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LETTER

Synthesis and complexation of a new chiral α-diimine-type bioxazoline ligand with C_2 symmetry

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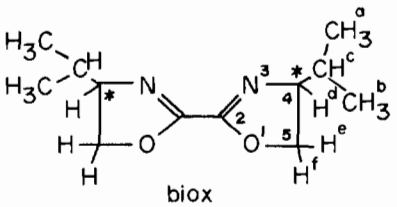
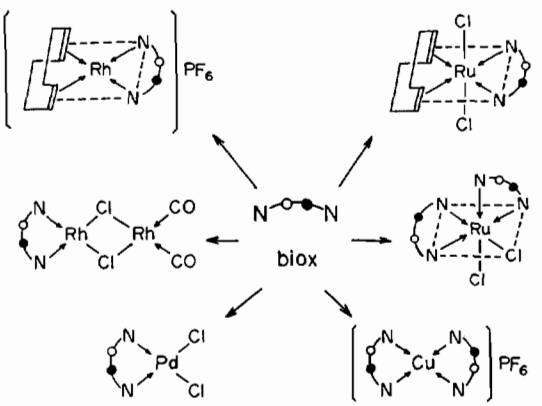
Catalytic asymmetric homogeneous reactions have been recognized as the most promising methods for obtaining optically active compounds [1]. Many articles [2] have been published concerning high efficient stereoselectivity in the asymmetric synthesis by use of transition-metal catalysts, especially with chiral C_2-symmetric bisphosphines such as DIOP and BINAP. Their efficiency would be explained on the basis of a reduced number of reaction intermediates in the presence of the C_2-symmetric ligands. In recent years, optically active chelating nitrogen ligands [3–8] have shown some asymmetric catalytic activities, such as in hydrosilylation [5, 7] and transfer hydrogenation [8]. Most of these nitrogen ligands have imine structures and in certain reactions gave even higher optical yields than those obtained with phosphorus ligands [7]. However, there have been only a few papers on chiral nitrogen ligands with C_2 symmetry [4]. We now communicate the preparation and characterization of a new chiral bioxazoline with a C_2-symmetric α-diimine structure having two bulky alkyl groups, and its complexation with rhodium(I), ruthenium(II), copper(I) and palladium(II). In spite of a non-C_2-symmetric structure, optically active 2-(2-pyridinyl)oxazolines [5, 6] have been used as efficient cocatalysts in some asymmetric homogeneous processes promoted by transition-metal complexes.

(2*S*,7*S*)-1,8-Dihydroxy-2,7-bis(1-methylethyl)-3,6-diazaoctane-4,5-dione was readily available from the reaction of diethyl oxalate with (*S*)-valinol, i.e. (*S*)-2-amino-3-methyl-1-butanol under toluene reflux (94% yield). White; m.p. 205–206 °C; ν(C=O), 1645 cm^{-1} (KBr). Subsequent reaction with $SOCl_2$ converted it to (2*S*,7*S*)-1,8-dichloro-2,7-bis(1-methylethyl)-3,6-diazaoctane-4,5-dione (95% yield). White; m.p. 223 °C; ν(C=O), 1655 cm^{-1} (KBr); ^{13}C NMR ($CDCl_3$): δ(ppm) 45.55 (1- and 8-C), 56.02 (2- and 7-C), 159.40 (4- and 5-C), 19.20 and 18.50 (CH_3), and 29.28 (CH). Then, a methanol solution of NaOH was mixed with the dichloro compound, and the mixture was boiled for 2 h. After removal of solvent under reduced pressure, ethyl ether extract of the residue gave white microcrystals of (4*S*,4′*S*)-(−)-4,4′,5,5′-tetrahydro-4,4′-bis(1-methylethyl)-2,2′-bioxazole, abbreviated to 4,4′-diisopropyl-2,2′-bioxazoline (biox) (75% yield), m.p. 57 °C; ^1H NMR (C_6D_6): δ(ppm) 0.65 (CH_3^a), 0.87 (CH_3^b), 1.45 (H^c), 3.60 (H^e), 3.68 (H^d), 3.80 (H^f); *J*(a-c) 6.6, *J*(b-c) 7.0, *J*(c-d) 6.7, *J*(e-d) 8.8, *J*(e-f) 8.6, *J*(d-f) 10.0 Hz; MS (EI), 224(M^+, 14), 181($M-C_3H_7$, 100); $[\alpha]_D^{19.5} = -171°$ (*c* = 1.12, EtOH); ν(C=N), 1618 cm^{-1} (KBr).



As complexation, 4,4′-diisopropyl-2,2′-bioxazoline was allowed to react with $[RhCl(cod)]_2$, $[RhCl(CO)_2]_2$, $[RuCl_2(cod)]_n$, $[RuCl_2(NCCH_3)_4]$, $[Cu(NCCH_3)_4]PF_6$ and $[PdCl_2(NCPh)_2]$ to yield $[Rh(cod)(biox)]PF_6$, $[(biox)RhCl_2Rh(CO)_2]$, [*trans*-$RuCl_2(cod)(biox)$], [*cis*-$RuCl_2(biox)_2$], $[Cu(biox)_2]PF_6$, and $[PdCl_2(biox)]$, respectively (Scheme 1).



Scheme 1. C_2-Symmetric biox is illustrated by analogy with twisted two-bladed propellers. The symbol ○ indicates the obverse side of the 2-oxazoline plane, over which the isopropyl group is located. The symbol ● indicates the reverse side of the plane.

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TABLE 1. Selected ^{13}C NMR data of biox and the complexes[a]

Compound	1-Methylethyl		Oxazoline ring		
	CH_3	CH	2-C	4-C	5-C
biox[b]	18.29 18.99	32.50	154.63	73.25	71.11
$[Rh(cod)(biox)]PF_6$[c]	14.29 18.93	29.90	162.04	69.37	73.53
$[(biox)RhCl_2Rh(CO)_2]$[c,e]	15.65 18.64	31.95 32.03	161.05	74.22	72.12
$[RuCl_2(cod)(biox)]$[d]	15.13 18.79	29.38	160.38	69.46	72.11
$[RuCl_2(biox)_2]$[b]	15.08 15.39 19.71 19.87	29.09 29.60	156.48 158.73	71.71 72.52	72.29 72.60
$[PdCl_2(biox)]$[c]	14.14 18.69	29.28	159.78	68.51	74.27
$[Cu(biox)_2]PF_6$[b]	17.59 18.49	31.99	158.06	71.34	73.91

[a]δ Values from TMS. [b]In $CDCl_3$. [c]In CD_2Cl_2. [d]In C_6D_6. [e]Carbonyl groups showed two resonances at δ 180.94 and 183.90, indicating the folded structure of the $RhCl_2Rh$ moiety.

Table 1 shows the ^{13}C NMR resonances of the biox moieties in these complexes. Detailed experimental procedures and other properties of the complexes will be described elsewhere. Our current research is directed towards the use of biox and these complexes as effective asymmetry-inducing catalysts for some homogeneous reactions.

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