

# Route to multicluster containing ancillary *ortho*-carborane-1,2-dithiolato ligands†

Jian-Qiang Wang, Chun-Xia Ren and Guo-Xin Jin\*

Received (in Cambridge, UK) 11th April 2005, Accepted 15th August 2005

First published as an Advance Article on the web 26th August 2005

DOI: 10.1039/b505041c

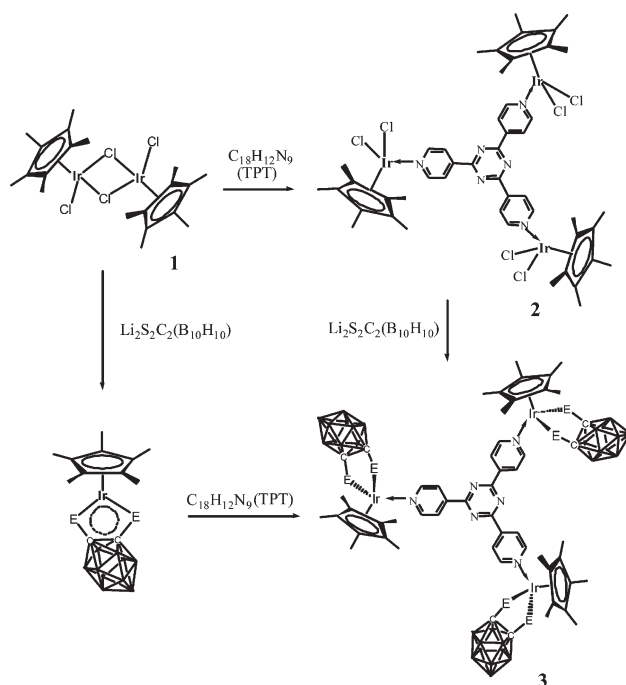
Multicluster molecules  $[\text{Cp}^*\text{IrS}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]_n(\text{L})$  [ $n = 3$  ( $\text{L} = \text{tpt}$ ),  $2$  ( $\text{L} = \text{bpy}$ )], connected with pyridyl-based ligands, were prepared and characterized by X-ray crystallography.

Derivatives of 1,2-dicarba-*closo*-dodecaborane(12) have aroused considerable interest in both their fundamental properties and their wide-ranging potential applications.<sup>1</sup> The rigid geometries of the *ortho*, *meta* and *para* isomers of  $\text{C}_2\text{B}_{10}\text{H}_{12}$ , together with the relative ease of derivatisation at the carbon vertices make them excellent candidates for crystal engineering.<sup>2</sup> For many of the potential applications of carborane derivatives an understanding of, and ideally control over, the solid-state structures of these compounds are vital. Among the types of target structures attracting attention are highly symmetrical, aesthetically appealing architectures, such as a star-shaped molecule.<sup>3</sup> The efforts to build cluster-supported molecular or supramolecular structures are expected to offer many fascinating research problems with potentially significant ramifications.<sup>4</sup> To our knowledge, only one case of an *ortho*-carboranyl-functionalised highly branched molecule has been reported, in researching efficient methods for assembling suitable organic or inorganic linkers into a desired target dendrimer.<sup>5</sup> Carboranes are obvious candidates for such an application because of their synthetic versatility and well-developed derivative chemistry. Our laboratory and Herberhold *et al.* have already reported on the synthesis of the 16 electron metal complexes  $[\text{Cp}^*\text{M}\{\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})\}]$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{E} = \text{S}, \text{Se}$ ),<sup>6</sup> and suggested that this species may have a deficiency at the metal center which can be used to build hetero-metallic clusters.<sup>7</sup> This has allowed the construction of polycarborane molecular architectures that take advantage of special attributes, such as an addition reaction at a metal atom in a dichalcogenolato metal heterocycle.<sup>6</sup> Herein, we report the stepwise assembly of two multicluster complexes **3**, **5** that contain two or three identical carborane ligands.

The syntheses of the multicluster complexes **3**, **5** take advantage of the linear or pseudolinear pyridyl based ligands (Scheme 1) which have been used as building blocks for discrete supramolecular assemblies.<sup>8</sup> Stirring a mixture of  $[\text{Cp}^*\text{Ir}_2\text{Cl}_2(\mu_2\text{-Cl})_2]$  (**1**) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 18 h produced an orange solution of **2** in a yield of 96%, which has been characterized by single crystal, NMR, IR spectroscopy, and elemental analysis. The molecule consists of

three  $(\text{Cp}^*\text{Ir})$  fragments linked by one tpt ligand in a star-shaped trimer. The  $\text{Cp}^*$  ligands are symmetrically bound to the iridium atoms.

The complex **3** is obtained by treatment of **2** with the dilithium 1,2-dithiolate carborane cluster in THF solution. Complex **3** can also be obtained from the reaction of  $[\text{Cp}^*\text{Ir}\{\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})\}]^{6a,9}$  with tpt in  $\text{CH}_2\text{Cl}_2$ . The formation of **3** is confirmed by the appearance of the  $^1\text{H}$  signal at 8.69, 8.98, and 1.76 ppm, which is ascribed to the pyridine and  $\text{Cp}^*$  ligands. Recrystallization of **3** from  $\text{CH}_2\text{Cl}_2$ /hexane affords the desired products as crystalline solids in excellent yields of 90%.<sup>§¶</sup> The solubility of **3** in common organic solvents is very similar to that of the corresponding dendrons. The enchanting molecular structure of **3** (Figs. 1 and 2) was crystallographically established by X-ray structure analysis. Three  $[\text{Cp}^*\text{Ir}\{\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})\}]$  units are symmetrically arranged around the periphery of one tpt core, thus forming a 'bowl-shaped' structure. All of the iridium centers adopt a three-legged piano-stool conformation, which has six-coordinate geometry, assuming that the  $\text{Cp}^*$  ligand functions as a three-coordinate ligand. The Ir–N bond lengths are 2.110(9)–2.107(14) Å, which are similar to those of **2**. Each tpt ligand connects three Ir atoms related by crystallographic three-fold symmetry of the tetragonal



Scheme 1 Preparation of **2**, **3**.

Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai, 200433, P. R. China. E-mail: gxjin@fudan.edu.cn; Fax: (+86)-21-65643776  
† Electronic supplementary information (ESI) available: Experimental details and crystal structure determination. See <http://dx.doi.org/10.1039/b505041c>

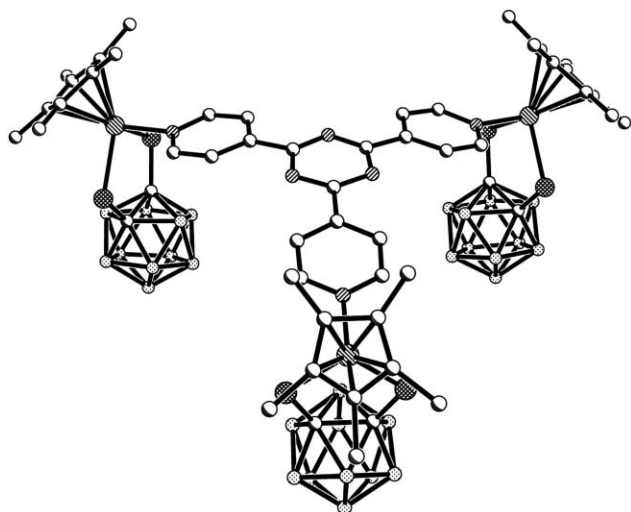


Fig. 1 Molecular structure of **3**.

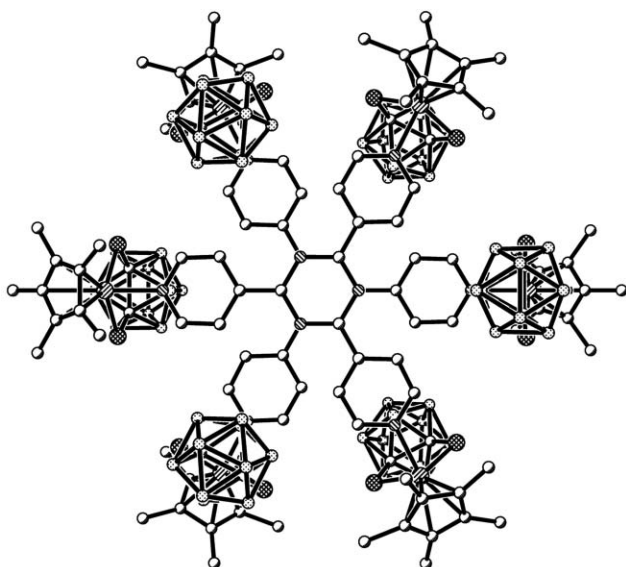


Fig. 2 Two units of **3** in a staggered disposition.

space group  $P4_2/nm$ . It is interesting that the tpt ligand acts in a bifunctional tridentate fashion in **3** through three N-donor atoms of the oligopyridyl and one triazine group. Two neighboring molecules of **3** are paired and staggered in a face-to-face fashion, with the separation between the central triazine rings being 3.46 Å, indicative of the presence of  $\pi$ - $\pi$  stacking interactions. The two neighboring molecules within the stack are rotated by about 60° with respect to each other, just like two buckled bowls.

Another remarkable feature of **3** is the packing pattern along the  $c$  axis. These 'buckled bowls' stack along the  $c$  axis to form an interesting stacking structure. As shown in Fig. 3, each of the eight molecules **3** is paired up to form two types of channels with the dimensions ranging from 3.6–4.0 Å. In other words, each molecule of **3** is locked into position by pairing up with neighboring molecules in the crystal lattice. The packing in the crystals is such as to create infinite tunnels. It is interesting that such channels are constructed with a double-stranded helix, which consists of repeating 'buckled bowl' molecules.

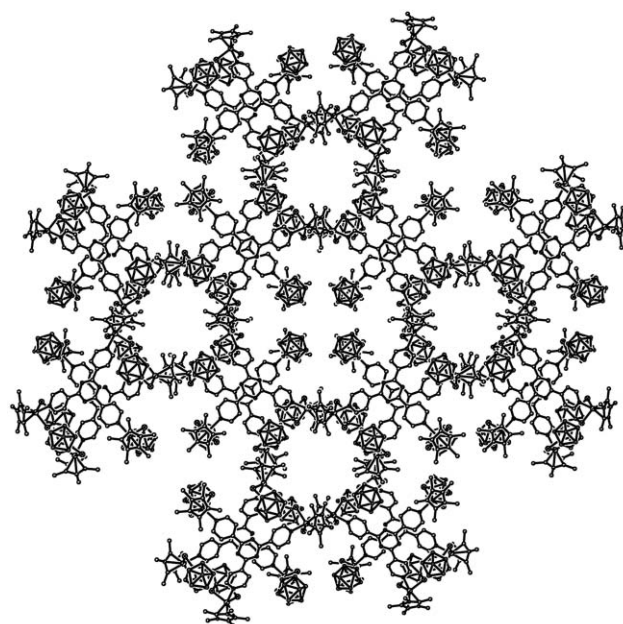


Fig. 3 Crystal structures of **3**, viewed down the  $c$  axis.

Changing the ligand from tpt to 4,4'-bipyridine (bpy), complex **5** is obtained through  $[\text{Cp}^*\text{IrCl}_2]_2(\text{bpy})$  (**4**). A perspective drawing of **5** is given in Fig. 4. The crystal unit has a crystallographically imposed inversion center in the middle of the Ir...Ir vector. The molecule has a dimeric structure connected by a 4,4'-bipyridyl ligand. The plane of the iridacycle has a dihedral angle of 90.8° with 4,4'-bipyridine, and the Ir...Ir distance is at 11.3 Å.

Interesting properties may be anticipated for these multicluster arrays. For example, **3** possessing a three-fold rotational symmetry, may display two-photon absorption properties<sup>10</sup> as well as improved second-order nonlinear optical properties.<sup>11</sup> Preliminary investigations of electronic absorption spectra for **3** show three bands at 238, 327, 575 nm. All these new complexes show no luminescence at room temperature in solution, presumably due to the presence of the carborane cluster moiety which quenches the potential emission, if there is any.<sup>12</sup>

In summary, we have presented here the formation of a multicluster containing  $o$ -carborane group assemblies from a

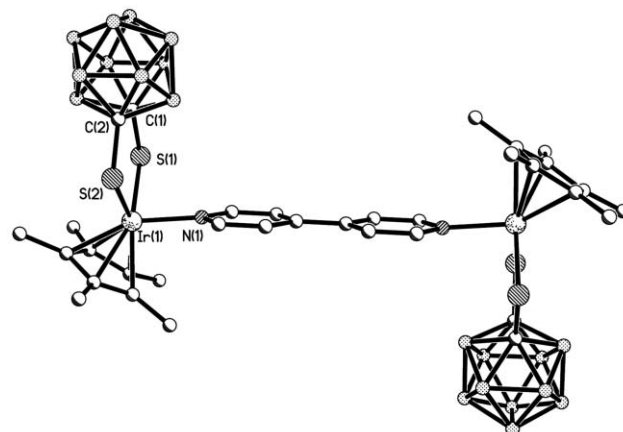


Fig. 4 Molecular structure of **5**.

central planar connector. The synthetic approach, based upon stepwise buildup of metal clusters with organic fragments, offers the potential for exquisite control over the detailed architecture of the materials, which may lead to a variety of unusual shapes and novel properties.

Financial support by the National Science Foundation of China for Distinguished Young Scholars (29925101, 20421303) and by the Doctoral Fund of the Education Ministry of China (No. 20020246011) is gratefully acknowledged.

## Notes and references

‡ Abbreviations: tpt: 2,4,6-tris(4-pyridyl)-1,3,5-triazine; bpy: 4,4'-bipyridine.

§ All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were purified by standard methods prior to use.  $[\text{Cp}^*\text{IrCl}_2]_2$ ,<sup>13</sup> 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt),<sup>14</sup> and  $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ <sup>6a</sup> were prepared according to the reported procedures. **Synthesis of 2, 3**: A mixture of **1** (0.15 mmol, 120 mg) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (0.1 mmol, 32 mg) was stirred in  $\text{CH}_2\text{Cl}_2$  at room temperature for 18 h. The solvent was removed under vacuum, producing an orange solid of **2** (145 mg, 96%). The component was recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane to give orange crystals of **2**. Elemental analysis calcd for  $\text{C}_{48}\text{H}_{57}\text{Cl}_6\text{Ir}_3\text{N}_6$  (%): C, 38.25, H, 3.81; found: C, 37.97, H, 3.69.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 1.63 (s, 45H,  $\text{C}_5\text{Me}_5$ ), 8.66 (br, 6H, tri-pyridyl), 8.97 (br, 6H, tri-pyridyl). A solution of  $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$  (0.15 mmol) in ethyl ether was added to the orange solution of **2** (76 mg, 0.05 mmol). The mixture was stirred for 24 h; the color changed from orange to violet. After removal of the solvent, the residue was extracted with  $\text{CH}_2\text{Cl}_2$ , to give **3** (86 mg, 90%). Recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane afforded air-stable violet crystals. Elemental analysis calcd for  $\text{C}_{54}\text{H}_{87}\text{B}_{30}\text{Ir}_3\text{N}_6\text{S}_6$  (%): C, 33.89; H, 4.58; Found: C, 33.75; H, 4.52.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 1.76 (s, 45 H,  $\text{C}_5\text{Me}_5$ ), 8.69 (br, 6 H, tri-pyridyl), 8.98 (br, 6 H, tri-pyridyl);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ): -8.6, -10.5. IR (KBr disk):  $\nu = 2058, 2069 \text{ cm}^{-1}$  ( $\nu_{\text{B-H}}$ ); UV/vis ( $\text{CHCl}_3$ ): 238, 327, 575 nm. **Synthesis of 4, 5**: A mixture of **1** (0.2 mmol, 160 mg) and 4,4'-bipyridine (0.1 mmol, 16 mg) was stirred in  $\text{CH}_2\text{Cl}_2$  at room temperature for 12 h. The solvent was removed under vacuum, producing an orange solid of **4** (89 mg, 93%). Elemental analysis calcd for  $\text{C}_{30}\text{H}_{38}\text{Cl}_4\text{Ir}_2\text{N}_2$  (%): C, 37.81; H, 4.02; found: C, 37.69; H, 3.91.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 1.66 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 7.85 (br, 4H, bipyridyl), 8.72 (br, 4H, bipyridyl). A solution of  $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$  (0.1 mmol) in ethyl ether was added to the solution of **4** (48 mg, 0.05 mmol). The mixture was stirred for 24 h, and the color changed from orange to dark red. After removal of the solvent, the residue was extracted with  $\text{CH}_2\text{Cl}_2$  to give **5** (53 mg, 87%). Recrystallization from  $\text{CH}_2\text{Cl}_2$ /benzene afforded air-stable red crystals. Elemental analysis calcd for  $\text{C}_{34}\text{H}_{58}\text{B}_{20}\text{Ir}_2\text{N}_2\text{S}_4$  (%): C, 33.37; H, 4.78; found: C, 32.98; H, 4.57.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 1.86 (s, 30 H,  $\text{C}_5\text{Me}_5$ ), 7.57 (d,  $^3J(\text{H}, \text{H}) = 5 \text{ Hz}$ , 4 H, dipyridyl), 8.77 (d,  $^3J(\text{H}, \text{H}) = 5 \text{ Hz}$ , 4 H, dipyridyl);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ): -6.3, -8.1, -8.7, -10.3. IR (KBr disk):  $\nu = 2053 \text{ cm}^{-1}$  ( $\nu_{\text{B-H}}$ ); UV/vis ( $\text{CHCl}_3$ ): 253, 330, 580 nm.

¶ Crystal data for **2**:  $\text{C}_{48}\text{H}_{57}\text{Cl}_6\text{Ir}_3\text{N}_6$ ,  $M = 1507.30$ , orange block, Trigonal, space group  $R\bar{3}m$ ,  $a = 24.096(7) \text{ \AA}$ ,  $b = 24.096(7) \text{ \AA}$ ,  $c = 7.479(3) \text{ \AA}$ ,  $\gamma = 120^\circ$ ,  $V = 3761(2) \text{ \AA}^3$ ,  $Z = 3$ ,  $\rho_{\text{calc}} = 1.997 \text{ Mg}\cdot\text{m}^{-3}$ ,  $\text{GOF} = 0.900$ ,  $R_1 = 0.0535$  ( $I > 2\sigma$ ),  $wR_2 = 0.1041$  (all unique reflections). For **3**:  $\text{C}_{54}\text{H}_{87}\text{B}_{30}\text{Ir}_3\text{N}_6\text{S}_6$ ,  $M = 1913.56$ , violet block, Tetragonal, space group  $P4_2/nm$ ,  $a = 35.258(6) \text{ \AA}$ ,  $b = 35.258(6) \text{ \AA}$ ,  $c = 16.150(4) \text{ \AA}$ ,  $V = 20076(6) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calc}} = 1.266 \text{ Mg}\cdot\text{m}^{-3}$ ,  $\text{GOF} = 1.151$ ,  $R_1 = 0.0704$  ( $I > 2\sigma$ ),  $wR_2 = 0.2177$  (all unique reflections). For **5**:  $\text{C}_{34}\text{H}_{58}\text{B}_{20}\text{Ir}_2\text{N}_2\text{S}_4\cdot 2\text{CH}_2\text{Cl}_2$ ,  $M = 1393.52$ , red block, Triclinic, space group  $P-1$ ,  $a = 10.223(2) \text{ \AA}$ ,  $b = 11.336(2) \text{ \AA}$ ,  $c = 13.688(3) \text{ \AA}$ ,  $\alpha = 101.052(2)^\circ$ ,  $\beta = 109.107(3)^\circ$ ,  $\gamma = 94.826(3)^\circ$ ,  $V = 1452.6(5) \text{ \AA}^3$ ,  $Z = 1$ ,

$\rho_{\text{calc}} = 1.593 \text{ Mg}\cdot\text{m}^{-3}$ ,  $\text{GOF} = 1.086$ ,  $R_1 = 0.0322$  ( $I > 2\sigma$ ),  $wR_2 = 0.0920$  (all unique reflections). Data were measured at 293 K on a Bruker SMART APEX CCD diffractometer [ $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$ ], graphite monochromator, the structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  using the SHELXTL program.<sup>15</sup> CCDC 267768–267770. See <http://dx.doi.org/10.1039/b505041c> for crystallographic data in CIF or other electronic format.

- (a) J. Plešek, *Chem. Rev.*, 1992, **92**, 269; (b) V. I. Bregadze, *Chem. Rev.*, 1992, **92**, 209; (c) M. F. Hawthorne and A. Maderna, *Chem. Rev.*, 1999, **99**, 3421; (d) Z. Xie, *Acc. Chem. Res.*, 2003, **36**, 1; (e) G.-X. Jin, *Coord. Chem. Rev.*, 2004, **248**, 587.
- (a) M. F. Hawthorne and Z. Zheng, *Acc. Chem. Res.*, 1997, **30**, 267; (b) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; (c) E. S. Alekseyeva, A. S. Batsanov, L. A. Boyd, M. A. Fox, T. G. Hibbert, J. A. K. Howard, J. A. H. MacBride, A. Mackinnon and K. Wade, *Dalton Trans.*, 2003, 475; (d) A. Franken, C. A. Kilner and J. D. Kennedy, *Chem. Commun.*, 2004, 328.
- (a) J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown and S. Wang, *Angew. Chem., Int. Ed.*, 2001, **40**, 4042; (b) C. Seward, W.-L. Jia, R.-Y. Wang, G. D. Enright and S. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 2933; (c) W.-L. Jia, R.-Y. Wang, D. Song, S. J. Ball, A. B. Mclean and S. Wang, *Chem. Eur. J.*, 2005, **11**, 832.
- (a) F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759; (b) B. K. Roland, H. D. Selby, M. D. Carducci and Z. Zheng, *J. Am. Chem. Soc.*, 2002, **124**, 3222; (c) B. K. Roland, C. Carter and Z. Zheng, *J. Am. Chem. Soc.*, 2002, **124**, 6234; (d) H. D. Selby, B. K. Roland and Z. Zheng, *Acc. Chem. Res.*, 2003, **36**, 933.
- (a) D. Armspach, M. Cattalini, E. C. Constable, C. E. Housecroft and D. Phillips, *Chem. Commun.*, 1996, 1823; (b) E. C. Constable, *Chem. Commun.*, 1997, 1073.
- (a) M. Herberhold, G.-X. Jin, H. Yan, W. Milius and B. Wrackmeyer, *J. Organomet. Chem.*, 1999, **587**, 252; (b) M. Herberhold, G.-X. Jin, H. Yan, W. Milius and B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 1999, 873; (c) X.-F. Hou, X.-C. Wang, J.-Q. Wang and G.-X. Jin, *J. Organomet. Chem.*, 2004, **689**, 2228; (d) Q. A. Kong, G.-X. Jin, S.-Y. Cai and L.-H. Weng, *Chin. Sci. Bull.*, 2003, **48**, 1733.
- (a) G.-X. Jin, J.-Q. Wang, Z. Zheng, L.-H. Weng and M. Herberhold, *Angew. Chem., Int. Ed.*, 2005, **44**, 259; (b) J.-Q. Wang, X.-F. Hou, L.-H. Weng and G.-X. Jin, *Organometallics*, 2005, **5**, 826; (c) J.-Q. Wang, L.-H. Weng and G.-X. Jin, *J. Organomet. Chem.*, 2005, **690**, 249.
- (a) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (b) G. F. Swieggers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; (c) J. A. R. Navarro and B. Lippert, *Coord. Chem. Rev.*, 2001, **222**, 219.
- J. Y. Bae, Y. I. Park, J. Ko, K. I. Park, S. I. Cho and S. O. Kang, *Inorg. Chim. Acta*, 1999, **289**, 141.
- S. Chung, K. Kim, T. Lin, G. C. He, J. Swiatkiewicz and P. N. Prasad, *J. Phys. Chem. B*, 1999, **103**, 10741.
- (a) J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, **94**, 77; (b) V. R. Thalladi, S. Brasselet, H.-C. Weiss, D. Bläser, A. K. Katz, H. L. Carrell, R. Boese, J. Zyss, A. Nangia and G. R. Desiraju, *J. Am. Chem. Soc.*, 1998, **120**, 2563.
- (a) R. V. Slone, K. D. Benkstein, S. Belanger, J. T. Hupp, I. A. Guzei and A. L. Rheingold, *Coord. Chem. Rev.*, 1998, **171**, 221; (b) S.-S. Sun, J. A. Anspach and A. J. Lees, *Inorg. Chim. Acta*, 2003, **351**, 363; (c) P. Thanasekaran, R.-T. Liao, Y.-H. Liu, T. Rajendran, S. Rajagopal and K.-L. Lu, *Coord. Chem. Rev.*, 2005, **249**, 1085.
- C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228.
- H. L. Anderson, S. Anderson and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2231.
- SHELXTL 6.10, Bruker Analytical Instrumentation, Madison, WI, USA, 2000.