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All manipulations involving chromium complexes were carried out under an inert atmosphere of dinitrogen using standard Schlenk line techniques. Commercial solutions of MeLi, nBuLi and PhLi were used as obtained. Vinyllithium was freshly prepared from tetravinyltin and MeLi in THF at -78°C, and used after subsequent removal of the THF *in vacuo*, and redissolution in toluene. Propargyl bromide was obtained from Fluka and vacuum distilled from P_2O_5 prior to use. (*S,S*)-1,2-dimethoxycyclopentane was prepared as detailed below. The chromium complexes were prepared by literature procedure.[1]

Experiment for (*S,S*)-1,2-dimethoxycyclopentane

In a 50 ml round-bottomed flask fitted with a condenser was placed NaH (0.53 g, 22 mmol, prewashed with pentane) and diethylether (10 ml), and the flask was cooled to 0°C. Then *trans*-(*S,S*)-1,2-cyclopentanediol (1.02 g, 10 mmol) was added dropwise with efficient stirring and cooling maintained. When the exothermic reaction had finished dimethylsulfate (3.64 ml, 20 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 5 hours. Purification can be achieved by distillation (135°C or 45°C at 15 mmHg) yielding 0.975 g (7.49 mmol, 75%) of the product.

^{1}H -NMR ($CDCl_3$, 298 K): 1.50-1.60 (m, 2H), 1.60-1.70 (m, 2H), 1.85-1.95 (m, 2H), 3.34 (s, 6H), 3.62-3.67 (m, 2H)

IR ($CHCl_3$): 3022s, 2938m, 2897m, 1456w, 1452w, 1370w, 1104s, 909s.

MS (m/z) 130 (15%), 98 (100%), 83 (15%)

High resolution MS: $C_7H_{14}O_2$; calc. 130.0994; found 130.0992

$[\alpha]_D^{20}$ ($CHCl_3$, c = 1.65): (+) 23

Two representative examples of a sequential nucleophile/electrophile addition in the presence of a chiral ligand are given below.

Nucleophile/Electrophile Addition Reaction Using an External Chiral Ligand with (phenyloxazoline)chromium tricarbonyl (1).

Experiment for alkyllithium and propargylbromide in the presence of (R,R)-2,3-Dimethoxybutane (4)

To a yellow toluene solution (10 ml) of complex **1** (1 mmol) and ligand **4** (2 equiv.) at -78°C was added dropwise a solution of RLi (1.1 equiv.). The mixture was maintained at this temperature for 4 hours with efficient stirring resulting in a color change to dark orange. At this point was added HMPA (10 equiv.) and propargyl bromide (6 equiv.) and the solution was then allowed to warm to ambient temperature overnight. Removal of all volatiles gave a dark brown oily residue which was extracted with Et_2O (3 x 10 ml) to give a lemon yellow solution, which was exposed to sunlight (~ 4 hours) until colorless and filtered over silica to remove the HMPA. After evaporation of the solvent *in vacuo*, the crude product was purified by column chromatography (hexane:ether, 5:1).

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Nucleophile/Electrophile Addition Reaction Using an External Chiral Ligand with (benzylidenecyclohexylamine)chromium tricarbonyl (7).

Experiment for alkyllithium and trimethylsilylpropargylbromide in the presence of (*S,S*)-1,2-Dimethoxy-1,2-diphenylethane (4)

To a yellow toluene solution (10 ml) of complex **7** (1 mmol) and ligand **6** (2 equiv.) at -78°C was added dropwise a solution of RLi (1.1 equiv.). The mixture was maintained at this temperature for 4 hours with efficient stirring resulting in a color change to orange. At this point was added HMPA (10 equiv.) and trimethylsilylpropargyl bromide (3 equiv.) and the solution was then allowed to warm to ambient temperature overnight. Removal of all volatiles gave a dark brown oily residue which was extracted with Et_2O 3 x 10 ml) to give a lemon yellow solution, which was exposed to sunlight (~ 4 hours) until colorless and filtered over silica to remove the HMPA. After evaporation of the solvent *in vacuo*, the crude product was hydrolyzed to the aldehyde by stirring in diethylether (10 ml) over silica (1 g and 0.1 ml H_2O was added) and then purified by column chromatography (hexane:ether, 5:1).

***trans*-6-phenyl-5-(3-trimethylsilanyl-prop-2-ynyl)-cyclohaxa-1,3-diene-carbaldehyde (8a)**

Nucleophile: Phenyllithium

Electrophile: trimethylsilylpropargyl bromide

^{1}H -NMR ($CDCl_3$, 298 K): 0.17 (s, 9H, $SiMe_3$), 2.24 (dd, 1H, J = 8.4, 16.7 Hz), 2.38 (dd, 1H, J = 6.4, 16.75 Hz), 2.72 (m, 1H), 4.11 (s, 1H, CH-Ph), 6.3 (m, 2H), 6.97 (dd, 1H, J = 1.2, 5.1 Hz), 7.1-7.3 (m, 5H, H arom), 9.55 (s, 1H, CHO).

^{13}C -NMR ($CDCl_3$, 298 K): 0.1 ($SiMe_3$), 25.1 (CH_2), 38.9 (CH), 41.9 (CH), 87.1 (alkyne C), 103.9 (alkyne C), 123.3 (CH arom), 126.9 (CH arom), 127.1 (CH arom), 128.6 (vinyl CH), 138.1 (C arom), 138.2 (vinyl CH), 141.0 (vinyl CH), 141.9 (vinyl<u>C</u>-CHO), 192.6 (<u>C</u>HO).

IR ($CHCl_3$): 3009w, 2961w, 2819w, 2719w, 2172m, 1676s, 1572m, 1492w, 1453w, 1405w, 1324w, 1251m, 1174m, 1034w, 845s.

MS (EI). 294 (M^+, 3%), 203 (26%)

HRMS: $C_{19}H_{22}OSi$; calc. 294.144, found, 294.145.

HPLC: Chiralcel OD, hexane/*i*-PrOH = 250/1, 1ml/min, retention time (5*R*,6*R*)-(-)-**8a**: 13.2 min (3.5%); (5*S*,6*S*)-(+)-**8a**: 15.2 min (96.5%).

***trans*-6-vinyl-5-(3-trimethylsilanyl-prop-2-ynyl)-cyclohaxa-1,3-diene-carbaldehyde (8b)**

Nucleophile: Vinyllithium

Electrophile: Trimethylsilylpropargyl bromide

^{1}H -NMR ($CDCl_3$, 298 K): 0.14 (s, 9H, $SiMe_3$), 2.14 (dd, 1H, J = 7.72, 16.55 Hz), 2.27 (dd, 1H, J = 7.35, 16.55 Hz), 2.60 (unresolved ddd, 1H, J = 7.72, 7.35, 5.89 Hz), 3.51 (d, 1H J = 6.99 Hz), 4.97 (m, 1H, J = 10.29, 1.47, 1.10 Hz), 5.05 (m, 1H, J = 17.28, 1.47, 1.10 Hz), 6.24 (dd, 1H, J = 5.15, 9.56 Hz), 6.32 (dd, 1H, J = 5.89, 9.56 Hz), 6.80 (dd, 1H, J = 0.74, 5.15 Hz), 9.54 (s, 1H, CHO).

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^{13}C -NMR ($CDCl_3$, 298 K): 0.04 ($SiMe_3$), 23.7 (CH_2), 37.2 (CH), 38.3 (CH), 86.6 (alkyne C), 104.0 (alkyne C), 115.0 (vinyl CH_2), 123.2 (vinyl CH), 136.5 (vinyl CH), 137.3 (vinyl C-CHO), 138.3 (vinyl CH), 140.7 (vinyl CH), 192.4 (CHO).

IR ($CHCl_3$): 3019w, 2961w, 2901w, 2818w, 2725w, 2172m, 1673s, 1570m, 1408w, 1320w, 1251m, 1175m, 1040w, 1020w, 988w, 921w, 845s.

MS (EI). 244 (M^+, 6%), 229 (5%), 203 (12%).

HRMS: $C_{15}H_{20}OSi$; calc. 244.128, found, 244.127.

GC: Lipodex E, 120 °C, carrier gas: H_2 (50 kPa), (5*R*,6*S*)-(-)-**8b**: 12.5 %; (5*S*,6*R*)-(+)-**8b**: 87.5 %.

trans-6-methy-5-(3-trimethylsilanyl-prop-2-ynyl)-cyclohaxa-1,3-diene-carbaldehyde (8c)

Nucleophile: Methyllithium

Electrophile: Trimethylsilylpropargyl bromide

^{1}H-NMR ($CDCl_3$, 298 K): 0.14 (s, 9H, $SiMe_3$), 0.99 (d, 3H, J = 7.36 Hz, Me), 2.10 (dd, 1H, J = 7.35, 16.55 Hz), 2.21 (dd, 1H, J = 7.35, 16.55 Hz), 2.39 (m, 1H), 2.88 (q, 1H, J = 7.36 Hz), 6.23 (dd, 1H, J = 5.15, 9.56 Hz), 6.31 (dd, 1H, J = 5.89, 9.56 Hz), 6.69 (dd, 1H, J = 0.74, 5.15 Hz), 9.49 (s, 1H, CHO).

^{13}C-NMR ($CDCl_3$, 298 K): 0.05 ($SiMe_3$), 18.45 (Me), 24.14 (CH_2), 28.55 (CH), 40.20 (CH), 86.18 (alkyne C), 104.41 (alkyne C), 122.72 (vinyl CH), 138.14 (vinyl CH), 139.79 (vinyl CH), 141.42 (vinylC-CHO), 192.80 (CHO).

IR ($CHCl_3$): 3025w, 3007w, 2962m, 2819w, 2724w, 2171m, 1667s, 1566m, 1452w, 1406w, 1326w,1249m, 1181m, 1030w, 974w, 909m, 844s.

MS (EI). 232 (M^+, 12%), 203 (22%).

GC: Lipodex E, 120 °C, carrier gas: H_2 (50 kPa), retention time (5*R*,6*S*)-(-)-**8c**: 15.5 min (4.5 %); (5*S*,6*R*)-(+)-**8c**: 16.1 min (95.5 %).

References and Notes

1. Kündig, E. P.; Ripa, A.; Liu, R.; Amurrio, D.; Bernardinelli, G. *Organometallics* **1993**, *12*, 3724.