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[Lewis Acid]$^{+}$[Co(CO)$_4$]$^{-}$ Complexes: A Versatile Class of Catalysts for Carbonylative Ring Expansion of Epoxides and Aziridines**

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General Considerations. All reactions and manipulations with air- and/or water-sensitive compounds were carried out under dry nitrogen using a drybox or standard Schlenk line techniques. NMR spectra were recorded on a Bruker AF-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometer, and referenced versus shifts of solvents containing residual protic impurities. Tetrahydrofuran, toluene, benzene, triglyme, 1,2-dimethoxyethane and hexanes were distilled from sodium/benzophenone under nitrogen. Methylene chloride was distilled from CaH_2 under nitrogen. [$Cp_2Ti(CO)_2$], [$Co_2(CO)_8$] and [Cp_2Co] were purchased from Strem Chemicals Inc. Propylene oxide (Aldrich), isobutylene oxide (Aldrich), 1,2-epoxybutane (Aldrich), 1,2-epoxy-5-hexene (Lancaster), epichlorohydrin (Aldrich) and, *cis- / trans*-2,3-epoxybutanes (Aldrich, Lancaster) were purchased and distilled over CaH_2 under nitrogen atmosphere. (*R*)-Propylene oxide was resolved from its racemic counterpart using Jacobsen's procedure in >98% ee.[1] [$NaCo(CO)_4$],[2] [PPh_4][$Co(CO)_4$],[3] [Cp_2Co][$Co(CO)_4$],[4] [$Cp_2Ti(THF)_2$][$Co(CO)_4$],[5] [(salph)$Al(THF)_2$][$Co(CO)_4$],[6] and cis-1-benzyl-2-(*tert*-butyldimethylsilyloxy)methyl-3-methyl-aziridine[8] were prepared according to literature procedures. 4-Methyl-1-benzyl-2-azetidinone,[7, 8] 4-methyl-1-tosyl-2-azetidinone,[9] *trans*-(7-

benzyl-7-azabicyclo[4.2.0.]octane-8-one),[10] *cis*-1-benzyl-4-(*tert*-butyldimethylsilyloxymethyl)-3-methyl azetidinone,[8] and *cis*-1-benzyl-3-(*tert*-butyldimethylsilyloxymethyl)-4-methyl azetidinone[8] were identified based on literature data.

2-Methyl-1-tosyl-aziridine. 2-Methylaziridine (3.6 ml, 51 mmol) was added to a 10% aqueous KOH solution (30 ml) and cooled in an ice bath for 30 min. To this solution p-toluenesulfonyl chloride (9.9 g, 52 mmol) was added rapidly while maintaining the temperature below 4 •C. The resulting mixture was stirred for 30 min at 0 •C, then stirred at room temperature overnight. The white precipitate was washed multiple times with cold water and dried under vacuum. The washed product was dissolved in hot petroleum ether and allowed to crystallize at 0 •C, yielding colorless crystals (6.3 g, 57 % yield).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (3H, d, *J* = 6.0), 2.02 (1H, d, *J* = 4.5 Hz), 2.44 (3H, s), 2.58 (1H, d, *J* = 6.9 Hz), 2.82 (1H, m), 7.31 (2H, d, *J* = 8.1 Hz), 7.80 (2H, d, *J* = 8.1 Hz).[11]

Synthesis of 7-benzyl-7-azabicyclo[4.1.0]heptane.

a) Synthesis of 2-Benzylamino-cyclohexanol. To a solution of cyclohexene oxide (5 g, 51 mmol) in 10 ml CH_3CN, anhydrous $LiClO_4$ (5.44 g, 51 mmol) was added and stirred until complete dissolution of the salt. The resulting solution was treated with the required amount of benzylamine (5.5 g, 51 mmol) at room temperature with stirring. The reaction mixture was then stirred for 24 h at room temperature. At the end of the reaction, 100 ml

water was added and the solution stirred for 30 min, extracted into diethyl ether (3 x 25) and finally crystallized from hot hexanes. (5.0 g, 50 % yield).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.93-1.10 (1H, m), 1.18-1.33 (4H, m), 1.71 (2H, m), 2.05 (1H, m), 2.15 (1H, m), 2.31 (1H, m), 3.20 (1H, m), 3.35 (1H, br), 3.68 (1H, d, *J* = 12.9 Hz), 3.95 (1H, d, *J* = 13.0 Hz), 7.23-7.35 (5H, m).[12]

b) Cyclization of 2-Benzylamino-cyclohexanol. Diethyl azodicarboxylate (Aldrich, 95 %, 3.6 ml, 22.6 mmol) was slowly added to a THF solution (50 ml) of 2-benzylamino-cyclohexanol (3.1 g, 15 mmol) and PPh_3 (5.94 g, 22.6 mmol) under N_2, with stirring, in an ice-bath. After addition, the ice bath was removed, and the mixture stirred at room temperature for 36 h. The resulting crystalline precipitate was filtered and the solvent removed from the filtrate by rotary evaporation to yield the crude product, which was purified by column chromatography (petroleum ether:diethyl ether = 95:5) (2.1 g, 75 % yield).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (4H, m), 1.63 (2H, m), 1.83 (4H, m), 3.48 (2H, s), 7.31 (5H, m).[8]

General procedure for the catalytic carbonylation of epoxides. A 100 ml Parr reactor was heated at 90 °C overnight, under vacuum. In a dry-box, the reactor equipped with a test-tube and magnetic stir bar were cooled in a –35 °C freezer for at least 2 h. The test-tube was charged with pre-cooled (-35 •C) epoxides or aziridines (1.92 mmol), catalyst (0.096 mmol) and 0.5 mL DME. Upon removal from a dry-box the reactor was pressured

with carbon monoxide (Matheson, Research Grade) and heated with stirring for the amount of time indicated, such that the final pressure of CO was ~900 psi. After the reaction time, the reactor was cooled in a bath of dry ice/acetone until the pressure reached a minimum and then slowly vented. The resulting reaction mixture was analyzed by ^{1}H NMR.

Identification of the regiochemistry of the lactone products derived from *cis*- and *trans*-2,3-epoxybutanes.

Trans-2,3-epoxybutane was subjected to 900 psi CO at 60°C for 10 hours in the presence of 5 mol % catalyst **1**, which yielded lactone **A**. *Cis*-2,3-epoxybutane under similar conditions gave lactone **B**.

Lactone **A** was distilled under vacuum after the removal of DME. The distillate was placed in a small, thick walled Pyrex tube equipped with an air-free valve and a 24/40 joint. This flask was frozen in liquid nitrogen, evacuated and heated to 175°C in an oil bath. After two hours the flask was cooled in an ice-bath and the volatiles transferred to a pre-cooled (liquid N_2) NMR tube charged with $CDCl_3$. ^{13}C NMR spectra showed exclusively *cis*-2-butene. Lactone **A** was thus identified as *cis*-3,4-dimethyloxetan-2-one. Similarly, **B** was identified as *trans*-3,4-dimethyloxetan-2-one.

***Cis*-3,4-dimethyloxetan-2-one** (**Lactone A**): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (3H, d, *J* = 7.5 Hz), 1.44 (3H, d, *J* = 6.6 Hz), 3.74 (1H,

m), 4.75 (1H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 8.24, 15.45, 47.45, 71.90, 172.76.

***Trans*-3,4-dimethyloxetan-2-one (Lactone B):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.39 (3H, d, *J* = 7.5 Hz), 1.55 (3H, d, *J* = 6.6 Hz), 3.22 (1H, m), 4.35 (1H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.53, 20.20, 52.38, 76.34, 172.10.

***Cis*-2-butene:** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.65 (6H, m), 5.45 (2H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.35, 124.70.

***Trans*-2-butene:** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.65 (6H, m), 5.45 (2H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.05, 126.05.

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