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Stereochemical aspects of the reactions of molybdenum complex CpMo(CO)2(syn-.eta.3-C3H4COCH3)

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The nature of **6** and **7** has been established by an X-ray analysis.[6] Some details are reported for **6**,[10] shown in Figure 2 with some relevant bond distances and angles.[11] The iminoacyl group does not change its structural parameters. The bonding scheme shown for the two metallacycles derived from the insertion of CO_2 into the V–C carbon bonds is supported by the structural parameters. The bidentate ligand in the metallacycle is the deprotonated form of an α-imino carboxylic acid. The appropriate sequence in the insertion reaction transformed the original aryl group into a doubly functionalized fragment. Insertion of carbon dioxide in a functionalized carbon ligand has so far been an unknown process.[12] Studies will continue for a complete definition of the chemistry of **2**, which is a rather unique iminoacyl derivative that does not have at the metal any ancillary ligand.

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Registry No. 1, 79738-18-4; 2, 127973-44-8; 3, 63064-23-3; 4, 127973-43-7; 6, 127973-45-9; 7, 127973-46-0; Bu^{t}NC, 7188-38-7; $C_6H_{11}NCO$, 3173-53-3.

Supplementary Material Available: Tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, thermal parameters, and hydrogen atomic coordinates for compounds 2 and 6 (12 pages); tables of observed and calculated structure factors for compounds 2 and 6 (23 pages). Ordering information is given on any current masthead page.

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[10] A THF (80 mL) solution of **2** (3.33 g, 5.06 mmol) was reacted with CO_2 at room temperature. The color suddenly changed to dark red. The solution was kept stirring for 30 min; then the solvent was evaporated to dryness. A dark solid was obtained, which, after extraction with diethyl ether, gave dark red crystals of **6** (40%). Anal. Calcd for $C_{44}H_{60}N_3O_4V$: C, 70.79; H, 8.04; N, 5.63. Found: C, 70.61; H, 7.97; N, 5.54. μ_{eff} = 2.87 μ_B at 288 K.

[11] Crystals of **6** are triclinic, space group $P\bar{1}$, with a = 11.253 (1) Å, b = 22.818 (2) Å, c = 8.538 (1) Å, α = 93.85 (1)°, β = 94.58 (1)°, γ = 100.95 (1)°, V = 2137.9 (4) Å^3, Z = 2, and d_{calcd} = 1.159 g/cm^3. The 4002 unique observed data ($I > 2\sigma(I)$) were collected with the use of the $\omega/2\theta$ scanning technique and nickel-filtered Cu Kα radiation (λ = 1.541 78 Å). The structure was solved as above and refined by full-matrix least squares anisotropically for all the non-hydrogen atoms. All the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. During the refinement the benzene rings were considered as regular hexagons.

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Stereochemical Aspects of the Reactions of $CpMo(CO)_2$(*syn*-η^3-$C_3H_4COCH_3$)

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Summary: Reduction of $CpMo(CO)_2$(*syn*-η^3-$\underline{CH_2CHCH}COCH_3$) (**1**) with $NaBH_4$ in MeOH produces (*RR*-(*SS*))-$CpMo(CO)_2$(*syn*-C^3-$\underline{CH_2CHCH}CH(OH)CH_3$) (**2**) with high diastereoselectivity. Treatment of the latter with 1 equiv of $(CF_3SO_2)_2O$ in ether at −45 °C stereospecifically generates the *s-trans*-η^4-*cis*-pentadiene cationic complex **3**, which adds nucleophiles regioselectively and stereospecifically at the α- or δ-carbons. The enolate of **1** generated with lithium diisopropylamide in THF undergoes diastereoselective aldol reactions.

Functionalization of $CpMo(CO)_2$(allyl) complexes in cyclic systems[1-3] has recently attracted considerable attention. Organic functional groups adjacent to the $CpMo(CO)_2$(η^3-allyl) unit can be transformed with excellent stereoselectivity and regioselectivity. In contrast, little has been reported concerning the acyclic allyl system. Faller et al.[4] have reported that condensation of CpMo(NO)(Cl)(*syn*-η^3-crotyl) with aldehydes yields the homoallylic alcohol with high regioselectivity and diastereoselectivity. Stereocontrolled functionalization of acyclic $CpMo(CO)_2$(η^3-allyl) systems represents a significant extension of this chemistry, and we report here stereochemical aspects of the reaction chemistry of $CpMo(CO)_2$(*syn*-η^3-$C_3H_4COCH_3$).

The complex $CpMo(CO)_2$(*syn*-η^3-$C_3H_4COCH_3$) (**1**) was conveniently synthesized by reaction of $CpMo(CO)_3Na$ with 5-chloro-3-penten-2-one (tetrahydrofuran at 0 °C) followed by decarbonylation with excess Me_3NO. The syn and anti isomers of **1**, formed in a ratio of 6:1, are readily separable by silica gel column chromatography. For the syn-η^3 isomer, the exo/endo ratio is 16:1. The presence of exo/endo isomers does not complicate the diastereoselectivity studies, because they are related to each other as conformers.[5] Reduction of the syn-η^3 isomer of **1** with $NaBH_4$ in CH_3OH produces (*RR*(*SS*))-$CpMo(CO)_2$(η^3-*syn*-$C_3H_4CH(OH)CH_3$) (**2**) in an exo/endo ratio of 2:1. The *RR*(*SS*) configuration is assigned to **2** by assuming that hydride adds to the carbonyl group trans to the CpMo-

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[1] (a) Pearson, A. J.; Khan, M. D.; Clardy, J. C.; He, C.-H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. (b) Pearson, A. J.; Blystone, S. L.; Nav. H.; Pinketon, A. A.; Rodeu, B. A.; Yoon, J. *Ibid.* **1989**, *111*, 134. (c) Pearson, A. J.; Khan, M. N. *Ibid.* **1984**, *106*, 1872.

[2] (a) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. (b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. (c) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *Ibid.* **1979**, *101*, 2570.

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[5] Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840.

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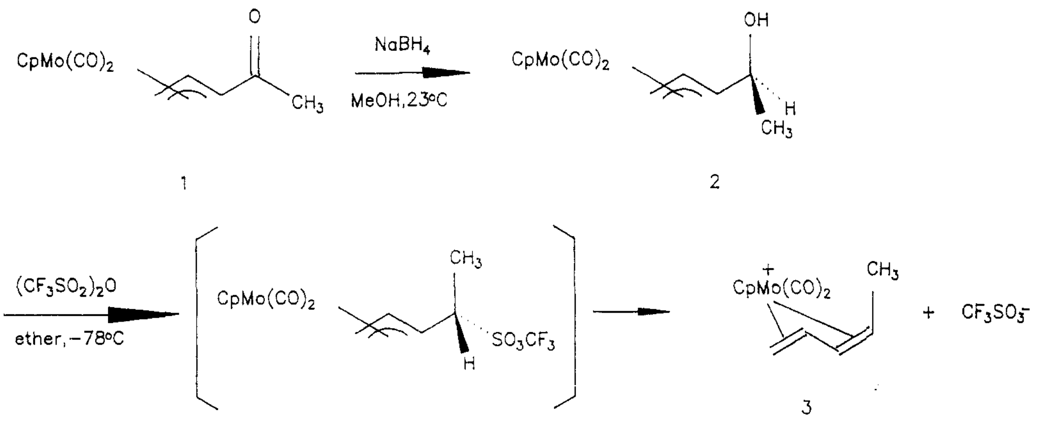
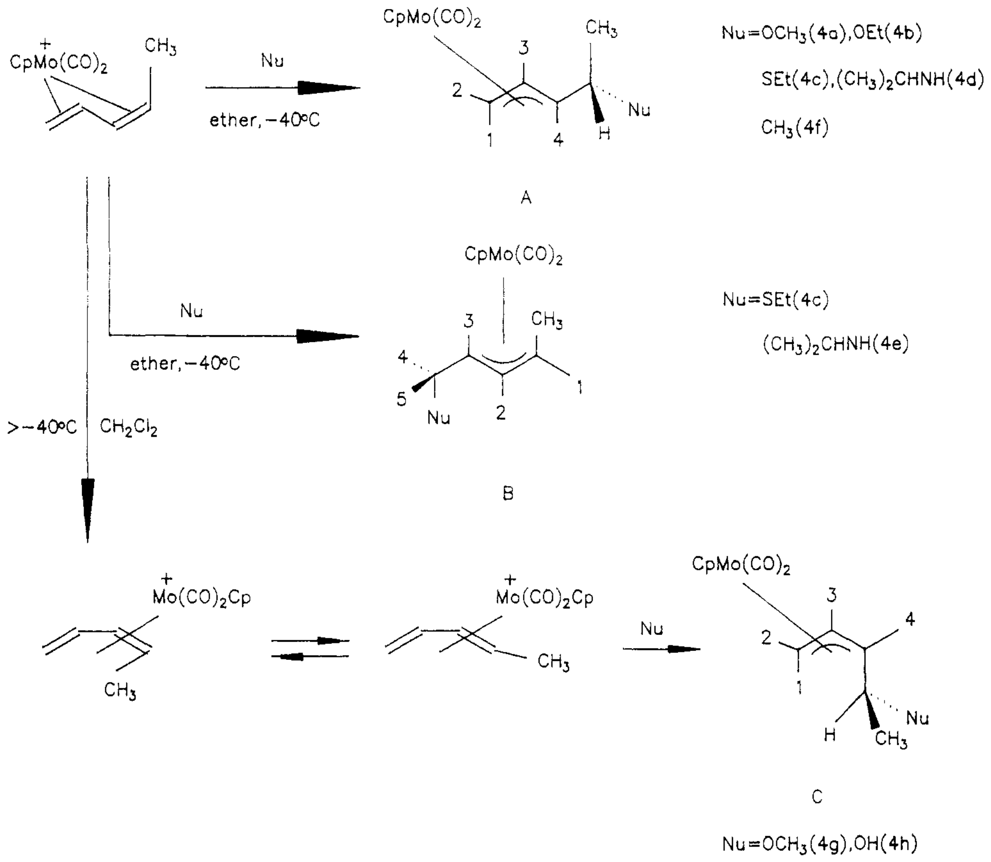
Scheme I



Scheme II



(CO)$_2$ unit. The ligand conformation of **1** has been clarified by an X-ray diffraction study,[6] which shows a sickle shape for the allyl and ketone carbon atoms as depicted in Scheme I.

Treatment of **2** with 1 equiv of $(CF_3SO_2)_2O$ at −45 °C in ether results in the stereoselective formation of the *s-trans*-η^4-*cis*-pentadiene complex **3** as a precipitate.[7,8]

Table I. Product Analysis of the Reaction between 3 and Nucleophiles

Nu (product)	product yield, % A	product yield, % B
H_2O (**2**)	75	
CH_3OH (**4a**)	67	
C_2H_5OH (**4b**)	59	
C_2H_5SH (**4c**)	34	24
$(CH_3)_2CHNH_2$ (**4d**)	57	
$[(CH_3)_2CH]_2NH$ (**4e**)		42
CH_3Li (**4f**)	49	

This *s-trans*-η^4-diene cation **3** is stable in the solid state at ambient temperatures. Attempts to characterize the *s-trans*-diene cation by NMR spectroscopy[9] at −40 °C in

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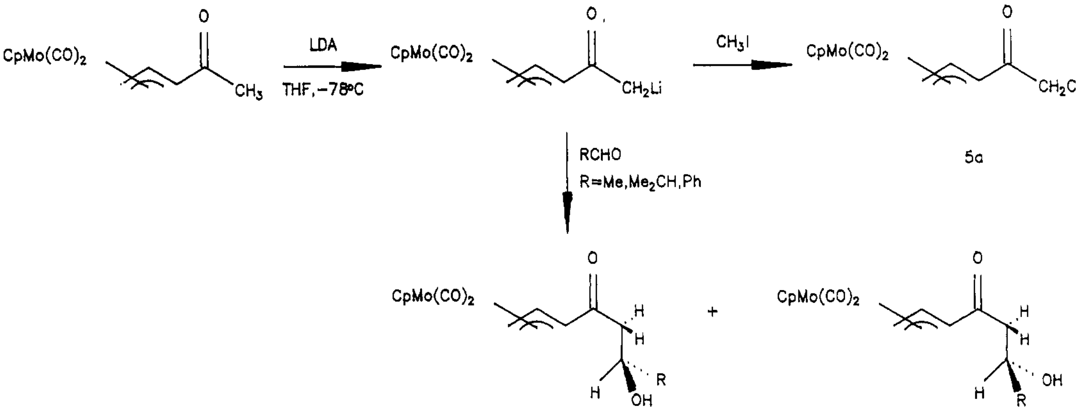
[6] Pale yellow crystals of **1** were grown from solution in ether solvent by cooling to −20 °C. The crystals belong to the triclinic system, space group $P\bar{1}$, with a = 7.0395 (1) Å, b = 7.891 (3) Å, c = 11.716 (8) Å, α = 98.67 (4)°, β = 92.50 (4)°, γ = 112.93 (3)°, V = 588.8 (5) Å^3, and Z = 2. Diffraction data were collected on a Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. A total of 2259 reflections were collected; of the 2076 unique reflections, 2006 were considered observed, having $I > 2\sigma(I)$. The position of the Mo atom was taken from a Patterson map. The remainder of the non-hydrogen atoms were located in difference Fourier maps; final R = 0.024 and R_W = 0.029.

[7] η^4-*s-trans*-Diene structures are only known for neutral complexes.[8] Recently, Green and co-workers reported the *s-trans*-η^4-diene cation $(C_5Me_5)Mo(CO)_2$(*s-trans*-η^4-*trans*-pentadiene); see: Benyunes, S. A.; Green M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268.

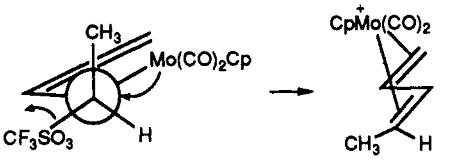
[8] (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6433. (b) Nakamura, A.; Yasuda, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (c) Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791.

Scheme III



CD_2Cl_2 encountered difficulties because of its facile rearrangement to the more stable *s-cis*-η^4-pentadiene cation. The solid form of the *s-trans*-diene cation in ether at −40 °C shows a remarkable reactivity toward diverse nucleophiles including H_2O, alcohols, amines, thiols, and alkyllithium. Analyses of the products (**4a–f**) resulting from the reaction enabled clarification of the cationic structure. The results are summarized in Table I. The nucleophiles may add at the α- or δ-carbons of the *s-trans*-diene cation. The regioselectivity depends heavily on the steric size of the entering group. Small nucleophiles such as H_2O, CH_3OH, C_2H_5OH, $(CH_3)_2CHNH_2$, and CH_3Li yield only type A products, whereas for $[(CH_3)_2CH]_2NH$ only type B is obtained. For C_2H_5SH, additions at both the α- and δ-carbons are possible and the two products (A + B) are separable by column chromatography. Type A complexes are assumed to have the same configuration, *RR*(*SS*), as **2** since hydrolysis of the *s-trans*-η^4-*cis*-pentadiene complex (**3**) regenerates **2**. This implies a trans-addition model during the nucleophilic attack. For complexes B, the anti methyl group is indicated by the coupling constant J_{12} = 7.0 Hz as well as a relatively upfield resonance (δ 1.00 ppm) in the exo isomer.[2b,5] The structures of A and B provide direct evidence for the formulation of **3** as the *s-trans*-η^4-*cis*-pentadiene cation. The more stable *s-cis*-η^4-pentadiene complex is expected to yield products other than A and B.[2b] We have examined its reaction with H_2O and CH_3OH at −40 °C. On the basis of spectroscopic data, compound C is produced in high yield and has the $CH(Nu)CH_3$ group in the anti position as indicated by the coupling constant J_{34} = 7.0 Hz.

It is instructive to consider the mechanism of formation of the *s-trans*-diene derived from **2**. Nucleophilic substitution with retention precludes the formation of a free carbocation at the α-carbon (*C*HCH_3). The Fisher projection represents the key conformation of the intermediate, which has CF_3SO_3 lying trans to the $CpMo(CO)_2$ unit. Apparently, the ionization process follows an intramolecular S_N2 mechanism. Thus, $CpMo(CO)_2$ acts as a base to displace the $CF_3SO_3^-$ anion from the opposite face of the C_4 unit and stabilizes the cation as it forms. This mechanism is essentially equivalent to those previously established for derivatives of ferrocene[5] and (butadiene)iron tricarbonyl[10] complexes.



Formation of the enolate anion $CpMo(CO)_2(syn\text{-}\eta^3\text{-}\underline{CH_2CHCH}COCH_2Li)$ is accomplished through deprotonation of **1** by lithium diisopropylamide in THF at −78 °C. This enolate reacts with 1 equiv of CH_3I to form $CpMo(CO)_2(syn\text{-}\eta^3\text{-}\underline{CH_2CHCH}COC_2H_5)$ (**5a**) in high yield. Reaction of this anion with 1 equiv of PCHO gives $CpMo(CO)_2(syn\text{-}\eta^3\text{-}\underline{CH_2CHCH}COCH_2CH(OH)R)$ (R = Ph (**5b**), CH_3 (**5c**), $(CH_3)_2CH$ (**5d**)) as two diastereoisomers in good yield. The two diastereoisomers are distinguishable by using the low-field proton resonances of the C*H*CO and C*H*R(OH) hydrogens. The ratio of the two diastereoisomers is 53:47 for R = $(CH_3)_2CH$, 89:11 for R = Ph, and 71:29 for R = CH_3. Good diastereoselectivity is observed in the phenyl case, and after fractional crystallization, **5b** can be obtained as a single diastereoisomer in 53% yield.

In summary, we have shown that functionalization of **1** proceeds in a highly stereospecific and regioselective manner. Since $CpMo(CO)_2$(allyl) has been recognized as a versatile complex in organic synthesis, use of $CpMo(CO)_2(syn\text{-}\eta^3\text{-}C_3H_4R)$ as a chiral auxiliary in acyclic systems deserves further attention.

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Supplementary Material Available: An ORTEP drawing, tables of bond distances and angles, crystal data, atomic coordinates, and thermal parameters for **1**, and a description of the elemental analyses and spectroscopic data for the compounds **1**, **2**, **4a–f**, and **5a–d** (10 pages); a table of structure factors for **1** (7 pages). Ordering information is given on any current masthead page.

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[9] **3a** freshly dissolved in CD_2Cl_2 exhibited a ill-defined broad ^1H NMR spectrum at −60 °C but at −40 °C exhibited a well-resolved spectrum assignable to an *s-cis*-η^4-pentadiene that contained both *anti*- and *syn*-methyl isomers. The four isomers were averaged to one isomer in a mechanism in which both exo–endo isomerization and butadiene-flipping processes are operative.[2b]

[10] For the related chemistry of $Fe(\eta^4\text{-butadiene})(CO)_3$, see the review paper: Gree, R. *Synthesis* **1989**, 341.