

Oxygen-Containing 10-, 15-, and 20-Membered Macrocyclic Cobalt Complexes from $\text{Co}_2(\text{CO})_6$ -Bispropargylic Alcohol

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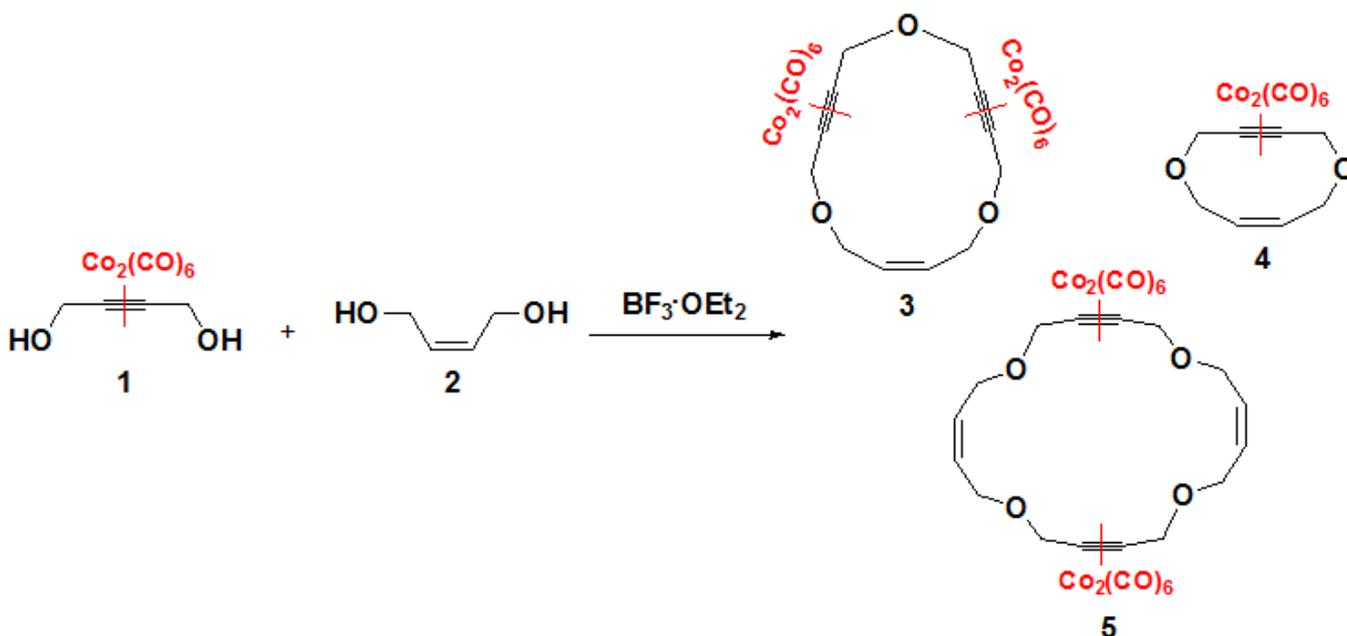
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Abstract: Novel 10-, 15-, and 20-membered oxygen-containing macrocyclic cobalt complexes (**3**, **4**, and **5** respectively) were obtained in moderate combined yield via double nucleophilic substitution of the hexacarbonyldicobalt-coordinated monoynone diol [$\{\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})\}$] (**1**) upon $\text{BF}_3\cdot\text{OEt}_2$ treatment in the presence of (*Z*)-2-butene-1,4-diol (**2**) at room temperature. The products distribution was found to be highly concentration dependent.

Keywords: Nicholas reaction, cobalt, alkyne complexes, macrocycles

The Nicholas reaction is a powerful and versatile synthetic tool in organic synthesis. It basically consists in the nucleophilic attack on a $\text{Co}_2(\text{CO})_6$ -propargylic cation, which is generated by adding either protic acids or Lewis acids, mainly trifluoromethane sulfonic acid, $\text{HBF}_4\cdot\text{OEt}_2$ and $\text{BF}_3\cdot\text{OEt}_2$ on $\text{Co}_2(\text{CO})_6$ -propargylic alcohols. The reaction works well with a variety of nucleophiles to form new bonds between the propargylic carbon and atoms that include carbon, oxygen, hydrogen and nitrogen. The procedure can be applied inter- or intra-molecularly in solution or in solid phase [1].



The treatment of the hexacarbonyldicobalt-coordinated monoynone diol [$\{\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})\}$] (**1**) [**2**] with two equivalents of $\text{BF}_3\cdot\text{OEt}_2$ and one equivalent of (*Z*)-2-buten-1,4-diol (**2**) at room temperature under diluted conditions afforded a mixture of the macrocycles **3**, **4**, and **5** in 62% combined yield. The ratio of the isolated macrocycles was found to be highly dependent on the concentration conditions. Thus, under 0.01M dilution, **4** was

obtained as the major product (see Experimental Section), whereas **5** was the major one under higher molar concentration (0.02M). The oxygen-containing macrocycles [**3**] were separated by silica gel column chromatography and their molecular weights confirmed by mass spectroscopy [**4**].

Experimental Section

General

^1H and ^{13}C NMR spectra were recorded at 25 °C on Bruker Avance-300 spectrometer in CDCl_3 as solvent, and chemical shifts are reported relative to Me_4Si . Low- and high-resolution mass spectra were obtained by using a Micromass Autospec spectrometer. Elemental analysis was performed on a Fisons Instrument EA 1108 CHNS-O analyzer. Infrared spectra were recorded on a Bruker IFS 55 spectrophotometer on compounds dispersed on a CaF_2 disc (20×2 mm). Column chromatographies were performed on Merck silica gel, 60 Å and 0.2–0.5 mm. Methylene chloride was dried by distillation over calcium hydride prior to use. All reagents were commercially available and used without further purification. Hexacarbonyldicobalt-coordinated monoyne diol [$\{\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})\}$] (**1**) was prepared as reported in the literature [**2**].

Synthesis of cobalt-complexed oxygen-containing macrocyclics **3–5**:

To a stirred solution of [$\{\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})\}$] (**1**) (200 mg, 0.54 mmol) in CH_2Cl_2 (54 mL, 0.01M) were consecutively added (*Z*)-2-butene-1,4-diol (**2**) (45 mL, 0.54 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (137 mL, 1.08 mmol) under an argon atmosphere at room temperature. The reaction mixture was monitored by TLC. The mixture was poured with vigorous stirring into a saturated solution of NaHCO_3 at 0 °C for 15 min and extracted with CH_2Cl_2 . The combined organic phases were washed with brine, dried (MgSO_4), concentrated, and the products separated by silica gel column chromatography. Macrocyclics **3**, **4**, and **5** were isolated as red oils in a ratio 1:10:4 respectively and 62% combined yield. Interestingly, under more concentrated conditions (0.02M) the ratio of the macrocyclics was found to be 1:3:8 respectively. It is worth to mention that traces of other cobalt complexes were also formed along with the isolated macrocyclics, although these minor products could not be isolated and characterized in the preliminary studies.

8,13-Bis-(hexacarbonyldicobalt)- μ_2 - $\{\eta^2$ -1,6,11-trioxa-cyclopentadec-3-ene-8,13-diyne $\}$ (**3**):

^1H NMR (300 MHz, CDCl_3) δ = 4.28 (m, 4H), 4.71 (s, 4H), 4.95 (s, 4H), 5.76 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ = 66.6 (t), 71.0 (t), 130.6 (d), 199.2 (s); IR (thin film) ν (cm^{-1}) 2093, 2053, 2022; FAB-MS m/z (relative intensity) 779 ($\text{M}+1$) $^+$ (8), 778 (M) $^+$ (30), 722 ($\text{M}-2\text{CO}$) $^+$ (12), 694 ($\text{M}-3\text{CO}$) $^+$ (10), 638 ($\text{M}-5\text{CO}$) $^+$ (13), 610 ($\text{M}-6\text{CO}$) $^+$ (17), 553 (100). HMRS calcd for $\text{C}_{24}\text{H}_{14}\text{Co}_4\text{O}_{15}$ ($\text{M}-1$) $^+$ 777.76606, found 777.76680.

3-Hexacarbonyldicobalt- μ_2 - $\{\eta^2$ -3,4-didehydro-2,5,7,10-tetrahydro-1,6-dioxecino $\}$ (**4**):

^1H NMR (300 MHz, CDCl_3) δ = 4.23 (m, 4H), 4.71 (s, 4H), 5.76 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ = 66.5 (t), 70.6 (t), 129.3 (d), 194.3 (s); IR (thin film) ν (cm^{-1}) 2094, 2054, 2022; FAB-MS m/z (relative intensity) 425 ($\text{M}+1$) $^+$ (22), 424 ($\text{M}-1$) $^+$ (18), 396 ($\text{M}-\text{CO}$) $^+$ (22), 368 ($\text{M}-2\text{CO}$) $^+$ (38), 365 (100), 340 ($\text{M}-3\text{CO}$) $^+$ (16), 312 ($\text{M}-4\text{CO}$) $^+$ (29). HMRS calcd for $\text{C}_{14}\text{H}_9\text{Co}_2\text{O}_8$ ($\text{M}-1$) $^+$ 422.89614, found 444.89578.

8,18-Bis-(hexacarbonyldicobalt)- μ_2 - $\{\eta^2$ -1,6,11,16-tetraoxa-cycloicosa-3,13-diene-8,18-diyne $\}$ (**5**):

^1H NMR (300 MHz, CDCl_3) δ = 4.45 (m, 8H), 4.88 (s, 8H), 5.86 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ = 66.6 (t), 71.0 (t), 130.6 (d); IR (thin film) ν (cm^{-1}) 2060, 2032, 2012; FAB-MS m/z (relative intensity) 849 ($\text{M}+1$) $^+$ (26), 848 (M) $^+$ (21), 820 ($\text{M}-\text{CO}$) $^+$ (20), 764 ($\text{M}-3\text{CO}$) $^+$ (33), 736 ($\text{M}-4\text{CO}$) $^+$ (30), 708 ($\text{M}-5\text{CO}$) $^+$ (29), 680 ($\text{M}-6\text{CO}$) $^+$ (21), 652 ($\text{M}-7\text{CO}$) $^+$ (21), 624 ($\text{M}-8\text{CO}$) $^+$ (26), 602 (100), 596 ($\text{M}-9\text{CO}$) $^+$ (20). Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{Co}_4\text{O}_{16}$: C, 39.65; H, 2.38. Found: C, 39.86; H, 2.51.

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