Inorg. Chem. **2003**, *42*, 8872–8877

A Chiral Alkyltris(pyrazolyl)borate Ligand: Synthesis of [(Ipc)B(pz)$_3$Mn(CO)$_3$] and [(Ipc)B(pz)$_3$Ru(*p*-cymene)]PF$_6$ (Ipc = Isopinocampheyl)

Philip J. Bailey,* Pedro Pinho, and Simon Parsons

Department of Chemistry, The University of Edinburgh, The Kings Buildings, West Mains Road, Edinburgh EH9 3JJ, U.K.

Received September 8, 2003

The application of the reagent (Ipc)BCl$_2$ (Ipc = isopinocampheyl) in the synthesis of a new tris(pyrazolyl)borate ligand having an Ipc substituent on boron is described. The sodium salt is a convenient precursor for the preparation of the complexes {(Ipc)tris(pyrazolyl)borato}tricarbonylmanganese and [{(Ipc)tris(pyrazolyl)borato}(*p*-cymene)-ruthenium]$^+$, whose X-ray crystal structures are reported. While little distortion of the B(pz)$_3$M unit is observed in these complexes, steric interaction between the Ipc group and the 3-positions of the pyrazolyl rings is noted to lead to distortion of the angles around the B–C bond.

Introduction

Anionic tris(pyrazolyl)borate ligands are well documented in the literature and widely recognized as an important class of ligands in coordination chemistry.[1] The simplest of these ligands, hydrotris(pyrazolyl)borate (Tp),[2] is also commercially available, clearly showing the interest in this family within the field. Other ligands of this class are also reported in the literature, and different properties are usually related to the introduction of different organic groups into the basic structure of the ligand. Most of the studied cases, however, relate to substitution in different positions of the pyrazole ring, and a wide variety of these, as well as their metal complexes, have now been reported.[3] Less common are ligands containing organic groups directly attached to the boron center, and the known cases are usually restricted to alkyl chains,[3] most commonly Me, *n*-Bu, *i*-Pr, *t*-Bu, or the simple phenyl ring[4] (Figure 1). This is mainly due to the restricted availability of adequate starting materials and difficulties associated with the synthesis of the required boron precursors. By far the most common method for synthesis of this class of ligands is the hydride route, involving reaction of the heterocycle with the corresponding alkali metal tetrahydroborate or substituted derivatives thereof, although there are a few examples of the use of boronic acids[3f,5] or boron halides.[3a,d]

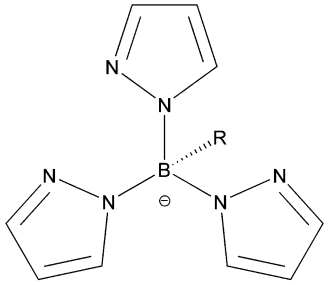


Figure 1. Common boron-substituted tris(pyrazolyl)borate ligands.

Isopinocampheyl (Ipc) boranes are widely recognized as synthetically useful compounds which are easily produced via hydroboration of α-pinene and can be modified into different intermediates that find application both in synthesis and catalysis.[6] Surprisingly, the isopinocampheylboron di-

(1) For reviews see: (a) Trofimenko, S. *Scorpionates-The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291−393. (c) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
(2) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.
(3) See for example: (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288. (b) Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S. *Inorg. Chem.* **2001**, *40*, 6509. (c) Han, R.; Perkin, G.; Trofimenko, S. *Polyhedron* **1995**, *14*, 387. (d) Janiak, C.; Braun, L.; Gigsdies, F. *J. Chem. Soc., Dalton Trans.* **1999**, 3133. (e) Murtuza, S.; Casagrande, O. L., Jr.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882. (f) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1983**, *22*, 1064. (g) Graziani, O.; Toupet, L.; Hamon, J.-R.; Tilset, M. *Inorg. Chim. Acta* **2002**, *341*, 127.
(4) Sohrin, Y.; Kokusen, H.; Matsui, M. *Inorg. Chem.* **1995**, *34*, 3928.
(5) White, D. L.; Faller, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 1548.
(6) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547.

10.1021/ic035061n CCC: $25.00
Published on Web 12/03/2003

halides [(Ipc)BX_2] or the corresponding alkali metal hydrides such as Na[(Ipc)BH_3][7] have never been reported as precursors for the preparation of tripodal ligands of the tris(pyrazolyl)-borate type. In fact until now there have been no reports of tris(pyrazolyl)borate ligands bearing a chiral group directly attached to boron. These ligands could therefore arise as a new subclass of ligands with interesting new properties, and it was decided to explore the synthetic possibilities to prepare these compounds. We wish herein to show that these new ligands are readily available and that transition metal complexes can also be prepared.

A useful precursor for the preparation of the desired transition metal complexes is clearly the alkali metal salt of the ligand. The synthesis of this can be envisaged through the reaction of the sodium (or other alkali metal) salt of pyrazole (sodium pyrazolide, NaPz) with the appropriate dihaloboron compound. Preparation of (Ipc)BX_2 can be achieved via one of three different routes: direct hydroboration with a dihaloborane;[8] hydroboration of α-pinene with borane followed by exchange of the remaining hydrides by halides;[9] hydroboration of α-pinene using boron trihalides and trialkylsilanes,[10] which effectively is an in-situ generation of dihaloborane followed by hydroboration. These routes are established procedures, but the choice of the most convenient one is directly linked with the desired enantiopurity of the final ligand precursor. To use the dihaloborane routes it is necessary that the starting olefin is enantiomerically pure, since no enrichment step is available. On the other hand, the exchange route intrinsically provides an enrichment step (see below), allowing the synthesis to be performed from a cheaper source of chirality. Both routes are clearly alternatives to each other, and although the dihaloborane route has not been explored, it is believed that this should not present any additional problems provided the required purity of the starting olefin is available. However, we chose to explore the exchange route using 91% ee (1*R*)-α-pinene as the starting olefin and the synthetic procedures are described in the next sections.

Experimental Section

Unless otherwise noted, reagents were used as obtained from the commercial suppliers. [{(Ipc)BH_2}$_2$(TMEDA)] was prepared according to the literature procedure.[9a] The release of (Ipc)BH_2 by treatment with BF_3·OEt_2 is also described in the same paper. All compounds were stored under nitrogen; TMEDA was dried and distilled from CaH_2, and boron trifluoride etherate was distilled. Ethereal HCl was prepared by bubbling HCl gas into dry ether and was standardized against methanolic sodium hydroxide, which in turn was standardized against aqueous HCl. Solvents were dried over Na/benzophenone (ether, hexane, and THF) or over CaH_2 (CH_3CN). Satisfactory elemental analyses (C, H, N) were obtained for all new compounds.

Sodium Pyrazolide. This was prepared using a procedure described in the patent literature as follows.[11] Pyrazole (4.0 g, 58.8 mmol) was dissolved in toluene (70 mL) under a nitrogen atmosphere. To this solution was added sodium hydride (2.30 g of a 60% suspension in paraffin, 57.5 mmol), and the mixture was heated to reflux for 12 h. The resulting mixture was cooled and the solvent removed in a vacuum. The resulting solid was washed with dry toluene (2 × 10 mL) and then hexane (2 × 10 mL) to remove paraffin and unreacted pyrazole and then dried under vacuum to yield the product as a free flowing colorless powder (4.80 g, 91%). δ_H (dmso-d_6): 7.31 (s, 2H), 5.89 (s, 1H).

Isopinocampheylboron Dichloride [(Ipc)BCl_2]. [{(Ipc)BH_2}$_2$-(TMEDA)] and (Ipc)BH_2 were prepared according to the literature procedure.[9a] Conversion to (Ipc)BCl_2 was achieved according to the patent procedure[9b] as follows. A solution of (Ipc)BH_2 obtained by treatment of [{(Ipc)BH_2}$_2$(TMEDA)] (17.32 g, 42 mmol) with BF_3·OEt_2 was cooled to −10 °C and treated dropwise with HCl in diethyl ether (2.54 M solution) until evolution of hydrogen ceased (64 mL, 162.6 mmol). The resulting solution was stirred at room temperature for 2 h and the ether then removed under vacuum. Vacuum distillation of the product through a Vigreaux column provided (Ipc)BCl_2 as a pyrophoric, colorless liquid (16.17 g, 88%, bp 52−55 °C at 0.1 mmHg). The ^{1}H NMR spectrum closely resembled that reported in the literature.[12]

Sodium Isopinocampheyltris(pyrazolyl)borate (1). Sodium pyrazolide (1.45 g, 16.1 mmol) was dissolved in dry THF (20 mL) under an atmosphere of nitrogen. To this solution was then added dropwise (Ipc)BCl_2 (13.3 mL, 0.4 M solution in hexane, 5.3 mmol) and the resulting mixture stirred at room temperature overnight. The solvent was then completely removed in a vacuum and replaced with dry hexane (75 mL). The hexane solution was filtered through vacuum-dried Celite to remove the formed sodium chloride and the filter cake washed with dry hexane (2 × 25 mL). The clear solution containing **1** was concentrated in a vacuum to afford the pure product as a very hygroscopic white solid (1.7 g, 87% yield). δ_H ($CDCl_3$): −0.40 (m, 1H), 0.42 (m, 3H), 1.08 (s, 3H), 1.10 (s, 3H), 1.44−2.29 (m, 7H), 6.19 (m, 3H), 7.17 (m, 3H) and 7.39 (m, 3H); δ_C ($CDCl_3$) 24.3, 27.9, 28.3 (m, C−B), 28.9, 30.0, 31.4, 37.3, 39.9, 42.4, 50.4, 105.3, 136.5 and 141.7. MS FAB: *m*/*z* 349 (M^-, 100).

{**Isopinocampheyltris(pyrazolyl)borato**}**tricarbonylmanganese (2).** A dry flask adapted with a reflux condenser was loaded with compound **1** (375 mg, 1.0 mmol) and dry acetonitrile (20 mL). To the solution under an atmosphere of nitrogen was then added [$Mn(CO)_5Br$] (280 mg, 1.02 mmol) and the clear orange solution heated to reflux for 2 h. During this time a yellow precipitate was formed. The volume of solvent was then reduced to one-fourth and decanted off. The remaining solid was partionated between water (40 mL) and CH_2Cl_2 (40 mL) and the water layer further extracted with CH_2Cl_2 (2 × 40 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to afford the desired product as a yellow solid (433 mg, 89% yield). δ_H ($CDCl_3$): 1.24 (s, 3H), 1.27 (d, 3H, J = 7.8 Hz), 1.29 (s, 3H), 1.42 (d, 1H, J = 10 Hz), 1.90−2.80 (m, 7H), 6.22 (m, 3H), 7.88 (m, 3H) and 8.18 (m, 3H). δ_C ($CDCl_3$): 23.3, 23.9 (m, C−B), 27.6, 28.5, 29.6, 32.2, 37.1, 40.0, 42.6, 52.1, 105.0, 135.9, and 144.5. IR (toluene, cm^{-1}): 1927, 2031. IR (KBr disk, cm^{-1}): 1934, 1942, 2031. MS+FAB:

(7) Brown, H. C.; Singaram, B.; Mathew, C. P. *J. Org. Chem.* **1981**, *46*, 2712.
(8) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384; For preparation of dihaloboranes, see: Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938.
(9) (a) Hydroboration followed by formation of the TMEDA adduct: Brown, H. C.; Schwier, J. R.; Singaram, B. *J. Org. Chem.* **1978**, *43*, 4395. (b) For preparation of $IpcBCl_2$: Brown, H. C. U.S. Patent 4,772,752, 1988.
(10) (a) Soundararajan, R.; Matteson, D. S. *J. Org. Chem.* **1990**, *55*, 2274. (b) Soundararajan, R.; Matteson, D. S. *Organometallics* **1995**, *14*, 4157.
(11) Hlatky, G. G. U.S. Patent 6,391,988 B1, 2002.
(12) Dhokte, U. P.; Brown, H. C. *Organometallics* **1995**, *15*, 3504.

m/*z* 488 (M^+, 8), 460 ($M^+ - CO$, 14), 432 ($M^+ - 2CO$, 10), 404 ($M^+ - 3CO$, 19).

(*p*-Cymene){isopinocampheyltris(pyrazolyl)borato}ruthenium Hexafluorophosphate (3). $[Ru(p\text{-cymene})Cl_2]_2$ (300 mg, 0.49 mmol) was dissolved under nitrogen in dry acetonitrile (70 mL). The solution was then allowed to stir at room temperature for 1 h after which time compound **1** (365 mg, 0.98 mmol) was added and the stirring continued for a further 2 h. At this point the solution was filtered under nitrogen through Celite to remove insoluble residues (consisting mainly of sodium chloride) and the solvent removed under vacuum. The intermediate complex was thereafter dissolved in methanol (20 mL) and treated with NH_4PF_6 (479 mg, 2.94 mmol); after 1 h the solid formed was allowed to deposit and washed once with cold methanol. After drying, an air-sensitive yellow solid was obtained (450 mg, 63% yield). δ_H ($CDCl_3$): 1.30 (d, 6H, $J = 6.81$ Hz), 1.36 (d, 3H, $J = 6.76$ Hz), 1.39 (s, 3H), 1.45 (s, 3H), 1.58 (d, 1H, $J = 10$ Hz), 2.09−2.89 (m, 7H), 2.41 (s, 3H), 3.95 (sep, 1H, $J = 6.81$ Hz), 5.85 (m, 4H), 6.34 (dd, 2H, $J = 5.08$ and 1.76 Hz), 8.12 (d, 3H, $J = 1.88$ Hz), and 8.22 (d, 3H, $J = 2.12$ Hz). δ_C ($CDCl_3$): 18.2, 22.3, 22.4, 23.2, 24.6 (m, C−B), 27.4, 30.8, 32.3, 37.7, 40.4, 43.2, 53.1, 87.6, 87.9, 88.0, 88.1, 102.4, 106.8, 108.3, 137.0, and 146.9. MS+FAB: *m*/*z* 586 (M^+, 86) 449 (M^+ − cymene, 18).

X-ray Crystallography. Single-crystal X-ray diffraction data were collected with Mo Kα radiation on a Bruker Smart Apex CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. Both structures were solved by Patterson methods (DIRDIF)[13] and refined by full-matrix least squares against $|F|^2$ using all data (SHELXTL)[14] with H atoms in idealized positions. All full-weight non-H atoms were modeled with aniostropic displacement parameters. In both cases the crystals were known to be enantiopure on the basis of their preparative routes. Crystallographic data for **2** and **3** are presented in Table 2.

The unit cell of **2** can be transformed into a metrically monoclinic *C* cell, but R_{int} for 2/*m* symmetry was 0.500. Structure determination was nonroutine because of the presence of twinning, disorder, and pseudosymmetry. The diffraction pattern was indexed using two orientation matrixes (GEMINI)[15] related by the twin law

$$\begin{pmatrix} -0.107 & 0 & -0.898 \\ -0.119 & -1 & 0.122 \\ -1.101 & 0 & 0.101 \end{pmatrix}$$

Note that this twin law is not related to the pseudomonoclinic symmetry of the lattice.

Both domains were integrated simultaneously,[16] and an absorption correction applied using the program TWINABS.[17] Overlap affected only 73 data, and these were simply omitted from the data set; only reflections of the principal domain were used in subsequent calculations. There were two molecules of **2** in the asymmetric unit, but with the exception of the isopinocampheyl moieties these were related by a pseudoinversion center. Modeling of these moieties was accomplished using a combination of Fourier difference syntheses and rigid body fitting (using coordinates from the structure of **3**; see below); in one of the crystallographically independent molecules this group is disordered over two orientations related by a rotation about the B−C bond. Part-weight atoms were refined with isotropic displacement parameters. Similarity restraints were applied to chemically equivalent bond distances and angles and to the displacement parameters of directly bonded light atoms. Rigid bond restraints were also applied. R1 = 0.0541 [based on $|F|$ and 4695 data with $|F| > 4\sigma(|F|)$] and wR2 = 0.1334 (based on $|F|^2$ and all 5836 data to $2\theta_{max} = 57.8°$). The final difference map extremes were +0.67 and −0.71 e Å^{-3}. The Flack parameter was 0.02(2).[18]

Table 1. Selected Bond Distances (Å) and Angles (deg) for **2** and **3**

Compound **2**			
Mn2−C15	1.804(5)	Mn2−N66	2.037(4)
Mn2−C35	1.807(4)	N26−B17	1.581(5)
Mn2−C25	1.809(4)	N76−B17	1.576(5)
Mn2−N16	2.023(4)	N126−B17	1.584(5)
Mn2−N116	2.027(3)	B17−C27	1.657(5)
C15−Mn2−C35	90.3(3)	C35−Mn2−N66	89.5(2)
C15−Mn2−C25	91.2(3)	N16−Mn2−N66	85.43(18)
C35−Mn2−C25	91.3(3)	N116−Mn2−N66	85.04(19)
C35−Mn2−N16	92.8(2)	N76−B17−N26	105.3(4)
C25−Mn2−N16	91.9(2)	N76−B17−N126	103.2(3)
C15−Mn2−N116	91.8(2)	N26−B17−N126	104.9(4)
C25−Mn2−N116	94.0(2)	N76−B17−C27	117.1(4)
N16−Mn2−N116	84.70(19)	N26−B17−C27	108.1(3)
C15−Mn2−N66	91.4(2)	N126−B17−C27	117.1(3)
Compound **3**			
Ru1−N13	2.081(2)	Ru1−C41	2.233(3)
Ru1−N14	2.084(3)	Ru1−C11	2.242(3)
Ru1−N12	2.107(3)	N22−B15	1.582(4)
Ru1−C51	2.194(3)	N23−B15	1.558(4)
Ru1−C21	2.000(3)	N24−B15	1.582(4)
Ru1−C61	2.000(3)	B15−C25	1.633(4)
Ru1−C31	2.002(3)		
N13−Ru1−N14	85.58(10)	N22−B15−N24	103.2(2)
N13−Ru1−N12	81.59(10)	N23−B15−C25	115.8(2)
N14−Ru1−N12	82.85(9)	N22−B15−C25	118.5(2)
N23−B15−N22	103.3(2)	N24−B15−C25	107.5(2)
N23−B15−N24	107.5(2)		

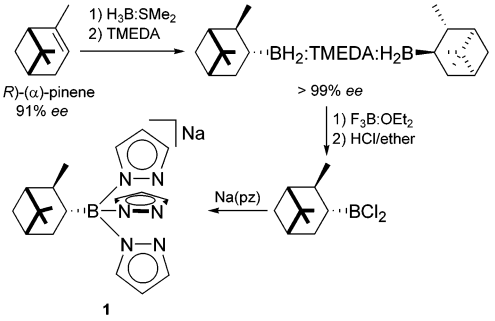
Table 2. Crystal Data for **2** and **3**

	2	**3**
cryst description	colorless prism	yellow block
empirical formula	$C_{22}H_{26}BMnN_6O_3$	$C_{33}H_{46}BF_6N_8PRu$
M_r	488.24	811.63
T (K)	150(2)	150(2)
cryst system	triclinic	orthorhombic
space group	$P1$	$P2_12_12_1$
a (Å)	11.0130(18)	10.4974(14)
b (Å)	11.6451(19)	14.713(2)
c (Å)	11.6288(19)	23.296(3)
α (deg)	60.555(3)	90
β (deg)	63.211(3)	90
γ (deg)	62.917(3)	90
V (Å^3)	1105.7(3)	3598.0(8)
Z	2	4
μ(Mo Kα) (mm^{-1})	0.635	0.548
indpdt reflcns	5836	22 537
data with $\|F\| > 4\sigma(\|F\|)$	4695	8193
abs corr	multiscan ($T_{min} = 0.788$, $T_{max} = 1$)	multiscan ($T_{min} = 0.684$, $T_{max} = 1$)
R1[a]	0.0541	0.0408
wR2[b]	0.1334	0.0975

[a] $R1 = \frac{\sum |F_0 - F_c|}{\sum |F_0|}$ Calculated using data with $|F| > 4s(|F|)$. [b] $wR2 = \left[\frac{\sum w (F_0^2 - F_c^2)^2}{\sum \omega (F_0^2)^2}\right]^{1/2}$ Calculated for all data (w = weight).

(13) Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *DIRDIF*; Crystallography Laboratory: University of Nijmegen, Nijmegen, The Netherlands, 1996.
(14) Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker AXS: Madison, WI, 2001.
(15) Sparks, R. A. *GEMINI*, version 1.05; Bruker-AXS: Madison, WI, 2000.
(16) *Bruker-AXS, SAINT*, version 7.01; Bruker AXS: Madison, WI, 2002.
(17) Sheldrick, G. M. *TWINABS*, version 1.02; University of Göttingen: Göttingen, Germany, 2002.

Scheme 1. Synthesis of Na[IpcB(pz)$_3$]



For **3** R1 = 0.0408 [based on $|F|$ and 8193 data with $|F| > 4\sigma(|F|)$] and wR2 = 0.0975 for 8629 independent reflections ($2\theta_{max} = 57.8°$) and 457 parameters. The final difference map extremes were +1.14 and −0.78 e Å^{-3}. The Flack parameter was 0.02(2). The absorption correction was carried out using SADABS.[19]

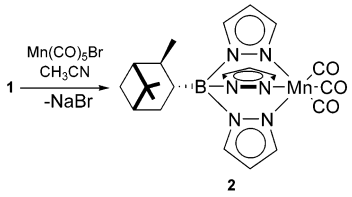
Crystallographic data for the structures reported in this paper have been submitted to CCDC and allocated reference numbers as follows: {isopinocampheyltris(pyrazolyl)borato}tricarbonylmanganese (**2**), ref 218508; [(*p*-cymene){isopinocampheyltris(pyrazolyl)borato}-ruthenium] hexafluorophosphate (**3**), ref 218509. These data may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

Results and Discussion

Hydroboration of α-pinene followed by formation of its TMEDA adduct [{(Ipc)BH$_2$}$_2$(TMEDA)] (80% yield) is a valuable method for preparation, enrichment, and storage of (Ipc)BH$_2$, which is otherwise unstable.[9a] Release of the monomeric species is easily achieved by treatment of this adduct with boron trifluoride etherate. Since all reactions are conducted in ether, the products are always the etherate complexes but for clarity represented throughout the article as the free species. The hydrides in (Ipc)BH$_2$ can be exchanged for chloride through reaction with hydrogen chloride in ether.[9b] Distillation affords the desired IpcBCl$_2$ (88% yield) in its free form as a colorless liquid and not as the etherate complex which is a white solid. This product is pyrophoric and reacts violently with water, protic solvents, or weak Lewis bases such as acetone. It is therefore recommended to store IpcBCl$_2$ as a dilute hexane solution, and in this form it offers no additional problems to the synthetic sequences to be performed. It is also possible to prepare standard solutions in other solvents, although coordinating solvents such as THF, ether, or Me$_2$S will form the corresponding adducts.

Reaction of (Ipc)BCl$_2$ with sodium pyrazolide, Na(Pz), proceeds without difficulties in dry THF to provide Na[(Ipc)B(Pz)$_3$] (**1**). Purification is easily achieved by removing the THF, redissolving the residue in hexane, and filtering to remove formed sodium chloride (Scheme 1); removal of the solvent provided the product in 87% yield. Alternative routes to **1** in which (Ipc)BCl$_2$ is treated with an excess of pyrazole

Scheme 2. Synthesis of [IpcB(pz)$_3$Mn(CO)$_3$]



were hampered by contamination of the product with pyrazole from which **1** is difficult to separate. However, signals for free pyrazole were absent from the ^{1}H and ^{13}C NMR spectra of **1** produced using preformed sodium pyrazolide. The boron bound carbon atom of the Ipc group appears as a broad signal at 28.3 ppm. A clear molecular ion ($m/z = 349$) for the [(Ipc)B(Pz)$_3$]$^-$ anion is observed in the negative ion FAB mass spectrum. The high solubility of **1** in all solvents hampered attempts at crystallization and crystals suitable for X-ray crystallography have not been obtained. Alternative routes to **1** from (Ipc)BH$_2$ and Na[(Ipc)-BH$_3$] which would avoid the need for its conversion to (Ipc)-BCl$_2$ were not explored as our previous attempts at the synthesis of related ligands by pyrolysis of precursor azole heterocycles with Na[(*n*-C$_4$H$_9$)BH$_3$] had shown that *β*-H elimination from the butyl group occurred at the temperatures required for these reactions. Such elimination would be predicted to be more fascile from the isopinocampheyl group which is bound to boron via a secondary carbon atom, and indeed this was observed to occur for Na[(Ipc)BH$_3$] during reactions in toluene under reflux.

The hygroscopic Na[(Ipc)B(pz)$_3$] (**1**) proved to be a convenient source of [(Ipc)B(pz)$_3$]$^-$ anion in the preparation of two different transition metal complexes. The reaction of **1** with [Mn(CO)$_5$Br] in acetonitrile under reflux provided [(Ipc)B(Pz)$_3$Mn(CO)$_3$] (**2**) and sodium bromide (Scheme 2).[20] Simple water extraction allows the sodium salt to be removed from the product, which is obtained in a virtually pure state. The boron bound carbon atom in **2** again provides a characteristically broad signal in the ^{13}C NMR spectrum at 24.5 ppm, and the mass spectrum contains a signal for the molecular ion at $m/z = 488$ and also those for successive loss of the three CO ligands. The toluene solution infrared spectrum of **2** contains bands at 1927 and 2031 cm^{-1} due to C−O stretching modes indicative of pseudo-C_{3v} symmetry at the metal center. However, in the spectrum recorded from a solid sample as a KBr disk, the lower energy band splits into two (1934 and 1942 cm^{-1}) while that at 2031 cm^{-1} remains unchanged. X-ray crystallography shows there to be two independent molecules of **2** in the unit cell (see below); however, if this were the cause of the difference between the solution and solid-state infrared spectra, both bands in the solution spectrum would be expected to split, a feature we have observed in the complex [{hydrotris-(methimazolyl)borato}tricarbonyl manganese].[21] It is there-

(18) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.
(19) Sheldrick, G. M. *SADABS*, version 2.04; University of Göttingen: Göttingen, Germany, 2002.
(20) Experimental procedure similar to that reported by the following: Bailey, P. J.; Lanfranchi, M.; Marchio, L.; Parsons, S. *Inorg. Chem.* **2001**, *40*, 5030.
(21) Bailey, P. J.; McCormack, C.; Parsons, S. *Inorg. Chim. Acta* **2003**, in press.

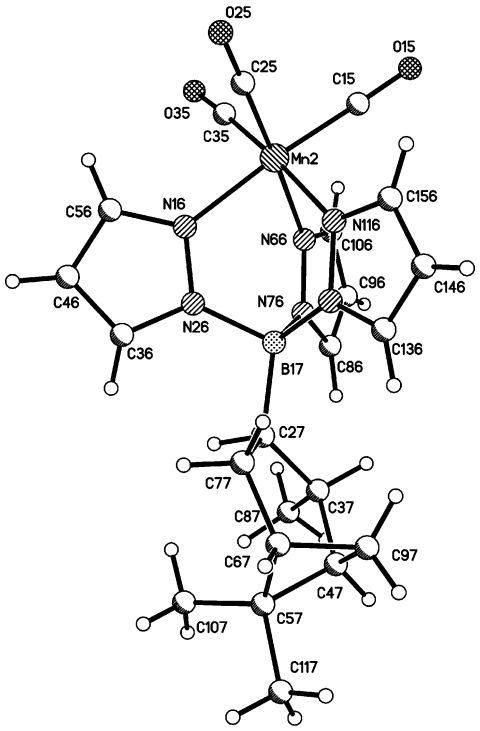
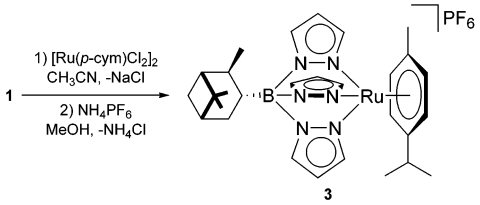


Figure 2. Crystal structure of $[IpcB(pz)_3Mn(CO)_3]$ (**2**).

Scheme 3. Synthesis of $[IpcB(pz)_3Ru(p\text{-cymene})]PF_6$



fore possible that while in solution the asymmetry of the Ipc group is not effectively communicated to the metal site; in the more constrained environment of the crystal the C_1 molecular symmetry of **2** is manifest in the three infrared bands.

Crystals of compound **2** were grown via slow diffusion of pentane into a solution of the complex in 1,2-dichloroethane. An X-ray crystal structure determination shows there to be two independent molecules in the unit cell, and the structure of one of these (containing Mn2) is represented in Figure 2. Selected bond lengths and angles are provided in Table 1. The planes of the pyrazole rings are parallel to the B−Mn vector, and no twisting distortion of the structure induced by the bulk of the Icp group is therefore evident. The most sterically demanding group within the Ipc unit, the methyl group attached to the carbon α to the boron bound carbon atom, is located neatly between two of the pyrazole rings. Slight distortion of the geometry at boron is indicated by the N−B−C27 angles [117.1(4), 117.1(4), 108.1(3) °], indicating some steric congestion between the pyrazole rings containing N76 and N126 and the Ipc group. A space-filling model indicates that this distortion is induced by the close approach of the axial hydrogen atom attached to C77 of the Ipc group and the hydrogen atom attached to C36 in the 3-position of the pyrazole ring containing N26. It is therefore

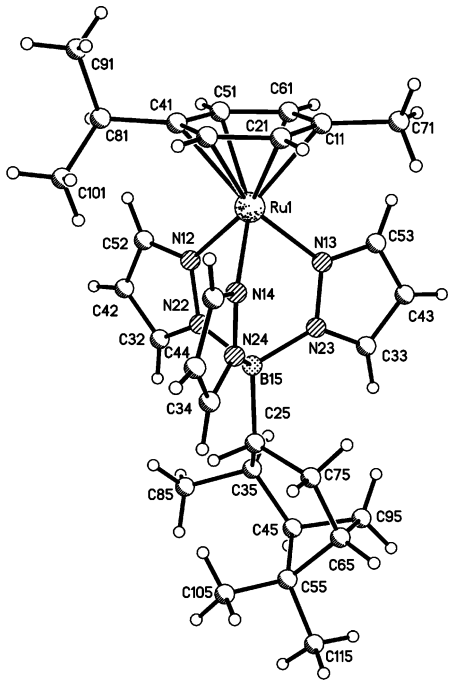


Figure 3. Crystal structure of $[IpcB(pz)_3Ru(p\text{-cymene})]PF_6$ (**3**).

clear that the presence of any substituents in the pyrazole 3-positions would result in severe congestion, resulting either in an inability of the pyrazole rings to adopt the orientations necessary for tripodal coordination or serious distortion of the resulting complexes. The absence of serious steric problems at the boron center is indicated by the B−C (1.657 Å) and B−N distances (range 1.576−1.584 Å) which are entirely normal. The geometry at the manganese center shows only small deviations from octahedral, the angles ranging from 84.70(19) to 94.0(2)°, thus indicating the close match of the tripodal ligand geometry to the size of the metal center.

Reaction of **1** with $[Ru(p\text{-cymene})Cl_2]_2$ in acetonitrile at room temperature produced $[(Ipc)B(pz)_3Ru(p\text{-cymene})]Cl$, which was not isolated but dissolved in methanol and treated with an excess of NH_4PF_6 to afford $[(Ipc)B(pz)_3Ru(p\text{-cymene})]PF_6$ (**3**) (Scheme 3).[22] The broad signal for the boron bound carbon atom appears at 24.6 ppm in the ^{13}C NMR spectrum, and the mass spectrum contains a molecular ion signal at $m/z = 586$ and a weaker one at $m/z = 449$ corresponding to loss of the arene ligand. The presence of the chiral Ipc group in the complex renders the *p*-cymene arene C−H protons pairwise diasteriotopic. However, the remoteness of the arene ligand from the Icp group means that little effect is observed in this AA′BB′ spin system. Crystals of compound **3** for X-ray diffraction were obtained by slow diffusion of ether into an acetonitrile solution, and the structure is represented in Figure 3. Bond lengths and angles are provided in Table 1. The orientation of the Ipc group relative to the $B(Pz)_3$ unit is very similar to that found in **2** as described above, and the N−B−C25 angles at boron are similarly distorted [115.8(2), 118.5(2), 107.5(2)°]. The N−M−N angles are somewhat more acute than those in **2**

(22) Experimental procedure similar to that reported by the following: Bhambri, S.; Tocker, D. A. *Polyhedron* **1996**, *15*, 2763.

consistent with the larger size of ruthenium. The arene ligand is rather unsymmetrically coordinated with bond lengths to the carbon atoms varying over a range of ca. 0.24 Å.

Conclusions

A new route toward boron-substituted tris(pyrazolyl)-borates has been developed not only affording an entry into a new class of ligands but also providing a general synthetic scheme that can be used to prepare other boron centered ligands. Our ultimate aim in this work is an exploration of the application of chiral tripod ligands in asymmetric catalysis at octahedral metal centers. For this to be effective complexes of C_3 symmetry are required and the chirality of the ligand must efficiently be communicated to the metal center. The C_1 symmetry of the isopinocampheyl group and its remoteness from the metal binding site in our new ligand suggest that asymmetric induction in complexes of this ligand would at best be inefficient. However, this was not our objective in preparing this ligand; rather we wished to demonstrate the effectiveness of (Ipc)BCl_2 as a reagent for the construction of borate-centered tripod ligands containing a chiral, boron bound substituent. Our next step is the use of alternative donor groups to provide ligands which generate C_3-symmetric complexes on binding to a metal center. The boron bound Ipc group may be employed to direct the chirality of the structure formed either during ligand synthesis or metal complexation. In the case of hydrotris(pyrazolyl)-borate ligands reduction of the pseudo C_{3v} symmetry of its complexes to C_3 has been achieved in two different ways. The introduction of bulky substituents into the pyrazole rings, as in the example of the tris(3,5-di-*tert*-butylpyrazolyl)-hydroborate ligand, induces a propeller-like twisting distortion of the metal−ligand unit due to intraligand repulsions between the *tert*-butyl groups.[23] Although this distortion is clearly not stereoselective in the parent Tp ligand, the presence of a homochiral group attached to boron would provide diasteroselective control of the induced twist. As alluded to above, the proximity of the Ipc group to the 3-positions of the pyrazole rings means that any substitution at this position would be expected to result in such a distortion. The Tp ligand containing menthyl rings fused to the 3,4-positions of the pyrazole donor groups (Tp^{menth}) has been explored extensively by Tolman.[24] The Cu(I) complex of this ligand has been shown to provide high enantioselectivity (up to 85% ee) in the cyclopropanation of styrene. The corresponding camphenyl derivative (Tp^{camph}) has recently been shown to provide 40% ee in the same reaction.[25] The utility of the (Ipc)BCl_2 reagent in the construction of tripodal borate ligands with a homochiral boron substiuent demonstrated here should therefore provide access to a range of C_3-symmetric tripod ligands containing pyrazole and other donor groups with potential applications in asymmetric catalysis, and we continue to explore these possibilities.

Acknowledgment. We acknowledge the financial support provided through the European Community's Human Potential Program under Contract HPRN-CT-2001-00187 (AC3S).

Supporting Information Available: Crystallographic information files (CIF) for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035061N

(23) Dowling, C. M.; Leslie, D.; Chisholm, M. H.; Parkin, G. *Main Group Chem.* **1995**, *1*, 29.
(24) (a) LeCloux, D. D.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, *115*, 153. (b) LeCloux, D. D.; Keyes, M. C.; Osawa M.; Reynolds, V.; Tolman, W. B. *Inorg. Chem.* **1994**, *33*, 6361. (c) LeCloux, D. D.; Tokar, C. J.; Keyes, M. C.; Osawa M.; Houser, R. P.; Tolman, W. B. *Organometallics* **1994**, *13*, 2855.
(25) Babbar, P.; Brunner, H.; Singh, U. P. *Indian J. Chem., Sect. A* **2001**, *40*, 225.