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A Simple Route to Chiral Carbohydrate-Cyclopentadienyl and -Indenyl Ligands.

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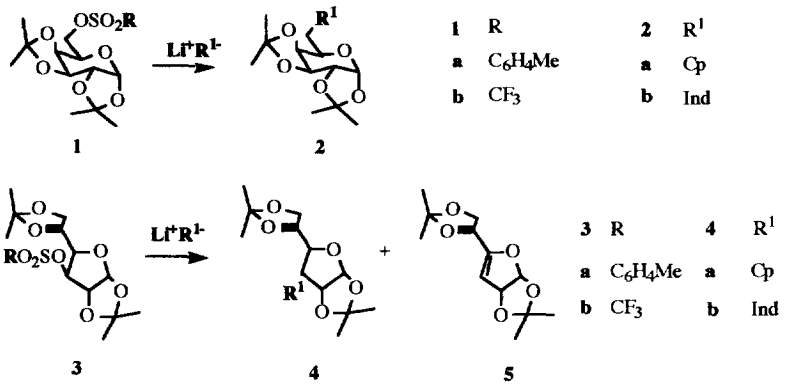
Abstract: Trifluoromethanesulfonates derived from acetal protected α-D-galactopyranose **1c** and α-D-glucofuranose **3c** react with cyclopentadienyl and indenyl lithium to give optically active carbohydrate-substituted cyclopentadienes **2a** and **4a** and indenes **2b** and **4b** in good to moderate yields; because of the double bonds tautomerism of the cyclopentadiene unit **2a** and **4a** have been characterised as their cyclopentadienyl molybdenum complexes **6** and **7** and the X-ray structure of **7** is reported. Copyright © 1996 Elsevier Science Ltd

There is a great deal of interest in the synthesis of optically active cyclopentadienyl transition metal complexes in which chirality originates from substituents attached to the cyclopentadienyl moiety (cyclopentadienyl-derived chirality)[1] and their application in asymmetric synthesis. In this context, the chiral pool is an important and attractive source of optically active ligands for synthetic chemists[2] and, indeed, some chiral cyclopentadienyl complexes have been derived from natural molecules. However, although enantiomerically pure complexes derived from carbohydrates have been reported and used as chiral auxiliaries in asymmetric reactions,[2-6] there is no mention of cyclopentadienyl-derived sugar complexes used as chiral auxiliaries. Only one report concerns the preparation of cyclopentadienyl C-glycosides as latent fulvenes. These compounds arise from attack of cyclopentadienyl anion on mannitol and ribitol derivatives to give epimeric cyclopentadienyl C-glycosides.[7]

We thought it could be of interest to obtain enantiomerically pure carbohydrate-derived cyclopentadienyl ligands by direct substitution of the alcohol functions of partially protected inexpensive sugars. Accordingly, we tried the nucleophilic displacement by cyclopentadienyl anion of primary or secondary sugar sulfonate esters of acetal protected α-D-galactopyranose **1** or α-D-glucofuranose **3** (Scheme 1).

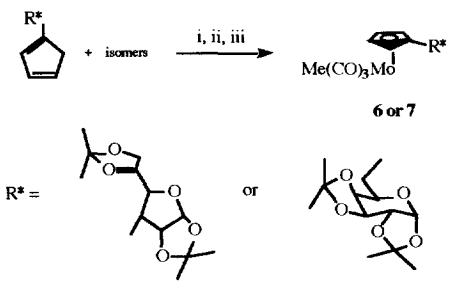
As expected from the literature,[8] primary and secondary sulfonate such as tosylate or mesylate derivatives of carbohydrates are not easily displaced by nucleophilic reagents. Indeed, when either **1a** or **3a** were treated in THF at reflux with CpLi, the starting sulfonate esters were recovered unchanged. After 15 hrs in boiling DMF, **1a** led to the cyclopentadiene derivative **2a** isolated as a mixture of isomers in 25% yield after purification on a silica gel column. In the same conditions, **3a** afforded **4a** (10%) and the elimination product **5** as shown by ^{1}H NMR analysis.[9] However, in boiling DMF, the triflate derivatives [10]**1b** and **3b** afforded **2a** and **4a** in 34% and 20%, respectively, after chromatographic purification. However, although reaction conditions were by no means optimized, we observed that an improvement of the reaction is achieved by performing the reaction at low temperature since at -15°C the yield of purified **2a** and **4a** reaches 55 and 52% .

Scheme 1



Furthermore, thin layer chromatography of the crude reaction mixture showed, after hydrolysis, that **1b** and **3b** had totally disappeared in less than 30 min.Although the substitution reaction of **1b** and **3b** is not possible in THF as the solvent, interestingly, for **1b** only, in THF at 25°C, in the presence of TMEDA (tetramethyethylenediamine) or DMF, **2a** is obtained in 32 and 72% yield, respectively. Since the ^{1}H NMR spectrum of **2a** or **4a** gives no reasonable structural information due to the double-bound tautomerism of the cyclopentadiene unit, the ligands were then characterised by ^{1}H and ^{13}C NMR spectroscopy after transformation into the corresponding molybdenum complexes, **6**[11] (30% yield) and **7**[11](50% yield) as shown on Scheme 2.

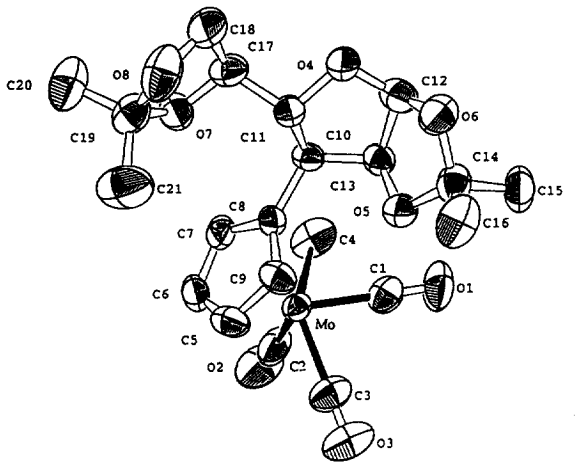
Scheme 2



i, BuLi, hexane, 0°C; ii, $Mo(CO)_6$, THF, 12h, reflux; iii, MeI, 1h, reflux.

The structure of **7** was additionally established by X-ray structural analysis (Fig. 1).[12]

Figure 1. Crystal structure of **7**.



Selected bond lengths (Å) :

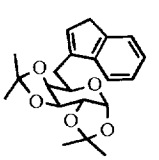
Mo-C(4)	2.339(8)
Mo-C(1)	1.977(5)
Mo-C(2)	1.986(7)
Mo-C(3)	2.022(5)
C(5)-C(6)	1.405(8)
C(6)-C(7)	1.405(8)
C(7)-C(8)	1.437(7)
C(8)-C(9)	1.422(8)
C(8)-C(10)	1.511(7)
C(1)-O(1)	1.153(6)
C(2)-O(2)	1.134(9)
C(3)-O(3)	1.093(7)

Selected bond angles(°) :

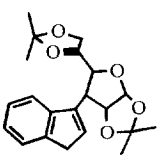
Mo-C(1)-O(1)	178.4(5)
Mo-C(2)-O(2)	176.1(5)
Mo-C(3)-O(3)	178.1(8)

$C_{21}H_{26}O_8Mo$. M = 502.38. Monoclinic, $P2_1$. a = 8.298(1); b = 8.712(2); c = 15.871(1)Å. β = 103.25(1)°. R = 0.029 and R_ω = 0.040.

Both **1b** and **3b** react with indenyl lithium to give **2b** and **4b**, in 65 % and 25% yield, respectively, after purification on a silica gel column. In contrast with the cyclopentadienes derivatives, **2b** and **4b** are obtained as single isomers, as unambiguously established by their ^1H and ^{13}C NMR spectra.[11]



2b



4b

Complexes **6** and **7** here reported as examples will be used as chiral auxiliaries as well as complexes with other transition metals of the optically active cyclopentadienes and indenes described in this paper.

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11. *Selected data: for* **2b:** $[\alpha]_D$ -71.8 (c 0.19, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.35 (3H, s, CH_3), 1.38 (3H, s, CH_3),1.53 (6H, s, CH_3), 2.92 (2H, dd, *J* 6.6, 1.6 Hz, $CH_2C_9H_7$), 3.37 (2H, d, *J* 1.63 Hz, =CH-CH_2), 4.23 (2H, m, H-5 and H-4),4.33 (1H, dd, *J* 2.3, 5.1 Hz, H-2), 4.61 (1H, dd, *J* 2.34, 7.75 Hz, H-3), 5.62 (1H, d, *J* 5.1 Hz, H-1), 6.5 (1H, m, =C*H*-CH_2), 7.3 (4H, m, Ar H). ^{13}C {^1H} NMR (50 MHz, $CDCl_3$) δ 24.6 (CH_3), 25.0 (CH_3), 26.0 (CH_3), 26.2 (CH_3), 28.6 ($CH_2C_9H_7$), 38.1 (C=CH-CH_2), 66.3 (C-4), 70.6 (C-2), 71.0 (C-3), 72.6 (C-5), 96.9 (C-1), 108.6 (CH_3-*C*), 109.2 (CH_3-*C*),119.0, 123.7, 124.6, 126.1 (C arom H), 129.9 (C=*C*H-CH_2), 140.4 (*C*=CH-CH_2), 144.3, 145.5 (Cq arom). **4b:** $[\alpha]_D$ +141.2 (c 0.12, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.30 (6H, s, CH_3), 1.36 (3H, s, CH_3), 1.57 (3H, s,CH_3), 3.16 (1H, qd, *J* 4.68, 10.51, 1Hz, H-3), 3.43 (2H, s, C=CH-CH_2), [3.89 (1H, dd, *J* 7.1, 8.1 Hz), 3.96 (1H, dd, *J* 6.5, 8.1 Hz) AB type spectrum OCH_2], 4.30 (1H, td, *J* 3.42, 6.67, 6.86 Hz, H-5), 4.65 (1H, dd, *J* 3.41, 10.6 Hz, H-4), 4.85 (1H,t, *J* 4.35 Hz, H-2), 5.99 (1H, d, *J* 3.64 Hz, H-1), 6.49 (1H, br s, =C*H*-CH_2), 7.36 (4H, m, Ar H). ^{13}C {^1H} NMR (50 MHz, $CDCl_3$) δ 25.4 (CH_3), 26.3 (CH_3), 26.5 (CH_3), 26.8 (CH_3), 38.4 (CH_2-CH=), 44.9 (C-3), 65.2 (CH_2-O), 76.3 (C-5), 80.0 (C-4), 81.1 (C-2), 105.3 (C-1), 109.6 (CH_3-*C*), 112.1 (CH_3-*C*), 118.7 (C arom H), 124.1 (C arom H), 125.0 (C arom H), 126.2 (C arom H), 132.4 (C=*C*H-CH_2), 137.0 (*C*=CH-CH_2), 144.0, 144.8 (Cq arom). **6**: $[\alpha]_D$ -79.7 (c 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.29(3H, s, CH_3Mo), 1.31 (3H, s, CH_3), 1.33 (3H, s, CH_3),1.44 (3H, s, CH_3), 1.51 (3H, s, CH_3), [2.43 (1H, dd, *J* 4.5, 15.4 Hz), 2.64 (1H, dd, *J* 8.8, 15.4 Hz) AB type spectrum $CH_2C_5H_4$], 3.8 (1H, ddd, *J* 1.8, 4.5, 6.9 Hz, H-5), 4.11 (1H, dd, *J* 1.8, 7.9 Hz, H-4), 4.29 (1H, dd, *J* 2.3, 5.1 Hz, H-2), 4.58 (1H, dd, *J* 2.3, 7.9 Hz, H-3), 5.11 (1H, m, Cp), 5.15 (1H, m, Cp), 5.21 (1H, m, Cp), 5.39 (1H, m, Cp), 5.51 (1H, d, *J* 5.1 Hz, H-1). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ -18.8 (Mo-CH_3), 24.6 (CH_3), 24.9 (CH_3), 26.1 (2 CH_3-C), 29.0 (CH_2-Cp), 67.9 (C-5), 70.4 (C-2), 71.0 (C-3), 72.4 (C-4), 89.4, 90.8, 92.2, 94.8 (CH, Cp), 96.77 (C-1), 108.6 (CH_3-*C*), 109.4 (CH_3-*C*), 112.1 (Cq Cp), 227.0, 227.2, 240.3 (CO).
7: $[\alpha]_D$ +143.7 (c 0.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.4 (3H, s, CH_3-Mo), 1.27 (3H, s, CH_3), 1.29 (3H, s,CH_3), 1.33 (3H, s, CH_3), 1.56 (3H, s, CH_3), 2.73 (1H, dd, *J* 4.1, 10.0 Hz, H-3), [3.70 (1H, dd, *J* 5.4, 8.5 Hz), 3.96 (1H, dd,*J* 6.9, 8.5 Hz) AB type spectrum OCH_2], 4.01 (1H, dd, *J* 5.6, 10.0 Hz, H-4), 4.15 (1H, q, *J* 5.5, 5.6, 6.5 Hz, H-5), 4.57 (1H, t, *J* 3.8 Hz, H-2), 5.19 (2H, t, *J* 2.3 Hz, Cp), 5.22 (1H, q, *J* 2.1 Hz, Cp), 5.55 (1H, q, *J* 2.1 Hz, Cp), 5.72 (1H, d, *J* 3.4 Hz, H-1). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ -21.2 (CH_3-Mo), 25.0 (CH_3-C), 26.0 (CH_3), 26.5 (CH_3), 26.9 (CH_3-C), 46.1(C-3), 66.4 (CH_2O), 76.7 (C-5), 82.6 (C-4), 85.1 (C-2), 90.5, 95.25, 95.3, 95.4 (CH, Cp), 104.4 (C-1), 106.7 (CH_3-*C*),109.7 (CH_3-*C*), 112.6 (Cq, Cp), 226.8, 227.3, 240.6 (CO).
12. Coordinates have been deposited at the Cambridge Crystallographic Data Centre

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