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Preliminary Communication

Asymmetric catalysis

LXXX *. An optically-active tetrakispyrazolylborate: Synthesis and use in Cu-catalysed enantioselective cyclopropanation

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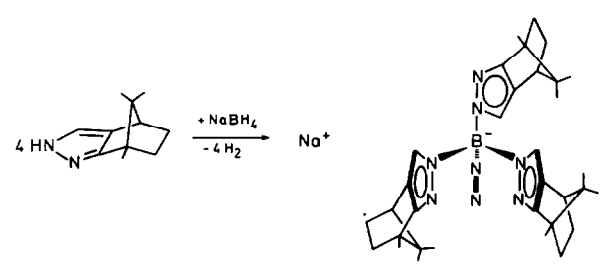
Abstract

The synthesis of the optically-active sodium salt of tetrakis(4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazolyl)borate, [NaB(camphpz)$_4$] (**1**) is reported. Cu-based *in situ* catalysts containing [NaB(camphpz)$_4$] give an enantiomeric excess of up to 62% in the enantioselective cyclopropanation of styrene with ethyl diazoacetate.

Polypyrazolylborates have been widely used in inorganic, bioinorganic, and organometallic chemistry [2] but to our knowledge there are no optically-active polypyrazolylborates [3]. We report here the synthesis and characterization of the optically-active sodium salt of tetrakis(4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazolyl)borate, [NaB(camphpz)$_4$] (**1**) and its use in the Cu-catalysed enantioselective cyclopropanation of styrene with ethyl diazoacetate.

NaB(camphpz)$_4$ (**1**) was prepared as described for KB(pz)$_4$ [2]. 4,5,6,7-Tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazole (camphorpyrazole) was synthesised by the published method [4–6]. NaB(camphpz)$_4$ was made by heating a mixture of $NaBH_4$ and 8 equivalents of camphorpyrazole at 220–240°C until four equivalents of hydrogen had been evolved (Scheme 1).

The IR spectra of dihydrobispyrazolylborates show BH_2 bands in the range 2200–2500 cm^{-1} and those of hydrotrispyrazolylborates show a BH band around 2500 cm^{-1} [2]. In contrast the IR spectrum of NaB(camphpz)$_4$ shows no BH bands, supporting its formulation as a tetrakis derivative, in accord with the elemental analysis. The negative ion FAB mass spectrum exhibits a m/z peak at 711 for the anion $[B(camphpz)_4]^-$. In principle, camphorpyrazole could be bonded to the boron atom either through nitrogen atom N(1) or through nitrogen atom N(2), giving rise to a range of isomers. It is generally accepted that unsymmetrical pyrazole ligands coordinate to metal ions through the less sterically hindered nitrogen atom [2]. By analogy, camphorpyrazole could be expected to bind via the less hindered N(1) nitrogen to the boron atom in NaB(camphpz)$_4$, but there have been recent reports that it can bind through either the more hindered nitrogen atom N(2) or the less hindered nitrogen atom N(1) (*e.g.* in pyridine derivatives), the isomers being differentiated on the basis of their ^1H NMR spectra [4,5,7–10]. As the ^1H NMR spectrum of NaB(camphpz)$_4$ shows only one singlet, at 6.54 ppm, for the C(5) proton, we formulate NaB(camphpz)$_4$ as shown in Scheme 1. In agreement with the ^{11}B NMR spectrum of KB(pz)$_4$ [11], only one sharp singlet ($h_{1/2}$ = 5.0 Hz) is observed at +0.7 ppm in the ^{11}B NMR spectrum of NaB(camphpz)$_4$. Thus the NMR spectra suggest that all four camphorpyrazole rings are coordinated identically through the less hindered N(2) nitrogen to the boron atom in NaB(camphpz)$_4$. Attempts to isolate the intermediates $NaH_2B(camphpz)_2$ and $NaHB(camphpz)_3$ are in progress.



Scheme 1. For the sake of clarity, the pyrazolyl substituent pointing away is denoted by N–N.

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* For Part LXXIX, see ref. 1.

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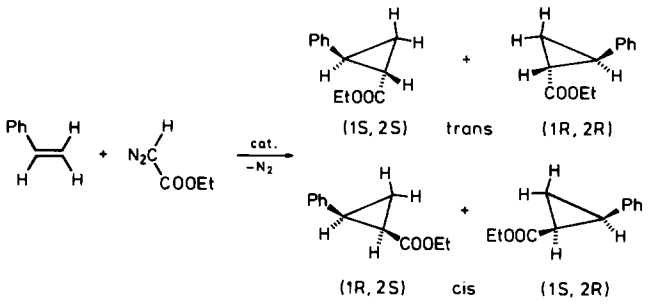
In continuation of our efforts to develop new optically-active ligands for enantioselective catalysis, we have examined the use the optically-active NaB(camphpz)$_4$ in cyclopropanation of styrene and ethyl diazoacetate brought about by Cu^I, Cu^{II} and Rh^I *in situ* catalysts (Scheme 2). The isolated complex Cu(CO)[B(camphpz)$_4$] was also used as a catalyst. The cyclopropanation of styrene and ethyl diazoacetate was performed by the reported methods [12]. The chemical yields, the cis/trans ratios and the enantiomeric excesses were determined as described previously [12,13].

As shown in Table 1 the product of the cyclopropanation is a mixture of *cis/trans* isomers, with the *cis* isomer the main component. The chemical yields are in the range 9–69%. The enantiomeric excess is 10–62% for the *cis* isomer and 0.5–42% for the *trans* isomer. The maximum enantiomeric excess is 62% for the *cis* isomer, obtained with a Cu^I–triflate/1 catalyst, and 42% for the *trans* isomer, obtained with a Cu^{II}–acetate/1 catalyst. However, the cocatalysts Cu(OAc)$_2$, CuI, and Cu(CF$_3$SO$_3$) give very similar results (Table 1, entries 1–3). With the isolated complex Cu(CO)[B(camphpz)$_4$] as the catalyst the enantioselectivity is a little lower, and with the *in situ* catalyst [Rh(cod)Cl]$_2$/1 it is appreciably lower (Table 1, entries 4, 5).



Scheme 2.

1. Experimental details

1.1. Synthesis of the sodium salt of tetrakis(4,5,6,7-tetrahydro-7,8,8-trimethyl-2H-4,7-methanoindazolyl)borate, NaB(camphpz)$_4$ (1)

A mixture of 0.403 g (10.63 mmol) of NaBH$_4$ and 15.05 g (85.04 mmol) of camphorpyrazole was heated at 220–240°C for 12 h until 4 equivalents of hydrogen gas had evolved. The white residue was washed several times with diethyl ether and dried under high vaccum at 180°C. Yield 90%. Anal. Found: C, 71.93; H, 7.97; N, 15.20%. $C_{44}H_{60}BN_8Na$ (mol. weight 734.78) calc.: C, 71.91; H, 8.23; N, 15.25%. IR (KBr, cm^{-1}): 2940, 2860 (C–H); 1570, 1475, 1430 (C=N, C=C). Optical activity $[\alpha]_D^{25} = +36.9$ ($c = 1$, pyridine). MS[NI-LISIMS(MNBA)] m/z 711, anion of [NaB(camphpz)$_4$]. ^{1}H NMR (DMF-d_7, int. TMS, 250 MHz): δ (ppm) = 6.54 (s, 4H, pzC5-H); 2.62 (d, 3.5 Hz, 4H, CH bridgehead); 1.99–1.95 (m, 4H, CH$_2$); 1.77–1.70 (m, 4H, CH$_2$); 1.22–1.14 (m, 4H, CH$_2$); 1.17 (s, 12H, CH$_3$); 1.05–0.99 (m, 4H, CH$_2$); 0.89 (s, 12H, CH$_3$); 0.67 (s, 12H, CH$_3$). ^{11}B NMR (DMF, ext. BF$_3$·OEt$_2$, 300 MHz): δ (ppm) +0.7 (s).

1.2. Synthesis of Cu(CO)[B(camphpz)$_4$]

NaB(camphpz)$_4$ (0.735 g, 1.0 mmol) was added to a suspension of CuCl (100 mg, 1.0 mmol) in CH$_2$Cl$_2$ (50 ml) at room temperature. CO was passed slowly through the suspension for 5 h. After filtration, the colourless solution was evaporated. The residue was washed with petroleum ether (40/60) and dried under vaccum. Yield 52%. Anal. Found: C, 67.13; H, 7.57; N, 13.65%. $C_{45}H_{60}BCuN_8O$ (mol. weight 803.34) calc.: C, 67.21; H, 7.46; N, 13.94%. IR (KBr, cm^{-1}): 2110 (CO).

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TABLE 1. Enantioselective cyclopropanation of styrene (8.7 mmol) with ethyl diazoacetate (10 mmol) using *in situ* catalysts Cu^I, Cu^{II}, and Rh^I/NaB(camphpz)$_4$ (1) = 1:1; styrene:Cu^I, Cu^{II}, and Rh^I = 190:1; temperature 55°C; reaction time 2 h, two runs in each case

In situ catalysts	Yield %	*cis / trans* ratio	%ee *cis / trans*
Cu(OAc)$_2$/1	68, 69	76/24, 76/24	57, 58 (1*R*, 2*S*)/40, 42 (1*R*, 2*R*)
CuI/1	48, 46	68/32, 69/31	54, 55(1*R*, 2*S*)/36, 35 (1*R*, 2*R*)
Cu(CF$_3$SO$_3$)/1	53. 53	76/24, 76/24	62, 62 (1*R*, 2*S*)/40, 39 (1*R*, 2*R*)
Cu(CO)[B(camphpz)$_4$][a]	39, 40	60/40, 60/40	45, 46 (1*R*, 2*S*)/29, 28 (1*R*, 2*R*)
[Rh(cod)Cl]$_2$/1	9, 8	44/56, 44/56	10, 10 (1*R*, 2*S*)/0.5, 0.4 (1*R*, 2*R*)

[a] Reaction temperature 25°C.

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