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# Multitopic third generation tris(pyrazolyl)methane ligands built on alkyne structural scaffolding: first preparation of mixed tris(pyrazolyl)methane/tris(pyrazolyl)borate ligands

**Daniel L. Reger,* James R. Gardinier, Selma Bakbak,† Radu F. Semeniuc, Uwe H. F. Bunz† and Mark D. Smith**

*Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA. E-mail: Reger@mail.chem.sc.edu*

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A series of new multitopic ligands with rigid linear geometry are formed by joining tris(pyrazolyl)methane and tris(pyrazolyl)borate units with arenyl and alkynyl linkers using Sonogashira and related alkynyl coupling reactions. These ligands are new examples of "third generation" poly(pyrazolyl)borate and poly(pyrazolyl)methane ligands, ligands functionalized at the non-coordinating "back" positions of either the boron or central carbon atoms. The reaction of $Na[OCH_2C(pz)_3]$ with propargyl bromide yields $HC_2CH_2OCH_2C(pz)_3$ (**2**) and homocoupling of this alkyne yields $[\text{-}C_2CH_2OCH_2C(pz)_3]_2$. The reaction of $Na[OCH_2C(pz)_3]$ with 3,5-$(BrCH_2)_2C_6H_3I$ yields 3,5-$[(pz)_3CCH_2OCH_2]_2C_6H_3I$ (**4**), which can be converted to 3,5-$[(pz)_3CCH_2OCH_2]_2C_6H_3(C_2H)$ (**6**) by reaction with $HC_2SiMe_3$ followed by removal of the $SiMe_3$ group. Compounds **4** and **6** can be combined to form {3,3′,5,5′-$[(pz)_3CCH_2OCH_2]_4$(1,1′-$C_6H_3C_2C_6H_3$) (**7**) and **6** homocoupled to form {3,5-$[(pz)_3CCH_2OCH_2]_2C_6H_3C_2$-}$_2$. Compound **6** reacts with *p*-$I_2C_6H_4$ to produce 3,3′,5,5′-$[(pz)_3CCH_2OCH_2]_4$[*p*-(1,1′-$C_6H_3C_2)_2C_6H_4$], which can also be formed by the reaction of **4** with bis(ethynyl)benzene. The reaction of **2** with Fe[(*p*-$IC_6H_4$)B$(pz)_3]_2$ yields the bitopic, metalloligand Fe$[(pz)_3CCH_2OCH_2$-$C_2$-$C_6H_4B(\kappa^3$-*N*,*N*′,*N*″-$pz)_3]_2$ (**10**) and a similar reaction with **6** yields the tetratopic metalloligand Fe[{3,5-$[(pz)_3CCH_2OCH_2]_2C_6H_3C_2$}$C_6H_4B(\kappa^3$-*N*,*N*′,*N*″-$pz)_3]_2$. The molecular structures of **2**, **4**, **7**, and **10** · $4CH_2Cl_2$ are reported and their supramolecular structures, organized by a series of CH···I and CH–π interactions, are detailed.

## Introduction

The design of solids with specific architectures is a current topic of research that has potential applications in diverse areas from catalysis to separations to gas storage. One approach to developing such materials is to take advantage of the coordination chemistry of metals with carefully designed multitopic ligands. The construction of robust and fairly predictable architectures can be achieved by synthetically tailoring the length between and geometric disposition of the ligating units in rigidly linked organic frameworks.[1] Studies using more flexible ligand architectures are less numerous but are potentially more attractive in the sense that one can envision shape-adaptable architectures whose final structure could be environmentally dependent, similar to proteins, for example.[2]

Our group has been developing the chemistry of semi-rigid, multitopic tris(pyrazolyl)methane ligands initially of the type $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ ($n$ = 2, 3, 4, 6; pz = pyrazolyl ring).[3] These ligands, when bound to metals, are structurally adaptive in that their final molecular and supramolecular structures depend on the nature of the metal, the anion, and included solvent, among other factors.[3a] The multiple coordination modes of the $C(pz)_3$ unit and inherent functionalities such as the π-systems, the acidic hydrogens of the arene and pyrazolyl groups as well as on the ethereal arms have resulted in a variety of structurally magnificent compounds organized by non-covalent interactions. In order to develop more sophisticated architectures based on intermolecular interactions it is necessary to introduce new functionalities into the ligand backbones. Alkynes are very attractive functional groups to build into these types of ligands because they have a fixed, linear geometry, they can become involved in π-stacking interactions, and they are good ligands to a variety of metals.

We now report the synthesis of a new family of semi-rigid linked tris(pyrazolyl)methane ligands that take advantage of Sonogashira coupling reactions[4] to give phenylalkynyl based systems. These compounds represent a new class of "third generation" poly(pyrazolyl)borate and poly(pyrazolyl)-methane ligands,[5] ligands specifically functionalized at the non-coordinating "back" position of the scorpionate.[5] In poly(pyrazolyl)methane chemistry, the derivatization of the central carbon in $HC(pz)_3$ to the alcohol $HOCH_2C(pz)_3$[3j] then to the linked ligands of the type $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ was our first development of "third generation" tris(pyrazolyl)methane compounds.[3] The use of Sonogashira coupling reactions with Fe[(*p*-$IC_2C_6H_4$)B(3-Mepz)$_3]_2$ to produce compounds of the formula Fe[(*p*-$RC_2C_6H_4$)B(3-Mepz)$_3]_2$ (R = H, $Me_3Si$, Ph) was our first development of "third generation" poly(pyrazolyl)borate ligands.[5] By utilizing this alkyne coupling methodology, we report here the preparation of the first compounds containing both a tris(pyrazolyl)methane and a tris(pyrazolyl) borate ligating unit that can be considered "third generation" at each site. Future studies will be directed at exploring the coordination chemistry of these ligands.

† Current address: School of Chemistry and Biochemistry, Georgia Institute of Technology, 770 State Street, Atlanta, GA 30332, USA. *Fax:* (+1) 404-385-1795.

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## Experimental

### General considerations

All operations were carried out under a nitrogen atmosphere by using either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 inert atmosphere dry box, unless otherwise specified. Solvents for synthetic procedures and spectroscopic studies were dried by conventional methods and distilled under $N_2$ atmosphere immediately prior to use. All chemicals were purchased from Aldrich Chemicals. The compounds $HOCH_2C(pz)_3$ (**1**),[3j] 3,5-di(bromomethyl)iodobenzene,[6] 4-ethynylphenyl-terpyridine,[7] and $Fe[(IC_6H_4)B(pz)_3]_2$,[8] were prepared by literature procedures. Robertson Microlit Laboratories performed all elemental analyses. Melting point determinations were made on samples contained in glass capillaries by using an Electrothermal 9100 apparatus and are uncorrected. Mass spectrometric measurements recorded in ESI(±) mode were obtained on a Micromass Q-Tof spectrometer whereas those performed by using direct probe analyses were made on a VG 70S instrument. NMR spectra were recorded by using either a Varian Gemini 300 or a Varian Mercury 400 instrument, as noted within the text. Chemical shifts were referenced to solvent resonances at $\delta_H$ 7.27 and $\delta_C$ 77.23 for $CDCl_3$; and $\delta_H$ 2.05 and $\delta_C$ 29.15 for acetone-$d_6$.

### Syntheses

**$HC_2CH_2OCH_2C(pz)_3$ (2).** Tris-2,2,2-(1-pyrazolyl) ethanol, $HOCH_2C(pz)_3$ (5.67 g, 23.2 mmol) was dissolved in 150 mL dry THF and was added dropwise over 30 min *via* cannula to a suspension of 0.930 g NaH (23.1 mmol) in 50 mL dry THF. The mixture was stirred and heated at reflux for 2 h, then propargyl bromide, $HCCCH_2Br$ (2.76 g, 23.2 mmol), was injected *via* syringe. After the mixture was heated at reflux for 24 h, 100 mL $H_2O$ was carefully added. The organic and aqueous portions were separated, the aqueous portion was extracted with two 100 mL portions of $CH_2Cl_2$, then the combined organic extracts were washed with 100 mL saturated $NaHCO_3$ solution and water (3 × 100 mL). After separation, the organics were dried over anhydrous $Na_2SO_4$, filtered, and the solvent was removed by rotary evaporation to give a brown solid residue. After chromatography on silica gel with hexane : ethyl acetate (1 : 1) as eluent 3.35 g (52%) of **2** was obtained as a colorless solid. Mp 75–76 °C. Anal. Calcd (Obs) for $C_{14}H_{14}N_6O$: C, 48.00 (48.32); H, 4.03 (3.89); N, 23.99 (24.26%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.67 (d, $J$ = 1 Hz, 3H, $H_3$-pz), 7.42 (d, $J$ = 2 Hz, 3H, $H_5$-pz), 6.38 (d of d, 3H, $J$ = 2,1 Hz, $H_4$-pz), 5.00 (s, 2H, $OCH_2C(pz)_3$), 4.20 (d, 2H, $J$ = 2.5 Hz, $OCH_2CC$), 2.43 (m, 1H, CCH); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta$ 141.6 ($C_3$-pz), 131.0 ($C_5$-pz), 106.8 ($C_4$-pz), 89.5 ($C_\alpha$), 78.7, 76.0 (C≡C), 73.0 ($CH_2$), 59.4 ($CH_2$). $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ 7.61 (d, $J$ = 1 Hz, 3H, $H_3$-pz), 7.47 (d, $J$ = 2 Hz, 3H, $H_5$-pz), 6.36 (d of d, 3H, $J$ = 2,1 Hz, $H_4$-pz), 5.17 [s, 2H, $OCH_2C(pz)_3$], 4.23 (d, 2H, $J$ = 2.4 Hz, $OCH_2CC$), 3.10 (m, 1H, CCH); $^{13}$C NMR (75.4 MHz, acetone-$d_6$): $\delta$ 141.2 ($C_3$-pz), 131.3 ($C_5$-pz), 106.6 ($C_4$-pz), 90.0 ($C_\alpha$), 79.3, 76.8 ((C≡C),), 72.9 ($CH_2$), 59.0 ($CH_2$); High Res ESI(+) MS Calculated for [M + Na] [$C_{14}H_{14}N_6ONa$], 305.1127, found 305.1134.

**[–$C_2CH_2OCH_2C(pz)_3$]$_2$ (3).** A mixture of 0.600 g (2.13 mmol) $HC_2CH_2OCH_2C(pz)_3$ and 3.86 g (21.0 mmol) anhydrous $Cu(OAc)_2$ in 30 mL acetonitrile was stirred at 70 °C for 6 h. The mixture was then partitioned between 150 mL each of $CH_2Cl_2$ and water, the organic fraction was collected and the aqueous fraction was extracted with three 50 mL portions of $CH_2Cl_2$. The combined organics were dried over $Na_2SO_4$, filtered and solvent was removed under vacuum to leave 0.540 g (90%) crude **3** as a pale yellow solid. Purification of the crude yellow solid by column chromatography on silica gel with $Et_2O$ as the eluent ($R_f$ = 0.6) afforded 0.502 g (84%) pure **3** as a colorless solid. Mp 143–145 °C. Anal. Calcd (Obs) for $C_{28}H_{26}N_{12}O_2$: C, 59.78 (59.39); H, 4.66 (4.89); N, 29.88 (29.53%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$7.67 (d, $J$ = 1.6 Hz, 6H, $H_3$-pz), 7.39 (d, $J$ = 2.5 Hz, 6H, $H_5$-pz), 6.35 (dd, 6H, $J$ = 2,1 Hz, $H_4$-pz), 5.19 [s, 4H, $OCH_2C(pz)_3$], 4.24 (s, 4H, $OCH_2CC$); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta$ 141.4 ($C_3$-pz), 130.7 ($C_5$-pz), 106.6 ($C_4$-pz), 89.5 ($C_\alpha$), 74.9, 73.4 (C≡C), 71.4 ($CH_2$), 60.0 ($CH_2$); Accurate ESI(+) MS Calculated for [M + H] [$C_{28}H_{27}N_{12}O_2$], 563.2380, found 563.2387.

**3,5-[$(pz)_3CCH_2OCH_2$]$_2C_6H_3I$ (4).** A solution of 0.463 g (1.19 mmol) 3,5-$(BrCH_2)_2C_6H_3I$ in 20 mL THF was added *via* cannula to a 40 mL THF solution containing 2.38 mmol $NaOCH_2C(pz)_3$ [generated *in situ* from 0.580 g (2.38 mmol) $HOCH_2C(pz)_3$ and an excess of NaH (0.067 g, 2.79 mmol)]. The resulting mixture was stirred and heated at reflux for 12 h. Water was carefully added, followed by 100 mL of methylene chloride. The aqueous and organic fractions were separated; the aqueous fraction was extracted with three 100 mL portions of $CH_2Cl_2$. The combined organic portions were washed with 100 mL, 6 wt% $NaHCO_3$ [to remove any unreacted $HOCH_2C(pz)_3$], then with 100 mL $H_2O$. The organics were dried over $MgSO_4$, filtered and solvent was removed by rotary evaporation to leave a pale yellow oil. The oil was adsorbed onto a pad of silica and loaded on a short pad of fresh silica. The plug was first flushed with $CH_2Cl_2$ to remove an unidentified impurity (TLC $R_f$ = 0.75), and then with $Et_2O$ to elute the desired product (TLC $R_f$ = 0.75). Removing diethyl ether by rotary evaporation left a colorless oil that was triturated with 5 mL hexanes to give a colorless solid. The hexane solution was decanted, and the remaining solid was dried under vacuum to give 0.768 g (90%) of pure **4** as a colorless solid. Crystals suitable for X-ray diffraction were grown by dissolving a portion in $Et_2O$ and adding an equal volume of hexanes and allowing the solution to evaporate slowly. Mp 124–127 °C. Anal. Calcd. (Obs.) for $C_{30}H_{29}N_{12}O_2I$: C, 50.29 (50.34); H, 4.08 (4.26); N 23.46 (23.28%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.67 (d, $J$ = 1 Hz, 6H, $H_3$-pz), 7.41 (d, $J$ = 3 Hz, 6H, $H_5$-pz), 7.38 (m, 2H, $C_6H_3I$), 6.92 (s, 1H, $C_6H_3I$), 6.36 (dd, 6H, $J$ = 3,1 Hz, $H_4$-pz), 5.11 (s, 4H, $OCH_2C(pz)_3$), 4.43 (s, 4H, $OCH_2CC$); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta$ 141.6 ($C_3$-pz), 139.7 (aryl), 136.2 (aryl), 131.1 ($C_5$-pz), 126.1 ($C_4$-aryl), 106.8 ($C_4$-pz), 94.7 ($C_i$-I), 89.7 ($C_\alpha$), 73.9 ($CH_2$), 73.3 ($CH_2$). Accurate ESI(+) MS Calculated for [M + H] [$C_{30}H_{30}N_{12}O_2I$] 717.1659, found 717.1653.

**3,5-[$(pz)_3CCH_2OCH_2$]$_2C_6H_3(C_2SiMe_3)$ (5).** A Schlenk tube containing 1.83 g (2.55 mmol) of 3,5-[$(pz)_3CCH_2OCH_2$]$_2$-$C_6H_3I$, 90 mg (0.13 mmol, 6 mol%) $Pd(PPh_3)_2Cl_2$, and 24 mg (0.13 mmol, 6 mol%) CuI was evacuated and backfilled with nitrogen three times. Dry THF (10 mL) and piperidine (5 mL) were added by syringe through a septum secured by copper-wire, the resulting mixture was frozen (−196 °C), evacuated, and backfilled with $N_2$. Next, 1.0 mL (7.2 mmol $HC_2SiMe_3$) was added to the frozen mixture under a $N_2$ blanket by syringe. The mixture was placed in an external 60 °C water bath (the stopcock was momentarily opened to the nitrogen line bubbler to relieve excess pressure) and was stirred at 60 °C for 8 h, then at room temperature overnight. The mixture was poured into 100 mL $H_2O$ and the aqueous phase was extracted with three 100 mL portions of $CH_2Cl_2$ followed by one 100 mL portion of $Et_2O$. The combined organics were dried over $MgSO_4$, filtered and solvent was removed to give a brown oil. The oil was subject to chromatography on $SiO_2$, the column was first eluted with methylene chloride to remove fast-moving impurities then with $Et_2O$ where the desired product elutes near the solvent front. A second chromatographic

separation on basic $Al_2O_3$ with $CH_2Cl_2$ as the eluent ($R_f$ 0.8) affords the desired compound as a colorless semi-solid (1.4 g 82%). Anal. Calcd. (Obs.) for $C_{35}H_{38}N_{12}O_2Si$: C, 61.20 (60.71); H, 5.58 (5.84%). $^1$H NMR ($CDCl_3$): $\delta$ 7.67 (d, $J = 1$ Hz, 6H, $H_3$-pz), 7.42 (d, $J = 2$ Hz, 6H, $H_5$-pz), 7.17 (br s, 2H, $C_6H_3I$), 6.92 (s, 1H, $C_6H_3I$), 6.34 (dd, 6H, $J = 2$, 1 Hz, $H_4$-pz), 5.11 (s, 4H, $OCH_2C(pz)_3$), 4.44 (s, 4H, $OCH_2CC$), 0.27 (s, 9H, $SiCH_3$); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta$ 141.6 ($C_3$-pz), 137.7 (aryl), 131.1 ($C_5$-pz), 130.9 (aryl), 127.1($C_4$-aryl), 123.7 ($C_i$-Si), 106.8 ($C_4$-pz), 104.7, 94.9 (C≡C), 90.0 ($C_\alpha$), 73.8 ($CH_2$), 73.7 ($CH_2$), 0.15 ($SiCH_3$). Accurate ESI(+) MS Calculated for [M + H] [$C_{35}H_{39}N_{12}O_2Si$], 687.3088, found 687.3080.

**3,5-[(pz)$_3$CCH$_2$OCH$_2$]$_2$C$_6$H$_3$(C$_2$H) (6).** A 4.4 mL (4.4 mmol) aliquot of a 1.0 M $NBu_4F$ solution in THF was added to a solution of **5** (3.00 g, 4.40 mmol) in 5 mL THF. After the mixture had stirred for 30 min, it was partitioned between 50 mL $CH_2Cl_2$ and 100 mL $H_2O$. The organic and aqueous phases were separated and the aqueous phase was extracted with three 50 mL portions of $CH_2Cl_2$. The combined organics were dried over $Na_2SO_4$, filtered and solvent was removed by rotary evaporation to leave 2.65 g (88%) **6** as a nearly colorless, pale yellow solid. Mp 102–103 °C. Anal. Calcd. (Obs.) for $C_{32}H_{30}N_{12}O_2$: C, 62.53 (62.22); H, 4.92 (4.91); N, 27.34 (27.27%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.67 (d, $J = 1$ Hz, 6H, $H_3$-pz), 7.43 (d, $J = 2$ Hz, 6H, $H_5$-pz), 7.20 (br s, 2H, $C_6H_3$), 6.95 (br s, 1H, $C_6H_3$), 6.35 (dd, 6H, $J = 2$, 1 Hz, 6H, 4-*H* pz), 5.13 (s, 4H, $OCH_2C(pz)_3$), 4.46 (s, 4H, $OCH_2CC$), 3.08 (s, 1H, CCH); $^{13}$C NMR ($CDCl_3$): $\delta$ 141.6 ($C_3$-pz), 137.9 (aryl), 131.1 ($C_5$-pz), 130.9 (aryl), 127.4 (aryl), 122.6 (aryl), 106.8 ($C_4$-pz), 90.0 ($C_\alpha$), 83.3 (C≡C), 77.7 (C≡C), 73.8 ($CH_2$), 73.6 ($CH_2$); Accurate ESI(+) MS: Calcd. for [M + H] [$C_{32}H_{31}N_{12}O_2$], 615.2693, found 615.2684.

**{3,3′,5,5′-[(pz)$_3$CCH$_2$OCH$_2$]$_4$(1,1′-C$_6$H$_3$C$_2$C$_6$H$_3$) (7).** A mixture of 5.00 g (7.00 mmol) **4** and 4.30 g (7.0 mmol) **6** was dissolved in THF (5 mL) and purged with $N_2$. Under a nitrogen blanket $Pd(PPh_3)_2Cl_2$ (100 mg, 2 mol%), CuI (67 mg, 5 mol%), and piperidine (5 mL) were each added to the mixture. The flask was flushed for 15 min with a slow stream of nitrogen then an additional 5 mL of THF was added. The mixture was stirred overnight in a 60 °C water bath, then 100 mL methylene chloride was added. After aqueous work up (washing with $H_2O$ and brine), crude **7** was obtained as a light yellow solid (8.85 g 74%). Purification was achieved by adsorbing crude **7** onto a pad of silica, loading the silica onto a pad of fresh silica, eluting with $Et_2O$ to remove any impurities, then with THF to give the desired product that moves with the solvent front. Removing solvent by rotary evaporation, triturating with $Et_2O$, filtering, and drying the colorless $Et_2O$ insoluble solid under vacuum afforded **7**·$H_2O$. Mp 207–209 °C (decomp.). Anal. Calcd (Obs) for $C_{62}H_{60}N_{24}O_5$: C, 60.97 (60.51); H, 4.86 (4.75); N, 27.52 (27.13%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.67 (d, $J = 1$ Hz, 12H, $H_3$-pz), 7.43 (d, $J = 2$ Hz, 12H, $H_5$-pz), 7.25 (s, 4H, $C_6H_3$), 6.96 (s, 2H, $C_6H_3$), 6.35 (dd, $J = 2$, 1 Hz, 12H, $H_4$-pz), 5.14 [s, 8H, $OCH_2C(pz)_3$], 4.48 (s, 8H, $OCH_2CC$), 1.62 (br s, 2H, $H_2O$); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta$ 141.6 ($C_3$-pz), 138.0 (aryl), 131.1 ($C_5$-pz), 130.5 (aryl), 127.1 (aryl), 123.6 (aryl), 106.8 ($C_4$-pz), 90.0 ($C_\alpha$), 89.4 (C≡C), 73.84 ($CH_2$), 73.79 ($CH_2$); Accurate ESI(+) MS Calculated for [7 + H], [$C_{62}H_{59}N_{24}O_4$], 1203.5151, found 1203.5127.

**{3,5-[(pz)$_3$CCH$_2$OCH$_2$]$_2$C$_6$H$_3$C$_2$-}$_2$ (8).** 2.47 g (12.4 mmol) $Cu(OAc)_2 \cdot H_2O$ was added to a solution of 0.760 g (1.24 mmol) **6** in 50 mL $CH_3CN$. The resulting heterogeneous mixture was stirred at 70 °C for 5 hours, then was added to 150 mL $H_2O$. The aqueous phase was extracted with three 100 mL portions $CH_2Cl_2$. The combined organics were dried over $MgSO_4$, filtered, and solvent was removed to leave a yellow oil. The yellow oil was adsorbed onto silica and then was added to a plug of fresh silica. The plug was fist eluted with $Et_2O$ to remove unidentified impurity, and then with THF to give the desired compound that moved with the solvent front. Solvent was removed by rotary evaporation and the residue was triturated with 10–20 mL $Et_2O$ to precipitate the product that was collected by filtration. The $Et_2O$ insoluble solid was washed with 5 mL hexanes, and dried under vacuum to leave 0.650 g (86%) of pure **8** as a colorless solid. Mp 180–182 °C. Anal. Calcd (Obs) for $C_{64}H_{58}N_{24}O_4$: C, 62.63 (62.38); H, 4.76 (4.69); N, 27.39 (27.15%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.68 (d, $J = 1$ Hz, 12H, $H_3$-pz), 7.43 (d, $J = 3$ Hz, 12H, $H_5$-pz), 7.23 (s, 4H, $C_6H_3$), 6.97 (s, 2H, $C_6H_3$), 6.36 (dd, $J = 3$, 1 Hz, 12H, 4-*H* pz), 5.13 (s, 8H, $OCH_2C(pz)_3$), 4.47 (s, 8H, $OCH_2CC$); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta$ 141.6 ($C_3$-pz), 138.1 (aryl), 131.2 (aryl), 131.1 ($C_5$-pz), 127.8 ($C_i$-aryl), 122.3 ($C_i$-aryl), 106.8 ($C_4$-pz), 90.0 ($C_\alpha$), 81.4, 74.3 (C≡C), 73.9 ($CH_2$); 73.6 ($CH_2$); ESI(+) MS Calculated for [M + H] [$C_{64}H_{39}N_{24}O_4$], 1227.5151, found 1227.5150.

**3,3′,5,5′-[(pz)$_3$CCH$_2$OCH$_2$]$_4$[p-(1,1′-C$_6$H$_3$C$_2$)$_2$C$_6$H$_4$] (9)**

***Method A.*** A mixture of 0.555 g (0.903 mmol) 3,5-[$(pz)_3CCH_2OCH_2]_2C_6H_3(C_2H)$ (**6**), 0.136 g (0.412 mmol) *p*-$I_2C_6H_4$, 0.023 g (0.033 mmol) $Pd(PPh_3)_2Cl_2$, 20 mL THF, and 10 mL piperidine was subject to two freeze–pump–thaw cycles and was frozen once more. Then, 2 mg (0.01 mmol) CuI was added under a nitrogen blanket, the vessel (sealed with a copper wire reinforced septum) was evacuated and the mixture was subject to two more freeze–pump–thaw cycles, then the flask was back filled with nitrogen. The mixture was heated to 60 °C with an external water bath, the stopcock was momentarily opened to the nitrogen line to relieve excess pressure, and the mixture was allowed to heat at 60 °C 12 h with stirring. The resulting yellow solution was added to 10 g of silica gel and solvents were removed by rotary evaporation. The dry silica gel was loaded onto a fresh pad of silica and eluted first with hexanes then $Et_2O$ to remove any unwanted impurities. Flushing the plug with with 2 : 1 (v : v) THF : hexanes elutes the desired compound in a pale yellow band (TLC $R_f = 0.8$; bright blue luminescence when irradiated with either 254 nm or 365 nm light). Evaporation of solvent, triturating the residue with hexanes, filtering and drying under vacuum afforded 0.529 g (95%) **9**·$2H_2O$ as a hygroscopic and solvophilic pale yellow solid. Mp 70 °C glass transition 95–100 °C (liq). Anal. Calcd (Obs) for $C_{70}H_{66}N_{24}O_6$: C, 62.77 (63.26); H, 4.97 (4.88); N, 25.10 (24.32%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.68 (d, $J = 1$ Hz, 12H, $H_3$-pz), 7.53 (s, 4H, $C_6H_4$), 7.44 (d, $J = 3$ Hz, 12H, $H_5$-pz), 7.26 (s, 4H, $C_6H_3$), 6.96 (s, 2H, $C_6H_3$), 6.36 (dd, $J = 3$, 1 Hz, 12H, 4-*H* pz), 5.15 (s, 8H, $OCH_2C(pz)_3$), 4.49 (s, 8H, $OCH_2CC$), 1.66 (br s, 4H, $H_2O$); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta$ 141.6 ($C_3$-pz), 138.0 ($C_6H_3$), 131.8 ($C_6H_3$), 131.1 ($C_5$-pz), 130.5 ($C_{2,3,5,6}$-$C_6H_4$), 127.1 ($C_i$-$C_6H_4$), 123.6 ($C_{4/i}$-$C_6H_3$), 123.3 ($C_{4/i}$-$C_6H_3$), 106.8 ($C_4$-pz), 91.1 (C≡C), 90.0 ($C_\alpha$), 89.6 (C≡C), 73.8 ($CH_2$); 73.7 ($CH_2$). Accurate ESI(+) MS Calculated for [**9** + H] [$C_{70}H_{63}N_{24}O_4$], 1304.5464, found 1304.5437;

***Method B.*** A 2.0 mL THF solution of 0.040 g (0.15 mmol) bis(trimethylsilylethynyl)benzene and 0.14 mL of a 1.0 M $NBu_4F$ in THF (0.14 mmol) was stirred for 30 min. The product mixture was partitioned between 50 mL each $CH_2Cl_2$ and $H_2O$, the organic phase is separated and the aqueous is extracted with an additional 50 mL $CH_2Cl_2$. The combined organics were dried over $Na_2SO_4$, filtered, and solvent was removed under vacuum, the residue (1,4-diethynylbenzene) was taken up in 10 mL THF and was transferred under nitrogen to a 4 mL nitrogen-purged solution of THF : piperidine (1 : 1) containing 0.20 g (0.28 mmol) **4**, and 5 mol% each $Pd(PPh_3)_2Cl_2$ and CuI. After the mixture had been stirred for

12 h at room temperature, it was worked up as described above to leave 0.10 g (0.074 mmol, 53% based on $NBu_4F$) of $\mathbf{9}\cdot 2H_2O$ as a yellow solid. The characterization data were identical to those found described under Method A.

### General procedure for alkyne coupling reactions involving iron borate compounds

A Schlenk flask is charged with the desired iron(II)(iodophenyl)tris(pyrazolyl)borate, $Pd(PPh_3)_2Cl_2$, terminal alkyne ($XC_2H$), THF and piperidine (*ca.* 20 mL, between 4 : 1 to 2 : 1 v/v). The reaction vessel is then subjected to three freeze–pump–thaw cycles. The reaction mixture is frozen once more, the vessel is backfilled with $N_2$, CuI is added under a $N_2$ blanket. After the reaction flask is sealed with a septum reinforced by copper wire, it is frozen, evacuated, backfilled with nitrogen once more and then placed in a 60 °C bath overnight. Then, the product mixture is adsorbed onto alumina, solvent is evaporated, and the alumina is added to a pad of fresh alumina. Eluting with hexanes eliminates any excess alkyne and homocoupled alkynyl impurities. Then, elution with $CH_2Cl_2$ affords the desired alkynylphenyl borate complex, $Fe[(X\text{-}C_2C_6H_4)B(pz)_3]_2$, in a fast moving purple band.

**$Fe[\{3,5\text{-}[(pz)_3CCH_2OCH_2]_2C_6H_3C_2\}C_6H_4B(\kappa^3\text{-}N,N',N''\text{-}pz)_3]_2$ ($\mathbf{10}\cdot CH_2Cl_2$).** This compound was prepared in quantitative yield (312 mg) as a pink solid by using 0.231 g (0.261 mmol) $Fe[IC_6H_4B(pz)_3]_2$, 0.162 g (0.574 mmol) $HC_2CH_2OCH_2C(pz)_3$, 15 mg (8 mol%) $Pd(PPh_3)_2Cl_2$, 4 mg (8 mol%) CuI, 40 mL THF and 10 mL piperidine. An additional heating period of 8 h at 80 °C was used in this case. Recrystallization by allowing a layer of MeOH to slowly diffuse into a $CH_2Cl_2$ solution at −20 °C afforded pink-purple needles of $\mathbf{10}\cdot CH_2Cl_2$. The needles lose the solvent of crystallization when collected, and this solid was used for the characterization. Mp 220 °C (decomp.), 255 °C liquefies. Anal. Calcd. (Obs.) For $C_{58}H_{52}N_{24}O_2B_2Fe$: C, 58.31 (57.71); H, 4.39 (4.12); N, 28.14 (27.84%). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.17 (part of AA′BB′, $J$ = 8 Hz, 4 H), 7.86 (d, $J$ = 1 Hz, 6 H, $H_3$-pz-C), 7.71 (br s, 6 H, $H_5$-pz-B), 7.69 (part of AA′BB′, 4 H), 7.51 (d, $J$ = 2 Hz, 6 H, $H_5$-pz-C), 7.02 (br s, 6 H, $H_3$-pz-B), 6.39 (dd, $J$ = 2,1 Hz, 6 H, $H_4$-pz-C), 6.26 (br s, 6H, $H_4$-pz-B), 5.35 (s, 4 H, $OCH_2Cpz_3$), 4.49 (s, 4 H, $OCH_2CC$). $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 149.9, 141.6, 138.7, 135.1, 131.5, 131.1, 122.1, 106.8, 89.9, 87.7, 73.1, 60.3, 46.9. Accurate ESI(+) MS: Calcd. For $M^+$: 1194.4260, Found: 1194.4302.

**$Fe[\{3,5\text{-}[(pz)_3CCH_2OCH_2]_2C_6H_3C_2\}C_6H_4B(\kappa^3\text{-}N,N',N''\text{-}pz)_3]_2$, (11).** This compound was prepared in 91% yield (301 mg) as a pink-orange solid by using 0.158 g (0.178 mmol) $Fe[IC_6H_4B(pz)_3]_2$, 0.243 g (0.395 mmol) $1\text{-}(HC_2)C_6H_3[3,5\text{-}CH_2OCH_2C(pz)_3]_2$, 25 mg (5 mol%) $Pd(PPh_3)_2Cl_2$, 6 mg (9 mol%) CuI, 10 mL THF and 5 mL piperidine. Mp 310 °C (decomp.). Anal. Calcd. (Obs.) for $C_{94}H_{84}N_{36}O_4B_2Fe$: C, 60.72 (60.32); H, 4.55 (4.59); N, 27.12 (26.28%). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.92 (br s), 8.06 (br s), 7.72 (s, 12H, $H_3$-pz-C), 7.67 (s), 7.49 (s, 12 H, $H_5$-pz-C), 7.41 (m, overlapping), 7.02 (s), 6.40 ($H_4$-pz-C), 6.36 (br, s, $H_4$-pz-B), 5.20 (s, 8H, $OCH_2Cpz_3$) , 4.56 (s, 8 H, $OCH_2CC$). ESI(+) MS: Calcd. For $M^{\bullet+}$: 1859, Found: 1859.

**Attempted preparation of $Fe[4\text{-}[4'\text{-}(4\text{-}\ C_2C_6H_4)(2,2':6,2''\text{-terpy})]C_6H_4B(\kappa^3\text{-}N,N',N''\text{-pz})_3]_2$ (12).** A mixture of 0.297 g (0.335 mol) $Fe[IC_6H_4B(pz)_3]_2$, 0.233 g (0.699 mmol) $4'\text{-}(4\text{-}HC_2C_6H_4)\text{-}2,2':6,2''$-terpy, 12 mg (8 mol%) $Pd(PPh_3)_2Cl_2$, 2 mg (5 mol%) CuI, 3 mL THF and 3 mL piperidine was heated for 8 h at 70 °C followed by 12 h at room temperature. The resulting purple solid was collected by filtration, washed with three 10 mL portions of MeOH, three 10 mL portions of $Et_2O$ and was air dried to afford 0.298 g of a very insoluble (trace solubility in either refluxing tetrachloroethane or refluxing DMF) purple solid mixture of the mono- and disubstituted compounds as identified by High Res. ESI(+) TOF MS. Calcd (obs) for $Fe[IC_6H_4B(pz)_3][(terpy)C_6H_4C_2C_6H_4B(pz)_3]$: 1091.2190 (1091.2190) and for $Fe[(terpy)C_6H_4C_2C_6H_4B(pz)_3]_2$ 1296.4338 (1296.4326).

### Crystallography

A colorless chunk sectioned from a larger crystal of $HC_2CH_2OCH_2C(pz)_3$ (**2**), an irregular colorless block sectioned from a larger crystalline mass of **4**, a colorless plate of **7**, and a purple plate of $\mathbf{10}\cdot 4CH_2Cl_2$ were each mounted onto the end of thin glass fibers using inert oil. X-Ray intensity data covering the full sphere of reciprocal space were measured at 150(1) K (**2**, **4**, **7**) or 100(1) K ($\mathbf{10}\cdot 4CH_2Cl_2$) on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda$ = 0.710 73 Å).[9] The raw data frames were integrated with SAINT+,[9] which also applied corrections for Lorentz and polarization effects. The final unit cell parameters for **2**, **4**, **7**, and $\mathbf{10}\cdot 4CH_2Cl_2$ are based on the least-squares refinement of 4515, 5607, 6918, and 9926 reflections, respectively, each with $I > 5\sigma(I)$ from the appropriate data set. Analyses of the data showed negligible crystal decay during data collection. Structures were solved by a combination of either direct methods for **2**, **7**, and $\mathbf{10}\cdot 4CH_2Cl_2$ or Patterson methods [10] for **4**, and subsequent difference Fourier syntheses, and refined by full-matrix least-squares against $F^2$, using SHELXTL.[11] Except where noted in the refinement of $\mathbf{10}\cdot 4CH_2Cl_2$, all non-hydro-

**Table 1** Summary of crystallographic data for **2**, **4**, **7**, and $\mathbf{10}\cdot 4CH_2Cl_2$

| | **2** | **4** | **7** | $\mathbf{10}\cdot 4CH_2Cl_2$ |
|---|---|---|---|---|
| Empirical formula | $C_{14}H_{14}N_6O$ | $C_{30}H_{29}IN_{12}O_2$ | $C_{62}H_{58}N_{24}O_4$ | $C_{62}H_{60}B_2Cl_8FeN_{24}O_2$ |
| Formula weight | 282.31 | 716.55 | 1203.32 | 1534.41 |
| $T$/K | 150(1) | 150.0(2) | 150.0(2) | 100(1) |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | *Cc* | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ |
| $a$/Å | 13.2954(8) | 8.7819(6) | 8.1473(5) | 8.5941(4) |
| $b$/Å | 12.4529(8) | 12.1248(8) | 34.148(2) | 13.4373(7) |
| $c$/Å | 8.5445(5) | 15.3073(10) | 11.3257(7) | 16.3188(8) |
| $\alpha$/° | 90 | 96.8400(10) | 90 | 103.9530(10) |
| $\beta$/° | 97.9170(10) | 99.5630(10) | 109.1850(10) | 98.3300(10) |
| $\gamma$/° | 90 | 105.9950(10) | 90 | 106.9990(10) |
| $V$/Å$^3$ | 1401.20(15) | 1521.48(18) | 2976.0(3) | 1701.26(15) |
| $Z$ | 4 | 2 | 2 | 1 |
| $\rho$(calcd.)/Mg m$^{-3}$ | 1.338 | 1.564 | 1.343 | 1.498 |
| $\mu$/mm$^{-1}$ | 0.091 | 1.103 | 0.091 | 0.600 |
| Final $R$ indices [$I > 2\sigma(I)$] $R1$, $wR2$ | 0.0294, 0.0625 | 0.0318, 0.0796 | 0.0639, 0.1656 | 0.0728, 0.2133 |
| $R$ indices (all data) $R1$, $wR2$ | 0.0314, 0.0630 | 0.0340, 0.0812 | 0.0815, 0.1752 | 0.0816, 0.2232 |

gen atoms were refined with anisotropic displacement parameters while hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. Crystallographic data are collected in Table 1 and further details of the structure solutions and refinement are noted for each below.

Systematic absences in the intensity data of **2** were consistent with the space groups $C2/c$ and $Cc$; intensity statistics indicated acentricity. The space group $Cc$ was verified by examination of the structure and checked with ADDSYM/PLATON.[12] Due to the lack of heavy atoms in the structure, Friedel opposites were merged during data processing and the absolute structure was not determined.

Compound **4** crystallizes in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure.

Systematic absences in the intensity data from **7** determined the space group $P2_1/c$. The molecule resides on a crystallographic inversion center. One of the pyrazolyl rings (N21–C23) is rotationally disordered about the N–$C_{methine}$ bond in equal proportions.

Compound **10**·$4CH_2Cl_2$ crystallizes in the triclinic system. The space group $P\bar{1}$ was assumed and eventually confirmed. Half of the iron cation located on an inversion center and two $CH_2Cl_2$ molecules of crystallization could be identified in the asymmetric unit. One $CH_2Cl_2$ is disordered over several orientations and was accounted for with the SQUEEZE program after several unsuccessful attempts at modeling the disorder. (61 electrons and 208.5 Å$^3$ solvent-accessible volume per unit cell.) The contribution of the disordered solvent was subtracted from the structure factors but was included in the final formula weight and calculated density. During the refinement a large residual electron density peak (2.88 e Å$^3$) persistently appeared near the midpoint of the C77–C78 triple bond, *ca.* 0.7 Å from each atom. The origin of this peak is unknown, but is responsible for the anisotropy of the displacement ellipsoids of atoms C77 and C78 as well as an unreasonably short (~1 Å) C–C bond. To correct for this, the atomic parameters for C77 and C78 were fixed at reasonable $U_{ij}$ values and a C–C bond length of 1.15 Å. This peak as well as the disorder in the crystal is the reason for the low quality of this refinement and the high final residuals.

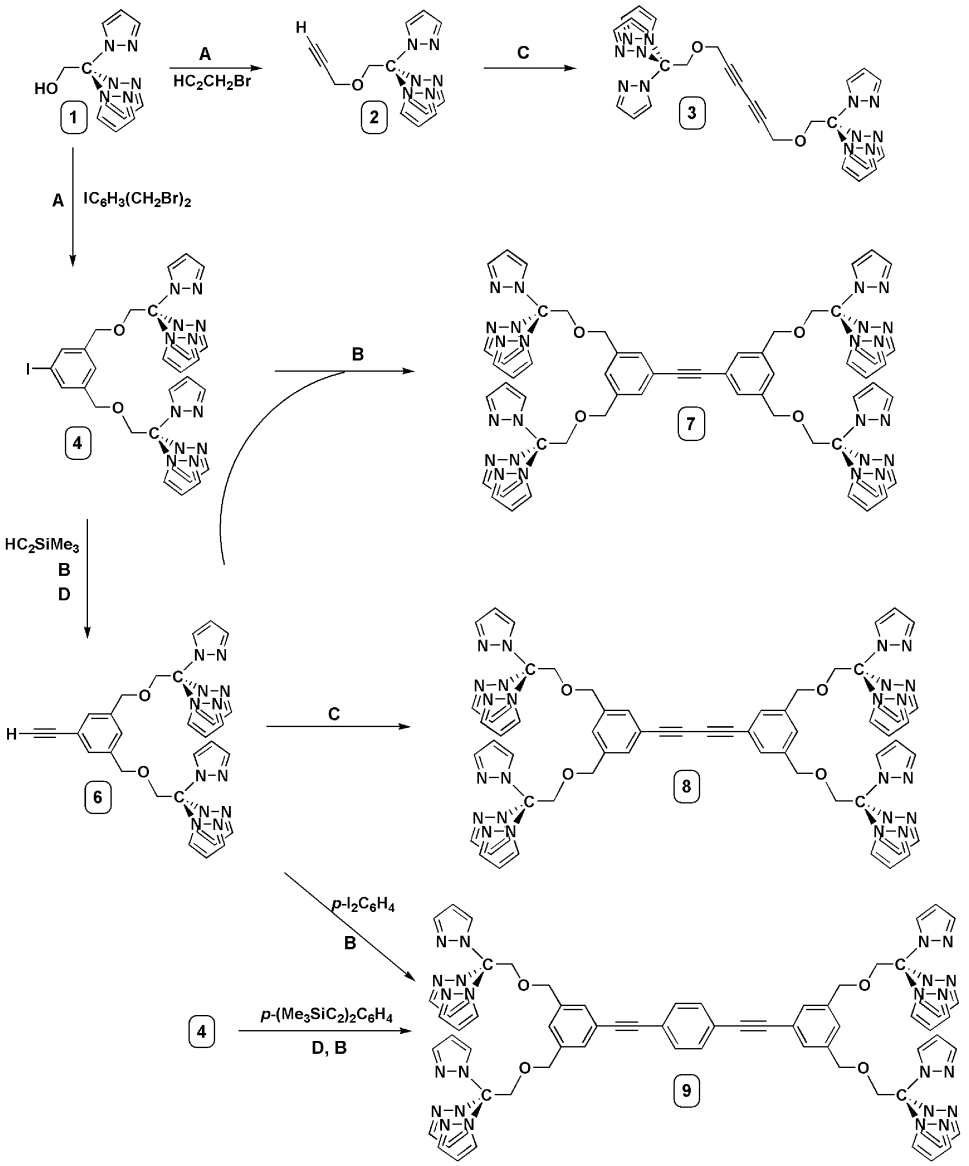
CCDC reference numbers 270421–270424.

See http://www.rsc.org/suppdata/nj/b4/b414770g/ for crystallographic data in CIF or other electronic format.

## Results and discussion

### Syntheses of tris(pyrazolyl)methane ligands

A summary of the routes to the new alkynyl-containing tris(pyrazolyl)methane ligands is given in Scheme 1. The reaction between the sodium alkoxide, $Na[OCH_2C(pz)_3]$ [prepared




**Scheme 1** Preparation of alkynyl-containing tris(pyrazolyl)methane ligands.

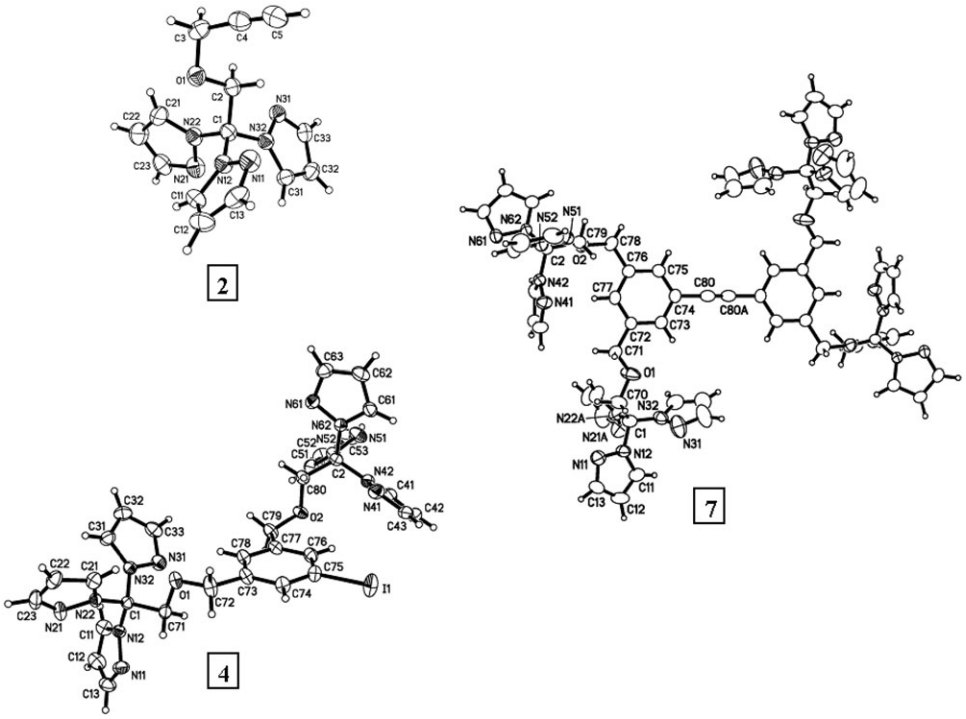



**Fig. 1** Molecular structures of alkynyl-containing tris(pyrazolyl)methane ligands.



*in situ* from NaH and the parent alcohol $HOCH_2C(pz)_3$ (**1**)], and either propargyl bromide or di(bromomethyl)–iodobenzene afforded the monotopic terminal alkyne **2** and ditopic iodophenyl derivative **4**, respectively, in high yields. The iodophenyl derivative **4**, was converted to the terminal alkynyl derivative **6**, by standard protocol (Sonogashira coupling with trimethylsilylacetylene followed by deprotection with tetrabutylammonium fluoride). Both terminal alkynes were subject to a number of coupling reactions. Thus, **2** and **6** were homocoupled with an excess of copper(II) acetate to give the ditopic derivative **3** and the tetratopic derivative **8**. Sonogashira coupling of **4** with **6** provided the tetratopic diphenylethynylene derivative **7**. The bright blue luminescent tetratopic derivative **9** was prepared in quantitative yield by coupling **6** with diiodobenzene or in modest yield by coupling **4** with diethynylbenzene. The identity of compounds **2**–**9** was established by a combination of elemental analyses, NMR spectroscopic methods, mass spectral data, and in the case of **2**, **4**, and **7** by single crystal X-ray diffraction.

### Structures of tris(pyrazolyl)methane ligands

ORTEP diagrams of **2**, **4**, and **7** are found in Fig. 1. While the intramolecular bond lengths and angles are rather unexceptional in these three compounds, the ability of the alkynyl and pyrazolyl groups to participate in non-covalent interactions is evident in the supramolecular structures.

In the case of **2**, the three-dimensional supramolecular structure is comprised of two sets of CH–π interactions. As shown by red lines on the left side of Fig. 2, CH–π interactions between a pyrazolyl hydrogen donor [H(21)] and the π-cloud of the pyrazolyl ring containing N(12) organize the molecules of **2** into chains that run along the *c* axis. The geometry of the interaction, CH(21)–Ct[N(12)] 2.93 Å, 137.8° (Ct = ring centroid), is within expected values[13,14]. These chains are shown rotated 90° into the *a*, *b* plane in the center of Fig. 2. The right side of the figure, also in the *a*, *b* plane, shows that the chains are organized into a three-dimensional structure by CH–π interactions (green lines) with the alkynyl hydrogens [H(5)] interacting with the pyrazolyl groups that contain N(31). The geometry of this type of interaction {CH(5)–Ct[N(31)] 3.12 Å, 166.8°} is also within accepted values.[15]

The supramolecular structure of **4** (Fig. 3) is that of sheets organized by CH–π and CH···I interactions in the crystal. A set of prototypical CH–π interactions (red lines, Fig. 3) between H(33) on a pyrazolyl ring and the π-cloud of the pyrazolyl ring containing N(61) {CH(33)–Ct[N(61)] 2.93 Å, 165.2°} organizes neighboring molecules of **4** into dimers

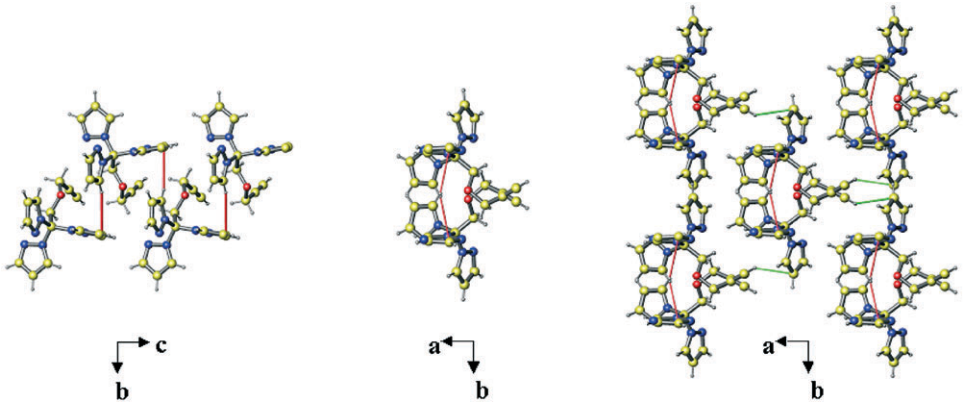



**Fig. 2** Three-dimensional supramolecular structure of $HC_2CCH_2OCH_2C(pz)_3$ (**2**) held together *via* pyrazolyl CH–π (pyrazolyl) interactions (red lines) and alkynyl CH–π (pyrazolyl) interactions (green lines).

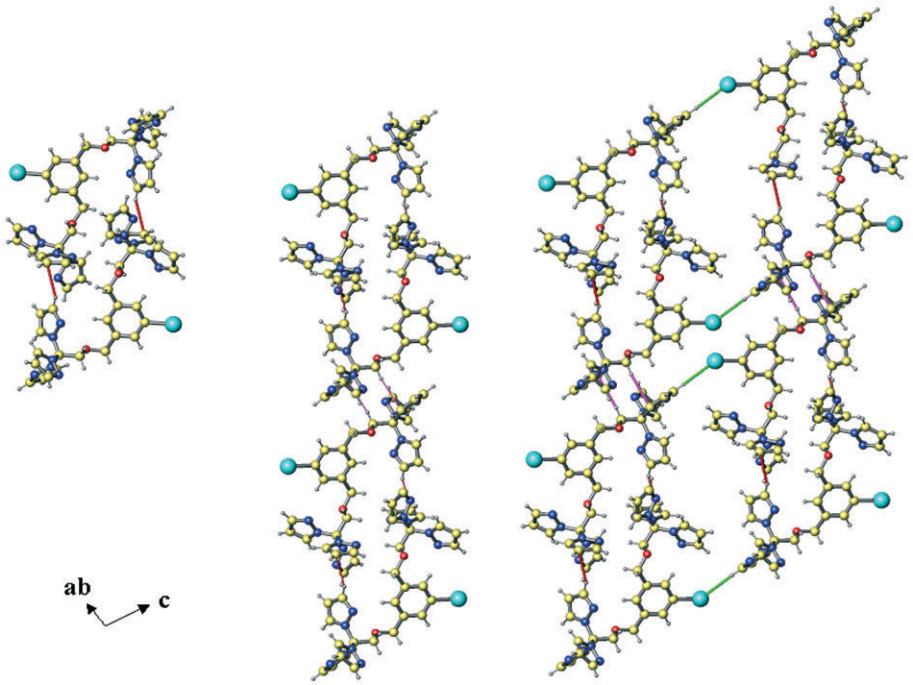



**Fig. 3** Two-dimensional sheet structure of $IC_6H_4[CH_2OCH_2C(pz)_3]_2$ (**4**) comprised of CH–π interactions (red and pink lines) and CH···I interactions (green lines).



(Fig. 3, left). These dimers are further organized into chains that run along the crystallographic [111] direction by another set of CH–π interactions (pink lines, Fig. 3, middle) that occur between H(71a) from a methylene group and the π-cloud of the pyrazolyl ring containing N(21), CH(71a)–Ct[N(21)] 3.09 Å, 148.1°. These chains are organized into sheets by a set of CH···I interactions (green lines, Fig. 3, right) along the *c* axis involving the acidic hydrogen at the 3-position of a pyrazolyl ring, H(23). The geometry of the interaction [CH(23)···I, 3.08 Å, 162.9°] is similar to that seen in other systems.[16]

Interestingly, it has not yet been possible to crystallize the related complex $1,3\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ (where a hydrogen replaces the iodine) which exists as an oil.[3d] This fact underscores the importance of introducing groups that can participate in non-covalent interactions (as in the case of the iodine group and allowing CH···I interactions) for the ultimate purpose of learning to control the crystal packing behavior of molecular solids. Another intriguing feature in the current system and its phenyl analogue, in terms of the future of 'crystal engineering' is that it remains unclear what role the orientation of the ethereal arms have on the crystal packing behavior or *vice versa*. Thus, **4** has the ether sidearms located above and below the plane of the central arene ring but the arms in the metal complex $\{1,3\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2(Mn(CO)_3]_2\}(BF_4)_2$[3d,f] have the opposite orientation with both on the same side of the arene ring.

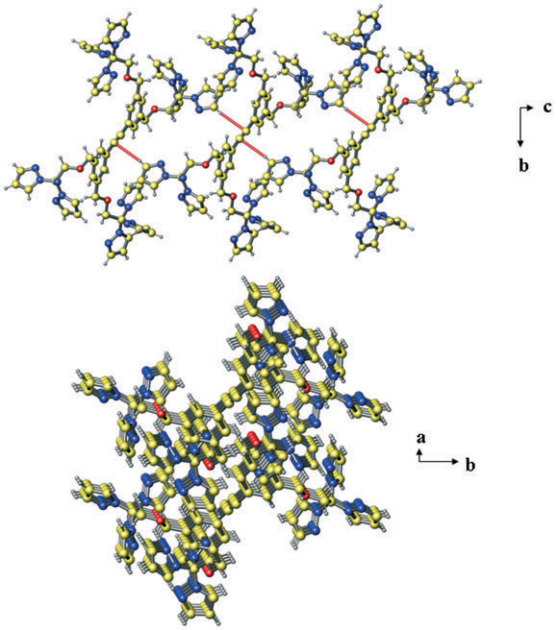
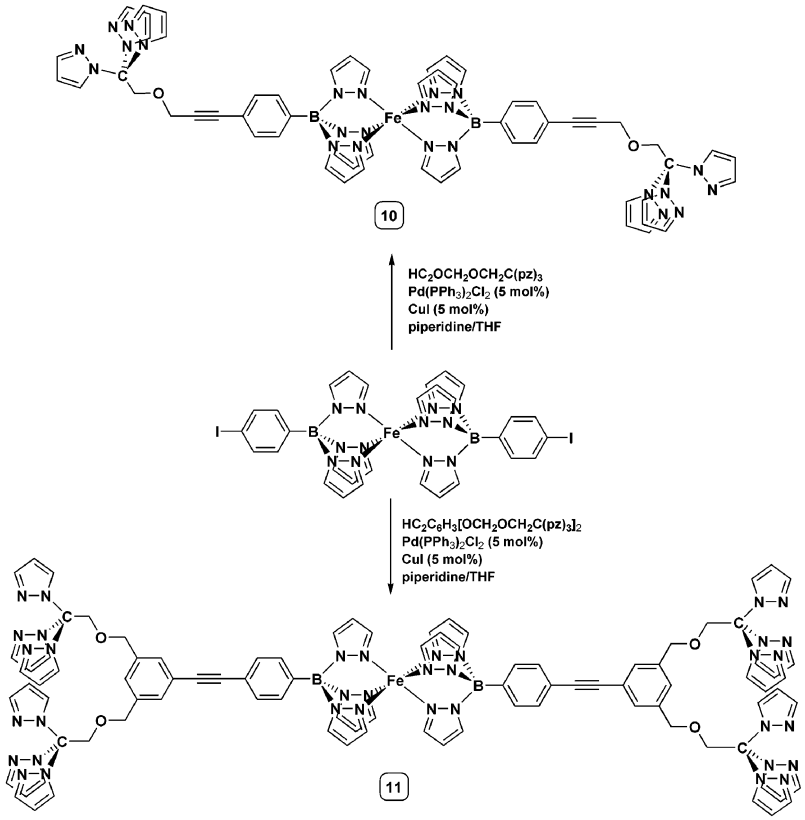



**Fig. 4** Supramolecular structure of $3,3',5,5'\text{-}[(pz)_3CCH_2OCH_2]_4(C_6H_3C_2C_6H_3)$ (**7**). Top: View emphasizing one chain created by CH(pz)–π (alkyne) interactions (red lines). Bottom: 3D network of **7**.

The supramolecular structure of **7** (Fig. 4) is three-dimensional, mainly as a result of CH–π interactions (Table 2), including some that involve the central alkynyl spacer as originally intended at the outset of this research. The building blocks are held in chains by CH–π interactions, which occur between the acidic hydrogen H(53) at the three positon of a pyrazolyl ring and the π-cloud of the alkyne fragment. The geometrical parameters for this interaction [CH(53)–C(80) distance of 2.74 Å, C–H–C angle of 149.9°] are in line with other CH–π alkyne interactions.[15] Given the fact that the molecule is centrosymmetric, this interaction links the molecular building blocks into chains positioned in the *bc* plane and running along the *c* axis of the unit cell. One chain, built up from three molecules, is shown at the top of Fig. 4, where the red lines represent the CH–π (alkyne) interactions. These chains are connected into a 3D network (bottom of Fig. 4) as a result of two sets of CH–π interactions. In contrast to the previous CH–π interaction where the acceptor π-cloud was located on the alkyne moiety, here in both cases the hydrogen atom acceptors are pyrazolyl rings. For the first set of interac-

**Table 2** Summary of intermolecular non-covalent interactions for **7**

| Donor(D)–H···Acceptor(A) | D–H···A/Å | D–H···A/° |
|---|---|---|
| Chain formation | | |
| C(53)–H(53)···C(80) | 2.74 | 149.9 |
| 3D network | | |
| C(12)–H(12)···Ct[N(41)] | 2.80 | 158.0 |
| C(78)–H(78a)···Ct[N(51)] | 3.07 | 145.4 |
| C(21b)–H(21b)···N(11) | 2.56 | 161.1 |




**Scheme 2** Preparation of mixed tris(pyrazolyl)methane–tris(pyrazolyl)borate ligands.



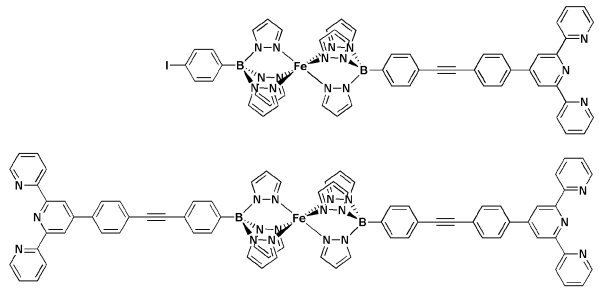
tions the hydrogen donor is the pyrazolyl ring containing the C(12) ring {C–H(12)···Ct[N(41)] distance = 2.80 Å and C–H···Ct angle = 158.0°}. For the second set, the hydrogen donor involves an ethereal methylene group located on one of the side arms of the compound {CH(78a)–Ct[N(51)], 3.07 Å, 145.4°}. It is worth mentioning that this arrangement is supported by CH–N interactions that occur between H(21b) of the rotationally disordered pyrazolyl ring and N(11) of a neighboring well-behaved pyrazolyl ring. The combination of these interactions build up the 3D network of **7**.

## Mixed tris(pyrazolyl)borate/tris(pyrazolyl)methane metallo-ligands

The chemistry used to build organic ligands in Scheme 1 can be extended to properly functionalized metal complexes. We have previously reported the syntheses of $Fe[(p\text{-}IC_6H_4)B(3\text{-}Rpz)_3]_2$ (R = H, Me) compounds with interesting spin-crossover properties (for R = Me).[8] The compound $Fe[(p\text{-}IC_6H_4)B(pz)_3]_2$ was smoothly converted to the dialkynlated bitopic $Fe[(pz)_3C\text{-}CH_2OCH_2\text{–}C_2\text{–}C_6H_4B(\kappa^3\text{-}N,N',N''\text{-}pz)_3]_2$ (**10**) by reaction with **2** and a similar reaction with **6** yields the tetratopic metalloligand $Fe[\{3,5\text{-}[(pz)_3CCH_2OCH_2]_2C_6H_3C_2\}C_6H_4B(\kappa^3\text{-}N,N',N''\text{-}pz)_3]_2$ (**11**) (Scheme 2) by using Sonogashira coupling reactions. These iron-containing unsubstituted pyrazolyl derivatives are purple, low spin diamagnetic species at room temperature, and the NMR spectra showed the expected resonances with chemical shifts in typical ranges 1–10 ppm.

The solid state structure of $\mathbf{10}\cdot 4CH_2Cl_2$ has been determined crystallographically, Fig. 5. While disorder problems precluded a high accuracy structure, the Fe–N average bond distance of 1.96 is typical of low spin iron(II), as expected from the color and NMR spectra. Disorder problems in the structure prevent further analysis of the crystal packing.

It was found that a similar Sonogashira coupling reaction between $HC_2C_6H_4$-terpy and $Fe[(p\text{-}IC_6H_4)B(pz)_3]_2$ afforded a highly insoluble solid mixture that showed signals in the



**Scheme 3** Iron-containing products obtained from attempted Sonogashira coupling reactions between $Fe[IC_6H_4B(pz)_3]_2$ and $HC_2C_6H_4$-terpy.

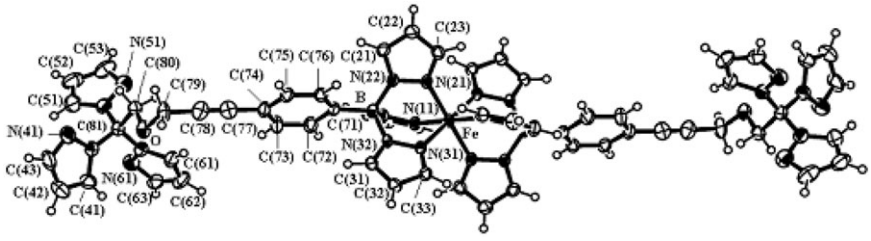



**Fig. 5** Molecular structure and atom labelling scheme of $Fe[(pz)_3CCH_2OCH_2C_2C_6H_4B(\kappa^3\text{-}N,N',N''\text{-}pz)_3]_2$.

ESI(+) mass spectra that could be attributed to the mono- and dialkynyl coupled products (Scheme 3). Considering the ease of the previous reactions, it is evident that the low solubility of the mono- and disubstituted (alkynylphenyl)terpy derivatives in every solvent hampered the completion of the reaction in addition to inhibiting the potential for product separation and characterization.

## Conclusion

We have prepared a new family of semi-rigid, multitopic ligands based on linking tris(pyrazolyl)methane units *via* central alkynyl spacers. Sonogashira coupling reactions were used to prepare phenylalkynyl based compounds while Glaser oxidative homocoupling reactions have been used to prepare butadiynyl based compounds. The main architectural feature of the new linked ligands is their overall rigid linear geometry, but with semi-rigid ending groups. The flexibility of these end groups is important to future chemistry as they provide solubility and structural adaptivity to metal complexes. In addition, we have shown that these compounds exhibit rich supramolecular (structural) chemistry that is a function of the added substituents along the ligand periphery—the addition of iodide allows for CH···I interactions whereas the addition of alkynyl moieties allows for extended structures based on CH–π interactions involving this electron rich group. While we have centred our chemistry on symmetrical multitopic ligands based on tris(pyrazolyl)methane units, the chemistry outlined here is applicable for other ligand systems; the syntheses of unsymmetrical analogs are in progress.

Importantly, we were able to use this chemistry to prepare new examples of "third generation" poly(pyrazolyl)borate and poly(pyrazolyl)methane ligands. First generation poly(pyrazolyl)borate ligands, initially introduced by Trofimenko,[17] are the simple $[HB(Rpz)_3]^-$ type ligands with non-bulky substituents at the 3-position. Second generation ligands, also introduced by Trofimenko,[18] are those with bulky substituents at the 3-position. Third generation ligands are designed to be those specifically functionalized at the non-coordinating, "back" position of the ligands, either at boron or carbon and a number of examples have been reported previously.[3,14,19] In this chemistry we have prepared the first third generation compound containing both the tris(pyrazolyl)methane and tris(pyrazolyl)-borate ligating units where the borate end was bound to iron(II). This chemistry opens up the door for further exploration into incorporating methyl-substituted pyrazolyls (which undergo spin transitions in iron(II) chemistry) or even other metal systems with the purpose of putting electro- and/or photoactive centers into highly organized coordination network solids.



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## References

1 (*a*) G. F. Swiegers and T. J. Malefeste, *Chem. Rev.*, 2000, **100**, 3483; (*b*) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*c*) S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1461; (*d*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; (*e*) C. T. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293; (*f*) R. D. Archer, *Coord. Chem. Rev.*, 1993, **128**, 49; (*g*) N. R. Champness and M. Schröder, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 419.

2 (*a*) P. S. Mukherjee, N. Das and P. J. Stang, *J. Org. Chem.*, 2004, **69**, 3526; (*b*) K. W. Chi, C. Addicott and P. J. Stang, *J. Org. Chem.*, 2004, **69**, 2910; (*c*) M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 1649.

3 (*a*) D. L. Reger, R. F. Semeniuc, V. Rassolov and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 537; (*b*) D. L. Reger, R. F. Semeniuc and M. D. Smith, *Inorg. Chem.*, 2003, **42**, 8137; (*c*) D. L. Reger, R. F. Semeniuc, I. Silaghi-Dumitrescu and M. D. Smith, *Inorg. Chem.*, 2003, **42**, 3751; (*d*) D. L. Reger, R. F. Semeniuc and M. D. Smith, *J. Organomet. Chem.*, 2003, **666**, 87; (*e*) D. L. Reger, R. F. Semeniuc and M. D. Smith, *Dalton Trans.*, 2003, 285; (*f*) D. L. Reger, R. F. Semeniuc and M. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2002, 476; (*g*) D. L. Reger, R. F. Semeniuc and M. D. Smith, *Inorg. Chem. Commun.*, 2002, **5**, 278; (*h*) D. L. Reger, R. F. Semeniuc and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 6545; (*i*) D. L. Reger, T. D. Wright, R. F. Semeniuc, T. C. Grattan and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 6212; (*j*) D. L. Reger, T. C. Grattan, K. J. Brown, C. A. Little, J. J. S. Lamba, A. L. Rheingold and R. D. Sommer, *J. Organomet. Chem.*, 2000, **607**, 120.

4 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467.

5 D. L. Reger, J. R. Gardinier, W. R. Gemmill, M. D. Smith, A. M. Shahin, G. L. Long, L. Rebbouh and F. Grandjean, *J. Am. Chem. Soc.*, in press.

6 (*a*) H. P. Dujkstra, M. D. Meijer, J. Patel, R. Kreiter, G. P. M. van Klink, M. Lutz, A. L. Spek, A. Canty and G. von Koten, *Organometallics*, 2001, **20**, 3159–3168; (*b*) A. V. Rukavishnikov, A. Phadke, M. D. Lee, D. H. LaMunyo, P. A. Petukov and J. F. Keana, *Tetrahedron. Lett.*, 1999, **40**, 6353.

7 (*a*) V. Grosshenny, F. M. Romero and R. Ziessel, *J. Org. Chem.*, 1997, **62**, 1491; (*b*) P. Korall, A. Boerje, P.-O. Norrby and B. Aakermark, *Acta Chem. Scand.*, 1997, **51**, 760; (*c*) C. A. G. Haasnoot, F. A. A. M. De Leeuw and C. Altona, *Tetrahedron*, 1980, **36**, 2783.

8 D. L. Reger, J. R. Gardinier, M. D. Smith, A. M. Shahin, G. J. Long, L. Rebbouh and F. Grandjean, *Inorg. Chem.*, 2005, **44**, 1852.

9 *SMART Version 5.625 and SAINT+ Version 6.02a*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1998.

10 P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. Israel, R. O. Gould and J. M. M. Smits, *The DIRDIF99 program system*, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.

11 G. M. Sheldrick, *SHELXTL (Version 5.1)*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.

12 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

13 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.

14 D. L. Reger, J. R. Gardinier, R. F. Semeniuc and M. D. Smith, *Dalton Trans.*, 2003, 1712.

15 (*a*) W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, Z. He and K.-Y., *Chem. Eur. J.*, 2003, **9**, 6155; (*b*) T. Steiner and M. Tamm, *J. Organomet. Chem.*, 1998, **570**, 235.

16 (*a*) F. Ugozzoli, A. Arduini, C. Massera, A. Pochini and A. Secchi, *New J. Chem.*, 2002, **26**, 1718; (*b*) M. Freytag, P. G. Jones, B. Ahrens and A. K. Fischer, *New J. Chem.*, 1999, **12**, 1137.

17 S. Trofimenko, *Scorpionates - The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.

18 S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1987, **28**, 1507.

19 (*a*) D. White and J. W. Faller, *J. Am. Chem. Soc.*, 1982, **104**, 1548; (*b*) C. P. Brock, M. K. Das, R. P. Minton and K. Niedenzu, *J. Am. Chem. Soc.*, 1988, **110**, 817; (*c*) C. Janiak, L. Braun and F. Girgsdies, *J. Chem. Soc., Dalton Trans.*, 1999, 3133; (*d*) J. L. Kisko, T. Hascall, C. Kimblin and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 1999, 1929; (*e*) N. C. Hardin, J. C. Jeffery, J. A. McCleverty, L. H. Rees and M. A. Ward, *New J. Chem.*, 1998, 661; (*f*) K. Niedenzu and S. Trofimenko, *Inorg. Chem.*, 1985, **24**, 4222; (*g*) F. Jäkle, K. Polborn and M. Wagner, *Chem. Ber.*, 1996, **129**, 603; (*h*) F. Fabrizi de Biani, F. Jäkle, M. Spiegler, M. Wagner and P. Zanello, *Inorg. Chem.*, 1997, **36**, 2103; (*i*) E. Herdtweck, F. Peters, W. Scherer and M. Wagner, *Polyhedron*, 1998, **17**, 1149; (*j*) S. L. Guo, F. Peters, F. Fabrizi de Biani, J. W. Bats, E. Herdtweck, P. Zanello and M. Wagner, *Inorg. Chem.*, 2001, **40**, 4928; (*k*) S. L. Guo, J. W. Bats, M. Bolte and M. Wagner, *J. Chem. Soc., Dalton Trans.*, 2001, 3572; (*l*) S. Bieller, F. Zhang, M. Bolte, J. W. Bats, H.-W. Lerner and M. Wagner, *Organometallics*, 2004, **23**, 2107; (*m*) D. L. Reger, K. J. Brown, J. R. Gardinier and M. D. Smith, *Organometallics*, 2003, **22**, 4973; (*n*) D. L. Reger, R. P. Watson, J. R. Gardinier and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 6609–6619.