Synthesis, NMR, and X-ray Molecular Structure of a Unique Chiral Propeller-Like Cobalt Complex $[(Co_2(CO)_4)\mu,\eta^2,\eta^2\text{-}(-H_2CC{\equiv}CCH_2-)(-dppm)_2][BF_4]_2$ and Differentiation of Its Enantiomers by the Trisphat Anion

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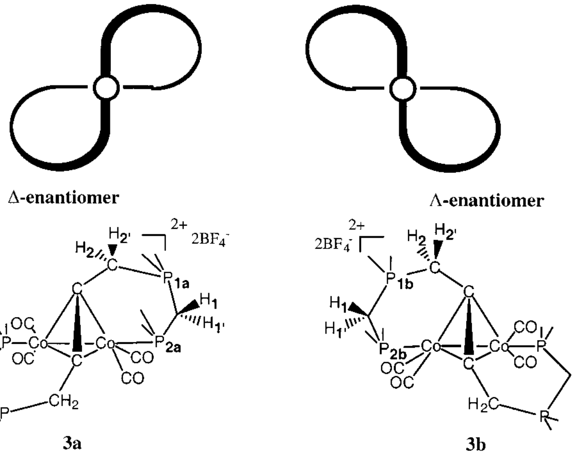
*Summary: The unusual chiral two-bladed propeller cobalt complex $[(Co_2(CO)_4)\mu,\eta^2,\eta^2\text{-}(-H_2CC{\equiv}CCH_2-)(-dppm)_2][BF_4]_2$ (**3**) has been prepared and its X-ray structure determined. Addition of the trisphat anion to a CD_2Cl_2 solution of **3** has led to the NMR nonequivalency of the two enantiomers **3a,b**. This is the first example in which a chiral propeller transition metal complex with C_2-symmetry has been differentiated by the trisphat anion.*



3a **3b**

Figure 1. Schematic representation of the two enantiomers **3a,b** of the chiral two-bladed propeller cobalt complex.

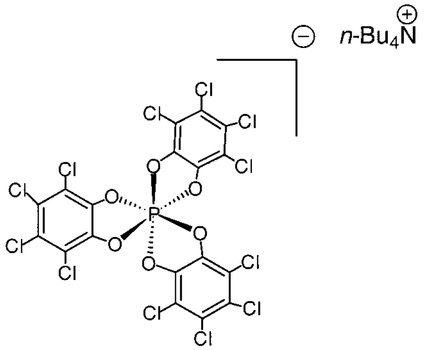


Figure 2. $[n\text{-}Bu_4N][\Delta\text{-trisphat}]$.

Chirality is a very old and ever fascinating topic.[1] Controlling the chirality at carbon centers is one of the most developed and central fields of organic chemistry, especially in the synthesis of natural products where several adjacent carbon atoms should have a predetermined chirality.[2] Other examples of chiral molecules lack a stereocenter, and among the more fascinating of these are those with spiral, propeller, and helical shapes. These helices or propellers will spiral either clockwise "Δ" or counterclockwise "Λ" depending on the direction of the twist; thus, the absolute configurations of **3a** and **3b** are, respectively, "Δ" and "Λ" (Figure 1). Predetermination of chirality at carbon centers is a well-developed area especially in asymmetric synthesis; however, less is known about predetermination of chirality at metal centers in coordination compounds.[3] In this paper, we report the synthesis of a rare chiral propeller-like cobalt complex $[(Co_2(CO)_4)\mu,\eta^2,\eta^2\text{-}(-H_2CC{\equiv}CCH_2-)(-dppm)_2][BF_4]_2$ (**3**) obtained as a racemic mixture from stepwise addition of dppm to a tetrahedral alkyne−dicobalt carbonyl complex. Complex **3** was completely characterized, and its X-ray molecular structure was determined. Addition to complex **3** of the optically pure Δ-trisphat-tetrabutylammonium (**1**) [trisphat = tris[tetrachlorobenzene-1,2-bis(olato)]phosphate] (Figure 2) as an NMR chiral reagent, discovered by Lacour,[4] allows the magnetic nonequivalency of the two enantiomers (**3a,b**) by formation of diastereomeric ion pairs. This was beautifully illustrated by ^1H and ^{31}P NMR analysis (vide infra).

Pursuing our research program in the area of cobalt−alkyne chemistry,[5a] we have prepared the known masked dicarbenium ion complex $[(Co_2(CO)_6)\mu,\eta^2,\eta^2\text{-}(Me_2S{-}CH_2C{\equiv}CCH_2{-}SMe_2)][BF_4]_2$[5e] (**2**). The structure of com-

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[1] von Zelewsky, A. *Stereochemistry of Coordination Compounds*; Wiley: Chichester, 1996; and references cited therein.

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plex **2** was also confirmed by X-ray study. Complex **2** crystallizes in the monoclinic space group $P2_1$/n.[6] A view of the cationic part of **2** with selected bond distances and angles is given in the Supporting Information. The structure shows that the Co_2C_2 core of $[(Co_2(CO)_6)\mu,\eta^2,\eta^2$-$(Me_2S-H_2CC{\equiv}CCH_2-SMe_2)]^{2+}$ adopts a tetrahedral geometry with C2−C3 attached to both metal centers. The Co1−Co2 distance is 2.4574(6) Å, typical of a Co−Co single bond.[7] Moreover, the C2−C3 distance, 1.349(4) Å, is lengthened owing to the loss of its triple bond character after complexation.

Treatment of the complex $[(Co_2(CO)_6)\mu,\eta^2,\eta^2$-$(Me_2S-H_2CC{\equiv}CCH_2-SMe_2)][BF_4]_2$ (**2**) with 2 equiv of dppm in CH_2Cl_2 gave the target cobalt complex $[(Co_2(CO)_4)\mu,\eta^2,\eta^2$-$(-H_2CC{\equiv}CCH_2-)(-dppm)_2][BF_4]_2$ (**3**) in 60% yield. This compound was identified by spectroscopic and microanalytical data. [8] The ^{31}P NMR spectrum of **3** recorded in CD_2Cl_2 exhibited two signals at δ 31.46 ppm attributed to P_1 ($P-CH_2$) appearing as a complex multiplet[9] and a broad signal at δ 43.51 ppm (Figure 3) attributed to the other phosphine unit P_2 coordinated to the metal center (P−Co); each corresponds to one phosphorus atom by integration. The ^1H NMR spectrum of **3** displayed a complex pattern. Hence ,^{31}P and ^1H decoupling experiments were carried out and allowed us to attribute the signal of the methylene groups of the alkyne unit and the dppm ligand, which appeared as two AB systems at $\delta_{H2'}$ 3.21, δ_{H2} 4.43 ppm and $\delta_{H1'}$ 3.57, δ_{H1} 3.90 ppm, respectively; the diastereotopic nature of the methylene protons confirmed that complex **3** is chiral. The chiral nature of complex **3** originates from its propeller-like structure. Further, the solid-state structure of **3**, determined by a single-crystal X-ray diffraction study, is consistent with its assigned solution structure. Suitable red crystals of **3** were grown from CH_2Cl_2/hexane solution. A CAMERON view of the $[(Co_2(CO)_4)\mu,\eta^2,\eta^2$-$(-H_2CC{\equiv}CCH_2-)(-dppm)_2]^{2+}$ cation of compound **3** together with selected bond distances and angles is shown in Figure 4. Complex **3** crystallizes in the monoclinic $P2_1/n$ space group.[10]

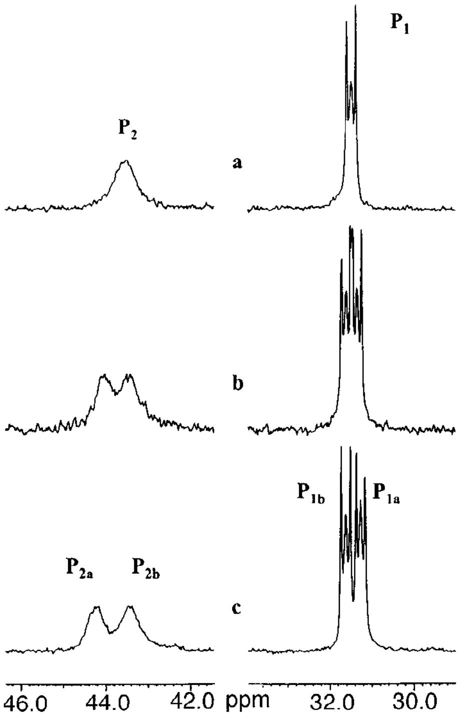

Figure 3. ^{31}P NMR spectra of racemic **3a,b** in the absence (a) and presence of Δ-trisphat (**1**) [0.6 equiv (b), 1.2 equiv (c)].

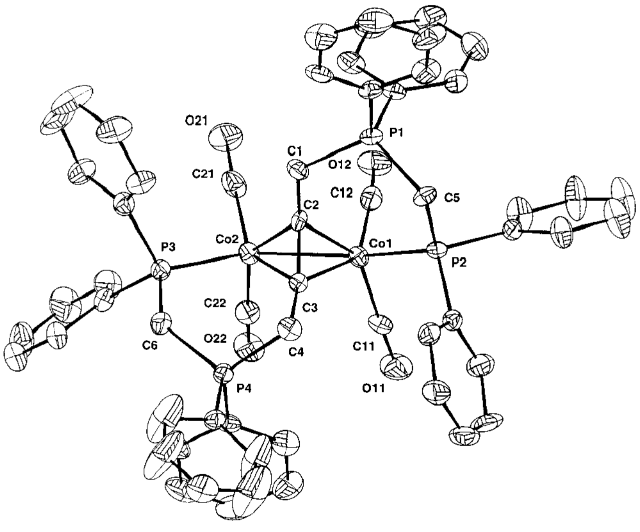

Figure 4. X-ray molecular structure of the cationic part of complex **3** with atom-numbering system. CAMERON view shows thermal ellipsoids at 30% probability, without hydrogens for clarity. Selected bond distances (Å) and angles (deg): Co1−Co2 = 2.447(2), Co1−C2 = 1.971(9), Co1−C3 = 1.941(9), Co2−C2 = 1.958(9), Co2−C3 = 1.965(9), C1−C2 = 1.50(1), C2−C3 = 1.37(1), C3−C4 = 1.50(1), C1−P1 = 1.81(1), P1−C5 = 1.793(9), P2−C5 = 1.854(9), Co1−P2 = 2.181(3), C4−P4 = 1.79(1), P4−C6 = 1.79(1), P3−C6 = 1.83(1), P3−Co2 = 2.188(3), C1−C2−C3 = 137.0(9), C2−C3−C4 = 134.6(8), C2−Co1−C3 = 41.1(4), C2−Co2−C3 = 41.0(4), Co1−C2−Co2 = 77.0(3), Co1−C3−Co2 = 77.6(3).

The structure of $[(Co_2(CO)_4)\mu,\eta^2,\eta^2$-$(-H_2CC{\equiv}CCH_2-)(-dppm)_2]^{2+}$ shows that the Co_2C_2 adopts a tetrahedral

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(6) Crystal data for **2**: red crystal, $C_{14}H_{16}B_2Co_2F_8O_6S_2$, fw = 635.9, monoclinic $P2_1/n$, a = 11.803(3) Å, b = 9.900(3) Å, c = 21.119(2) Å, β = 99.99(1)°, V = 2430(1) Å^3, Z = 4, ρ = 1.74 g/cm^3, T = 295 K, μ(Mo Kα) = 16.14 cm^{-1}, R (R_w) = 0.0362 (0.0450). Crystal dimensions 0.10 × 0.40 × 0.80 mm; Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (λ = 0.710 69 Å) collection range 2θ = 2−50°. Absorption correction was applied on the basis of a ψ-scan curve. The structure was determined by direct methods and subsequent difference Fourier syntheses and refined by full-matrix least-squares methods on F^2 by using the programs of the PC version of CRYSTALS.[12] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located on a difference Fourier map and their coordinates were refined with an overall isotropic thermal parameter.

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(8) Spectroscopic data for **3**: $^1H\{^{31}P\}$-NMR (CD_2Cl_2) δ 3.21 (d, $2H_2'$, AB, $-CH_2$-alkyne), 3.57 (d, $2H_1'$, AB $-CH_2P$) 3.90 (d, $2H_1$, AB $-CH_2P$), 4.43 (d, $2H_2$, AB $-CH_2$-alkyne), 8.01−7.23 (m, 40H, H_{Ar}). Anal. Calcd for $C_{58}H_{48}B_2Co_2F_8O_4P_4$: C, 56.68; H, 3.92. Found: C, 56.97; H, 4.11.

(9) The peculiar aspects of both signals P_1 and P_2 arise from unresolved couplings (^1J and ^3J, respectively) with the quadrupolar ^{59}Co nucleus (I = 7/2; natural abundance 100%). This precludes the determination of the homonuclear $^2J_{P-P}$ coupling; nevertheless, the latter was observed through the $^{31}P-^{31}P$ COSY spectrum.

(10) Crystal data for **3**: deep-red crystal, $C_{58}H_{48}B_2Co_2F_8O_4P_4$, fw = 1224.4, monoclinic $P2_1$/n, a = 11.446(4) Å, b = 33.872(9) Å, c = 14.698(3) Å, β = 101.11(1)°, V = 5592 (3) Å^3, Z = 4, ρ = 1.45 g/cm^3, T = 295 K, μ(Mo Kα) = 7.75 cm^{-1}, R (R_w) = 0.0662 (0.0721). Crystal dimensions

geometry with C2−C3 attached to both metal centers. Further, there is a C_2-axis passing through the center of the tetrahedron and bisecting the C2−C3 and Co1−Co2 skew bonds. The Co1−Co2 distance is 2.447(2) Å, slightly shorter than that found for complex **2**, whereas the C(2)−C(3) distance is 1.37(1) Å, longer than that in complex **2**. The structure confirms that two dppm ligands chelate symmetrically to the alkyne-dicobalt unit such that one-half of each phosphine ligand is coordinated to the cobalt center while the other, pendant half of the ligand is attached to the $-CH_2^+$ group, describing beautifully a two-blade propeller form. This propeller-like structure starts at P2−Co1−Co2−P3 and twists left through the dppm ligand to continue via the bridging alkyne-unit above the metal−metal bond and then twists right through the second dppm ligand. To demonstrate the chiral nature of **3**, we decided to use a chiral NMR reagent.

Most chiral NMR reagents have been made to complex organic substrates and interact less strongly with transition metal complexes. However, recently, Lacour and co-workers have designed the chiral trisphat anion and have shown the NMR nonequivalency of the two enantiomeric pairs of cationic tris(bisimine)ruthenium(II) complexes possessing D_3-symmetry.[11] In this work, we employed this method to differentiate for the first time a chiral propeller-like cobalt complex with C_2-symmetry.

Sequential addition in small portions of up to 1.2 equiv of trisphat to $[(Co_2(CO)_4)\mu,\eta^2,\eta^2\text{-}(-H_2CC{\equiv}CCH_2-)(-dppm)_2][BF_4]_2$ (**3**) in CD_2Cl_2 was monitored by ^1H and ^{31}P NMR spectroscopy at room temperature. As shown by Figure 3, resolution of both enantiomers was achieved. The ^{31}P spectra show the evolution of two signals at 31.46 and 43.51 ppm during the addition of trisphat. For example, the multiplet at δ 31.46 ppm (P_1) is remarkably split into two identical multiplets respectively shielded at δ 31.26 ppm (P_{1a}) and deshielded at 31.61 ppm (P_{1b}) with respect to the original one (Figure 3c). Similarly, the broad signal at 43.51 ppm attributed to the P−Co is beautifully split into two large twin peaks centered at 43.40 and 44.30 ppm, respectively. It is interesting to note that for each enantiomer this signal moved in the opposite sense relative to the one mentioned above as secured by a $^{31}P-^{31}P$ COSY experiment. In conclusion, the signals of one of the enantiomers of **3a**,**b** are centered at 31.26 ppm (P_{1a}) and at δ 44.30 ppm (P_{2a}) while for the other one they are at 31.61 ppm (P_{1b}) and at δ 43.40 ppm (P_{2b}). On the other hand, the ^1H NMR spectra (spectra are given in Supporting Information) were very informative and showed that the two AB systems attributed to the methylene groups each change into two identical doublets, thus confirming the NMR nonequivalency of the two enantiomers **3a**,**b** by forming a pair of diastereomers with the resolved Δ-trisphat. The propeller like-complex $[(Co_2(CO)_4)\mu,\eta^2,\eta^2\text{-}(-H_2CC{\equiv}CCH_2-)(-dppm)_2][BF_4]_2$ (**3**) represents a rare example in transition metal chemistry. Further, its NMR differentiation by trisphat ion is the first example reported for a chiral propeller-like complex.

In summary, in this paper we have reported the synthesis and X-ray molecular structure of a unique propeller-like chiral complex. Further, by NMR analysis (^1H and ^{31}P) we have extended the use of trisphat anion as a chiral shift reagent to differentiate, for the first time, the Δ-enantiomer **3a** from the Λ-enantiomer **3b** of complex $[(Co_2(CO)_4)\mu,\eta^2,\eta^2\text{-}(-H_2CC{\equiv}CCH_2-)(-dppm)_2][BF_4]_2$ (**3**). Future efforts are directed to resolve these enantiomers and to obtain the X-ray structure of one of them as a trisphat salt.

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Supporting Information Available: Experimental details, ^1H NMR spectra of **3**, 2D COSY $^{31}P-^{31}P$ spectra of **3**, and X-ray crystallographic and structural data for complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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0.20 × 0.30 × 0.50 mm. Absorption correction was applied using the program DIFABS[13] and provided the best resolution for **3**. The structure was determined by direct methods and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated overall refinable isotropic thermal parameters.

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