleophile has added to different ends of the η^3-allyl group yielding 48% (*R*)-**4** and 52% (*S*)-**5** after, decomplexation. A sample of pure (*R*)-**4** can be isolated via preparative TLC (silica, $CHCl_3$). The relative configuration of (*S*)-**5** was determined by using a chiral NMR shift reagent and observing the separation of the diastereomeric methyl ester singlets. These results were compared to those from a sample of (*R*)-**5** prepared by using $Mo(CO)_6$ as the allyl alkylation catalyst where the catalytic cycle proceeds through a net-retention mechanism.[6a]

[13] (a) The regiochemistry of the addition is controlled by the relative position of the NO group. The separation of diastereomers and the ability of the NO to override the steric directing effect of the *i*-Pr group will be discussed in a forthcoming full paper.[13b] (b) Faller, J. W.; Linebarrier, D.; Lambert, C., manuscript in preparation.

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Unusually Long-lived Cobalt(II) and Cobalt(I) Species Identified during Electrochemical Reduction of Neopentyl B_{12} Costa-Type Models

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Summary: Unusually long-lived complexes, which are formally in cobalt(II) and cobalt(I) oxidation states, are identified spectrally and electrochemically during the cathodic reduction in acetonitrile of a Costa-type organocobalt(III) B_{12} model with a particularly bulky alkyl axial ligand, namely, neopentyl. The solution behavior is different from that reported for other similar complexes in that intermolecular alkyl transfer processes are essentially prevented by the bulky neopentyl axial ligand.