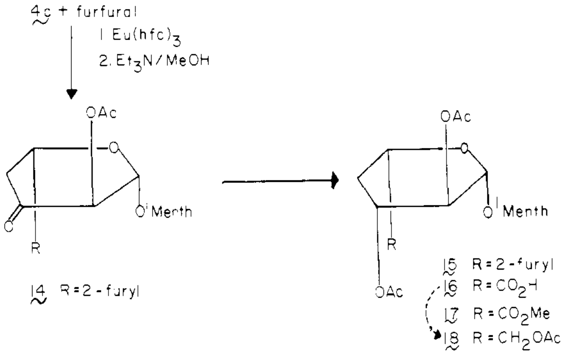
The data are provided in Scheme II. *Here, a clear interactivity of the two chiral elements is manifested. Indeed, the modest intrinsic "D-pyranose" selectivity of the l-menthyloxy auxiliary is expressed as a strong "L-pyranose" preference by intereaction with the chiral catalyst.* Thus, the increase in facial selectivity is not simply another instance of double diastereoselection,[7] in which two isolated complementary steric biases provide a mutual reinforcement. Our results involve a phenomenon[8b] wherein the inherent facial bias of the chiral auxiliary is inverted upon interaction with the chiral catalyst.

It had been recognized[8c] that, in principle, there can be interactivity between various stereo-biasing elements. Given such interactivity, overall stereodifferentiation[8c] may be quite different from the arithmetic sum of its isolated elements. The particularly novel dimension of our finding is that the interactivity is maximal when the individual biases are of *opposite* sense.

The factors that underlie this striking interactivity remain to be sorted out. Conceivably, if the basis for the phenomenon could be understood, even more discriminating combinations might be identified. However, it already seems likely that the phenomenon can play a valuable role in many kinds of synthetic objectives. We illustrate the shape of future events by the synthesis of optically pure **18** which is a β-4-deoxy-L-glucoside of *l*-menthol.

Cyclocondensation of *l*-menthyloxy diene **4c** with furfural, mediated by $Eu(hfc)_3$ in the usual way, affords a cycloadduct which was worked up with triethylamine–methanol[3a,9] (axial protonation), providing a 75% yield of the optically pure ketone **14**:[10] mp 126–127 °C; $[\alpha]^{23}_{D}$ + 65.2° (*c* 1.3, $CHCl_3$). Reduction of this ketone with K-selectride[11] (Aldrich) followed by acetylation provides, in 77% yield, the diacetate **15**:[10] mp 127–129 °C; $[\alpha]^{23}_{D}$ −5.3° (*c* 0.8, $CHCl_3$). Ozonolysis of the furan **15** afforded the 4-deoxyglucuronic acid derivative **16**, best characterized as its methyl ester **17**:[10] mp 143–145 °C; $[\alpha]^{23}_{D}$ −32.0 (*c* 0.6, $CHCl_3$). Reduction of **16** with borane–THF followed by acetylation afforded a 75% yield (from **15**) of **18**:[10] mp 103–105 °C; $[\alpha]^{23}_{D}$ −26.6 (*c* 0.7, $CHCl_3$).



Thus, the chiral auxiliary–chiral catalyst combination can be used to synthesize optically pure saccharides, including L-*glycosides, without recourse to formal resolution or glycosylation.*[13] Clearly this approach to rare and important sugars holds out considerable promise and is, accordingly, receiving close attention in our laboratory.

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Supplementary Material Available: Characterizations and spectral data for compounds **13b**, **13c**, **13d**, **14**, **15**, **17**, and **18** (1 page). Ordering information is given on any current masthead page.

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[9] NMR analysis indicates an 87:13 ratio of **14** and its D-pyranose facial isomer. Compound **14** is obtained as a homogeneous entity by chromatography and crystallization.

[10] The structure of this compound is supported by spectral data which are provided as supplementary material.

[11] NMR analysis indicates the presence of ca. 9% of axial alcohol in the K-Selectride (Aldrich) reduction.

[12] For the use of a 2-furyl group as a latent carboxylic acid, see: Schmid, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 259.

[13] For the application of the thermal hetero Diels-Alder reaction to the synthesis of a disaccharide without glycosylation, see: David, S.; Lubineau, A.; Vitale, J. M. *Nouv. J. Chim.* **1980**, *4*, 547 and references therein.

Double Oxidative Addition of β or γ Methyl Groups of Coordinated Fischer-Type Carbenes on a Triruthenium Cluster. Synthesis of $Ru_3[(\mu\text{-}H)_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)](CO)_9$ and $Ru_3[(\mu\text{-}H)_2,\eta^2,\mu_3\text{-}C(OEt)N(Me)C(H)](CO)_9$

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Recent isolation of the Fischer-carbene cluster complex $Os_3[\eta^1\text{-}C(OMe)Me](\mu\text{-}H,\mu\text{-}O{=}CMe)(CO)_9$,[1] led us to investigate the synthesis of a triruthenium analogue; we isolate instead the two title complexes as summarized in Scheme I.

Titration of $Ru_3[\mu\text{-}H,\mu\text{-}O{=}C(CH_3)](CO)_{10}$ (**1**)[2] with $LiCH_3$ (1.6 N in diethyl ether) in dry, freshly distilled diethyl ether at −30 °C leads to its instantaneous conversion to the anion $[Ru_3[\eta^1\text{-}C(O)CH_3][\mu\text{-}H,\mu\text{-}O{=}C(CH_3)](CO)_9]^-$ (**2a**).[3] The resulting solution is warmed to room temperature and treated with 2 equiv of $C_2H_5OSO_2CF_3$.[4] IR spectra show no initial change, and 48 h of stirring is required to see the complete disappearance of the absorptions of **2a**. The solvent is removed at this point and the solid residue extracted with 30 mL of pentane. Crystallization by evaporation of the orange-red pentane extract gives orange crystals of $Ru_3[(\mu\text{-}H)_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)](CO)_9$ (**3**) in 80% yield. This is summarized in the sequence **1**–**2a**–A–**3** in Scheme I. The molecular weight of **3** is determined by mass spectroscopy and its structure deduced from spectroscopic evidence.[5] Compound **3** is a heteroatom-substituted homologue of ethyne complexes earlier observed in the reaction of acetylenes[6] or olefins[7] with $Ru_3(CO)_{12}$. The coordinated C_2 fragment in **3** shows ^{13}C resonances at 78 and 218 ppm (with respect to tetramethylsilane); ^{13}C–H coupling of 159 Hz is observed on the 78-ppm resonance

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[1] Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982**, *104*, 4679–4680.

[2] Boag, N. M.; Kampe, C. E.; Lin, Y. C.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1706–1708.

[3] For [Li][**2a**]: (a) IR ν_{CO} (cm^{-1}) (Et_2O) 2075 m, 2033 s, 2008 s, 1999 vs, 1968 m, 1932 m, 1571 w (η^1-acyl group), ($CHCl_3$) 1424 (μ-acyl). (b) ^1H NMR (obtained as are all other ^1H NMR reported here at 89.55 MHz) in $CDCl_3$ (ppm relative to Me_4Si) 2.70(s, 3) ($\mu\text{-}Co{=}C(CH_3)$, 2.41 (s, 3) $\eta^1\text{-}C(O)C\mathit{H}_3$, 14.46 (s, 1) Ru–*H*–Ru. (c) $\{^1H\}^{13}C$ NMR (obtained as are all other ^{13}C NMR reported here at 22.29 MHz) in $CDCl_3$ with $Cr(acac)_3$, (ppm relative to Me_4Si) 266.3 ($\mu\text{-}O{=}\mathit{C}CH_3$), 249.1 ($\eta^1\text{-}O{=}\mathit{C}CH_3$), 202.0, 198.4, 190.9, 189.1 (CO, fluxional), 47.5 ($\mu\text{-}O{=}C\mathit{C}H_3$), 41.0 ($\eta^1\text{-}O{=}C\mathit{C}H_3$).

[4] Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 173–180.

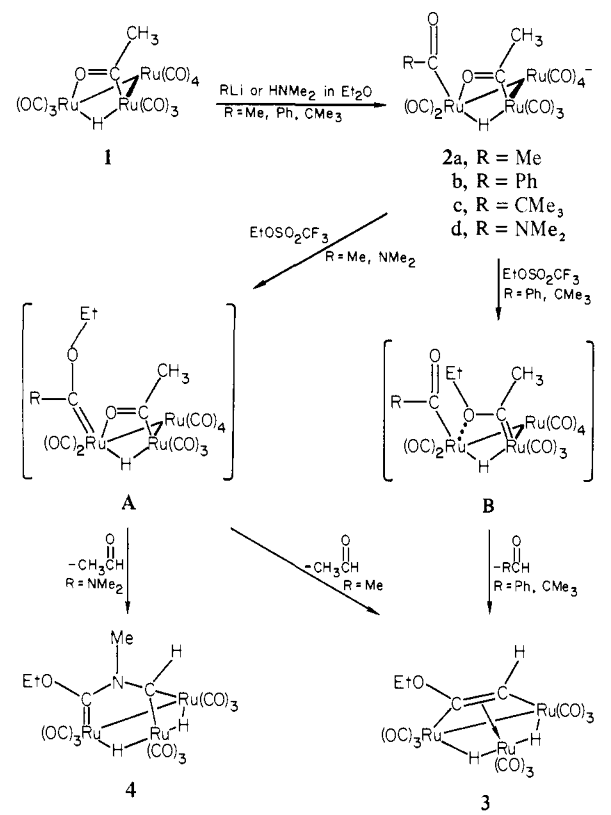
[5] For **3**. (a) IR (petroleum ether) ν_{CO} (cm^{-1}) 2108 (w), 2080 (s), 2056 (vs), 2040 (s), 2034 (w), 2018 (m), 2013 (w), 2008 (m), 1995 (w), 1988 (vw). (b) ^1H NMR (C_6D_6, ppm relative to Me_4Si) 5.75 (s, 1, CH=), 3.49 (q, 2, $OC\mathit{H}_2CH_3$), 1.03 (t, 3, $OCH_2C\mathit{H}_3$), −17.98 (s, 2, equilibrating Ru–H–Ru). (c) ^{13}C NMR with $Cr(acac)_3$ $\{^1H\}^{13}C$ (C_6D_6, ppm relative to Me_4Si) 218 ($={\mathit{C}}(OEt)$), 197.0, 192.6, 190.6 (CO, fluxional), 74.2 ((CH)=), 67.0 ($O\mathit{C}H_2CH_3$), 14.2 ($OCH_2\mathit{C}H_3$); off-resonance decoupled 218.0 (s), 197.0 (s), 192.6 (s), 190.6 (s), 74.2 (d), 67.0 (t), 14.2 (q); −90 °C (CD_2Cl_2, carbonyl region only) 200.9, 199.4, 196.7, 193.9, 191.2, 190.6, 189.3, 187.4, 185.6. (d) Mass spectrum, parent ion *m/e* 627 (^{101}Ru) followed by nine multiplets spaced 28 mass units apart and a large *m/e* 72 peak ($[EtOCH{=}CH_2{}^+]$). No higher mass signals are observed.

[6] Cetini, G.; Gambino, O.; Sappa, E.; Valle, M. *J. Organomet. Chem.* **1969**, *17*, 437–443.

[7] (a) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415–1419. (b) For a recent review of other cluster complexes of these and related fragments, see: Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.*, in press.

0002-7863/83/1505-6969$01.50/0

Scheme I



of a regiospecifically ^{13}C-labeled derivative, as described below. We thus assign the 1,2-ethyne(1-(OEt),2-H) structure to the C_2 fragment in **3** rather than an isomeric 1,1′-vinylidene(2-(OEt),2′-H) form.[7a] The acetaldehyde that accompanies formation of **3** is identified by GC-MS. The yield is separately determined to be essentially quantitative.[8]

In order to trace the origins of the μ-alkoxyalkenylene group and of the μ-H atoms in **3** we used $LiCD_3$[9] in the first step of Scheme I. This gives rise to acetaldehyde containing *no* label[8] and the trinuclear product **3**-d_3: $Ru_3[(\mu\text{-}D)_2,\eta^2,\mu_3\text{-}C(OEt){=}C(D)](CO)_9$. Conversely, titrating $Ru_3[\mu\text{-}H,\mu\text{-}C(O)CD_3](CO)_{10}$ (**2**-d_3) with $LiCH_3$ in the first step of Scheme I leads to formation of $CD_3C(O)H$[28] and *no* deuterium incorporation into the triruthenium product. This specificity denotes that there is no exchange between η^1- and μ-acyl groups in the intermediate anion **2a**. Furthermore no acetaldehyde-d_4 nor mixed hydride–deuteride of **3** is obtained. These results indicate that loss of the μ-acyl group and the bridging hydrogen as acetaldehyde must precede oxidative addition of the methyl C–H bonds of the carbene group in the alkylated cluster complex.

Two further labeling studies were performed. By using $Li^{13}CH_3$[9] in the first step of Scheme I, trinuclear product shows specifically enhanced intensity of its 74 ppm ^{13}C resonance ($J^{13}C\text{–}H$) = 159 Hz): $Ru_3[(\mu\text{-}H)_2,\eta^2,\mu_3\text{-}C(OEt){=}{}^{13}C(H)](CO)_9$. The other resonance of the C_2 group at 218 ppm in **3** is replaced by a doublet ($J(^{13}C\text{–}^{13}C)$ = 124 Hz) confirming the C–C bonded nature of the C_2 group. The $^{13}C\text{–}^{13}C$ and $^{13}C\text{–}^{1}H$ coupling constants ($J(^{1}H\text{–}^{13}C)$ = 159 Hz observed in the ^1H NMR) indicate sp^2 hybridization of *C*OEt. In a second study we employed unlabeled $LiCH_3$ with $Ru_3[\mu\text{-}H,\mu\text{-}O{=}C(^{13}CH_3)](CO)_{10}$ in the first step of Scheme I. Trinuclear product **3** shows *no* ^{13}C incorporation. These experiments confirm that it is the acyl group of the starting complex that is lost as aldehyde in the formation of **3**.

The reaction of **1** with two other organolithium reagents was investigated. With LiPh or $LiCMe_3$ followed by alkylation with $C_2H_5OSO_2CF_3$ we obtain **3** as product along with the corresponding aldehyde RC(O)H.[8] This result must derive from alkylation at oxygen of the *bridging* acyl group as indicated in proposed intermediate B in Scheme I. This is paralleled by the protonation of a μ-acyl group in $Cp_2Zr(\eta^2\text{-}O{=}CMe)Mo(CO)_3Cp$[10a] and O-alkylation at the triply bridging acyl group in $[Fe_3(\mu_3\text{-}O{=}CCH_3)(CO)_9^-]$,[10b] denoting a significant contribution from an oxycarbene resonance form of such a group. In the case of the *tert*-butyl derivative, **2c**, it is steric hindrance that directs alkylation to the oxygen of the bridging acyl group. Similar direction of alkylation occurs in the case of the phenyl derivative **2b** due to deactivation of the oxygen atom in the phenacyl group.

When $HNMe_2$ is used in the first step of Scheme I and is followed by alkylation as indicated, deep orange crystals of **4** are isolated.[11] Thus as represented both by **3** or **4** we observed double-oxidative addition of a methyl group occasioned by the loss of a four-electron donor on the metal cluster complex. Both these processes occur at 25 °C. We are aware of several precedents for such double oxidative addition all of which occur at temperatures of 110 °C or higher.[12-14] We thus demonstrate the low-temperature occurrence of such double oxidative addition which was masked in the earlier studies by the higher temperatures required to achieve coordinative unsaturation on the metal. Our work may also provide clues to the extensive transformation reported by E. O. Fischer and co-workers[15] in isolation of the complex $Ru_3[\mu\text{-}H,\mu,\eta^3\text{-}C(Ph)C_6H_4](CO)_9$ from the reaction of $Ru_3(CO)_{12}$ with LiPh. In these connections we also call attention to the dehydrogenation of triethylamine by $Os_3(CO)_{10}(NCCH_3)_2$ leading to $HOs_3(\mu\text{-}^-CHCH{=}^+NEt_2)(CO)_{10}$ in refluxing benzene.[16] Studies in progress indicate that the oxidative additions in our system are *prevented* under an atmosphere of CO: the coordinately unsaturated intermediate(s) formed in the loss of aldehyde can obviously be intercepted defining a limit on the rate of the internal oxidative additions observed here.

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Supplementary Material Available: Additional experimental details and spectroscopic data (7 pages). Ordering information is given on any current masthead page.

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(8) GC/MS (KRATOS MS-25) and Hewlett-Packard 5880A GC were employed for identification and quantification of the aldehydes, see supplementary material for details.

(9) $LiCD_3$ and $Li^{13}CH_3$ are prepared from CD_3I (Aldrich) and $^{13}CH_3I$ (Merck Sharp and Dome) by treatment with equimolar *n*-butyllithium in hexane, cf.: McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 1057–1061.

(10) (a) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209–210. (b) Wong, W.-K.; Chiu, K. W.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1557–1563.

(11) for **4**: (a) IR (petroleum ether) ν_{CO} (cm^{-1}) 2109 (w), 2082 (s), 2058 (vs), 2037 (s), 2021 (m), 2008 (s), 1995 (w). (b) ^1H NMR (C_6D_6, ppm relative to Me_4Si) 6.98 (s, 1, C(H), 4.42 (q, 2, OCH_2CH_3), 3.02 (s, 3, NCH_3), 1.18 (t, 3, OCH_2CH[3), −14.97 (s, 2, equilibrating Ru–H–Ru). (c) ^{13}C NMR with $Cr(acac)_3$ $\{^1H\}^{13}C$ (C_6D_6, ppm relative to Me_4Si) 252.3 (EtO)*C*N), 196.4, 191.6 (CO, fluxional), 64.7 (CH_3CH_2O), 39.9 (CHN), 37.2 ($N(CH_3)$)), 14.1 ($OCH2C_3$); off-resonance decoupled 252.3 (s), 196.4 (s), 191.6 (s), 66.7 (t), 42.0 (d) 38.2 (q), 14.1 (q).

(12) Trinuclear reaction intermediates containing double oxidatively added groups are postulated in the H/D exchange in amines catalyzed by $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ at 150 °C: Laine, R. M.; Thomas, D. W.; Cary, L. W.; Buttrill *J. Am. Chem. Soc.* **1978**, *100*, 6527–6528.

(13) $Os_3(\mu\text{-}H)_3[\mu_3\text{-}C(H)](CO)_9$ obtained in thermolysis of the following: (a) $Os_3[\mu\text{-}H,\mu\text{-}O{=}C(CH_3)](CO)_9$ or $Os_3[\mu\text{-}H,\mu\text{-}O(CH{=}CH_2)](CO)_9$ at 150 °C Deeming, A. J.; Azam, K. A. *J. Mol. Catal.* **1977**, *3*, 207–213). (b) $Os_3[\mu\text{-}H,\mu\text{-}CH_3](CO)_{10}$ at 100 °C (Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225–5226).

(14) $Os_3[(\mu\text{-}H)_2,\eta^2,\mu_3\text{-}C(R)P(R')_2](CO)_9$ obtained in the thermolysis at 150 °C of $Os_3(CO)_{11}P(R')_3$: Deeming, A. J.; Underhill, M. *J. Chem. Soc. Dalton Trans.* **1973**, 2727–2730.

(15) Parkins, A. W.; Fischer, E. O.; Huttner, G.; Regler, D. *Angew. Chem.* **1970**, *82*, 635.

(16) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewycz, R. A. *J. Organomet. Chem.* **1978**, *162*, C39–C42.