APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 209–210
DOI:10.1002/aoc.841

Crystallographic report

[*N*,*N*′-Bis-(6-methylpyrid-2-ylium)-(1*R*,2*R*)-1,2-diaminocyclohexane] bis-[(*p*-cymene)-trichlororuthenate(II)]

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Received 6 September 2004; Accepted 14 September 2004

The chiral compound (H_2cydiampy)[$RuCl_3$(*p*-cymene)]$_2$ has been obtained in high yield by treating [$RuCl_2$(*p*-cymene)]$_2$ with an excess of hydrochloric acid in the presence of one equivalent of *N*,*N*′-bis-(6-methylpyrid-2-yl)-(1*R*,2*R*)-1,2-diaminocyclohexane (cydiampy). It crystallizes in the chiral tetragonal space group $P4_32_12$, with half of the atoms of the dication related to the other half by a crystallographic C_2 axis that also makes equivalent the two anionic metal moieties.

KEYWORDS: ruthenium; atropisomeric compounds; chiral compounds; crystal structure

COMMENT

Transition metal complexes containing atropisomeric ligands have been used widely as catalyst precursors in asymmetric catalytic processes.[1] An important class of such chiral ligands are *N*,*N*′-disubstituted-1,2-diaminocyclohexanes.[2]

In addition to the synthesis of the atropisomeric ligand *N*,*N*′-bis-(6-methylpyrid-2-yl)-(1*R*,2*R*)-1,2-diaminocyclohexane (cydiampy), we now report that while studying the synthesis of chiral ruthenium complexes derived from cydiampy, in an attempt to crystallize the cationic complex [RuCl(cydiampy)(*p*-cymene)][BF_4] (unpublished results), we observed that the use of dichloromethane as a solvent led to decomposition of the desired product, yielding a small amount of orange crystals that were identified as (H_2cydiampy)[$RuCl_3$(*p*-cymene)]$_2$ (**1**). This compound was prepared subsequently in high yield by treating [$RuCl_2$(*p*-cymene)]$_2$ with an excess of hydrochloric acid in the presence of one equivalent of cydiampy.

Compound **1** crystallizes in the chiral tetragonal space group $P4_32_12$, with half of the atoms of the dication related to the other half by a crystallographic C_2 axis that also makes equivalent the two anionic metal moieties. Hydrogen bonds have been identified between all the N–H groups of the dicationic unit and the chlorine atoms Cl2 and Cl3 of both anionic fragments, the distances being: H100–Cl2, 2.49(9); H100–Cl3, 2.62(9); H200–Cl3, 2.51(5) (Figure 1).

EXPERIMENTAL

N,*N*′-bis-(6-methylpyrid-2-yl)-(1*R*,2*R*)-1,2-diaminocyclohexane (cydiampy)

A mixture of (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (570 mg, 5.0 mmol), 2-bromo-6-methylpyridine (1.75 g, 10.1 mmol), [Pd(dba)$_2$] (360 mg, 0.394 mmol), 1,3-bis-(diphenylphosphino)propane (320 mg, 0.776 mmol) and NaO^{t}Bu (2.68 g, 27.9 mmol) in 50 ml of toluene was stirred at 70 °C for 36 h. The solvent was removed under vacuum and the brown residue was extracted with dichloromethane (5 × 30 ml). The solvent was concentrated under reduced pressure to ∼2 ml and the residue set onto the top of a chromatographic column (silica gel, 2 × 20 cm, packed with hexanes). Elution with dichloromethane–diethyl ether (2:1) yielded 947 mg (64%) of the desired compound, which was obtained as a white solid upon precipitation with hexanes. Anal. calc. for $C_{18}H_{24}N_4$ (296.41): C 72.93, H 8.16, N 18.90. Found: C 72.90, H 8.17, N 18.92. MS (*m*/*z*): 296 [M^+]. Specific rotation: +182 $[^\circ]_D$ (0.01 g ml^{-1}). ^{1}H

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Contract/grant sponsor: Spanish MCyT; Contract/grant number: BQU2002-2623.

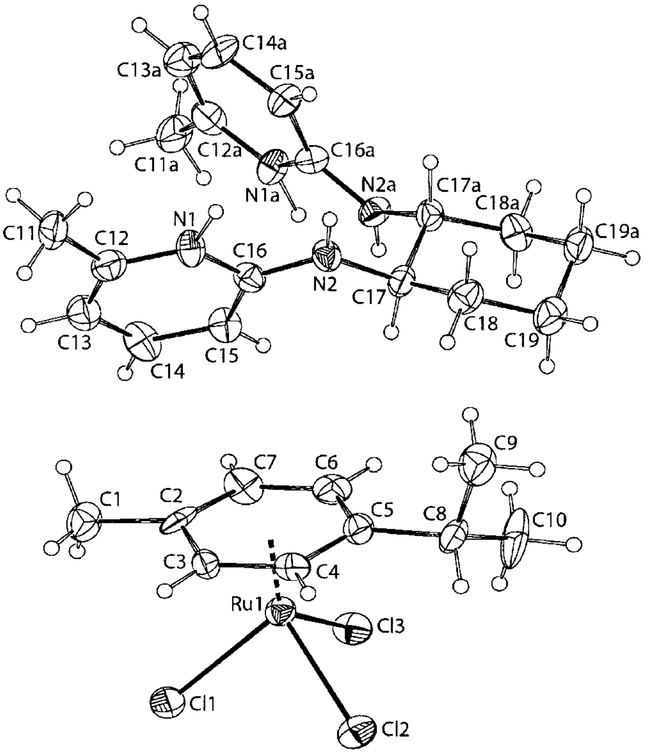

Figure 1. The dication (top) and one of the two identical monoanions (bottom) of compound **1**. Selected distances: C2–Ru1, 2.213(8); C3–Ru1, 2.173(8); C4–Ru1, 2.169(8); C5–Ru1, 2.206(9); C6–Ru1, 2.166(9); C7–Ru1, 2.168(10); Cl1–Ru1, 2.436(2); Cl2–Ru1, 2.418(2); Cl3–Ru1, 2.439(2); N2–C16, 1.34(1); N2–C17, 1.45(1). Symmetry operations: $-y+2$, $-x+2$, $-z+3/2$.

NMR (CD_2Cl_2): 7.20 (t, $J = 7.8$ Hz, 1H, C*H*), 6.35 (d, $J = 7.8$ Hz, 1H, C*H*), 6.13 (d, $J = 7.8$ Hz, 1H, C*H*), 5.06 (s, br, 1H, N*H*), 2.36 (s, 3H, CH_3), 2.23 (m, 1H, C*H*), 1.84 (m, 2H, CH_2), 1.40 (m, 2H, CH_2). DEPT $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 158.5 (C), 156.9 (C), 137.6 (CH), 111.7 (CH), 104.7 (CH), 55.4 (CH) 32.4 (CH_2), 24.7 (CH_2), 24.6 (CH_3).

(H_2cydiampy)[$RuCl_3$(*p*-cymene)]$_2$ (1)

An excess of concentrated aqueous HCl (~0.1 ml) was added to a solution of [$RuCl_2$(*p*-cymene)]$_2$ (50 mg, 0.082 mmol) and *N,N*′-bis-(6-methylpyrid-2-yl)-(1*R*,2*R*)-1,2-diaminocyclohexane (25 mg, 0.084 mmol) in dichloromethane (20 ml) and the mixture was stirred at room temperature for 20 min. The solvent was removed under vacuum and the orange residue washed with diethyl ether (4 × 20 ml) and dried under vacuum to yield 82 mg (78%) of the desired compound as an orange solid. Anal. calc. for $C_{38}H_{54}Cl_6N_4Ru_2$ (981.71): C 46.49, H 5.54, N 5.70. Found: C 46.55, H 5.60, N 5.62. ^1H NMR (CD_2Cl_2): 12.07 (s, br, 1H, NH_{py}), 7.64 (t, $J = 7.6$ Hz, 1H, C*H*), 7.22 (d, $J = 7.6$ Hz, 1H, C*H*), 6.15 (d, $J = 7.6$ Hz, 1H, C*H*), 5.50 (d, $J = 5.8$ Hz, 2H, C$H_{p\text{-}cym}$), 5.29 (d, $J = 5.8$ Hz, 2H, C$H_{p\text{-}cym}$), 3.76 (s, br, 1H, N*H*), 3.09 (sept, $J = 6.8$ Hz, 1H, C$H_{p\text{-}cym}$), 2.32 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.22 (m, 1H, C*H*), 1.80 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.37 (d, 6H, C$H_{3(p-cym)}$). Diffraction data were collected on a Nonius Kappa-CCD diffractometer using Cu Kα radiation. $C_{38}H_{54}Cl_6N_4Ru_2$, $M = 981.69$, tetragonal, $P4_32_12$, $a = b = 10.1388(2)$, $c = 41.0460(9)$ Å, $V = 4219.33(15)$ Å^3, $Z = 4$, 3847 unique data (θ_{max} 68.20°), 3388 data with $I > 2\sigma(I)$, $R = 0.048$ (obs. data), $wR_2 = 0.150$ (all data); Flack parameter: −0.02(3). Programs used: DIRDIF-96, XABS2, SHELXL-97, PLATON, WINGX. CCDC deposition number: 246229.

Acknowledgment

This work has been supported by the Spanish MCyT (grant BQU2002-2623).

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