Synthesis, reactivity and complexation studies of N,S *exo*-heterodisubstituted *o*-carborane ligands. Carborane as a platform to produce the uncommon bidentate chelating (*pyridine*)N-C-C-C-S(*H*) motif†‡§

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Received 5th October 2007, Accepted 14th November 2007
First published as an Advance Article on the web 6th December 2007
DOI: 10.1039/b715362g

The synthesis of N,S-heterodisubstituted 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ compounds (R = Et, **2**; R = ^{i}Pr, **3**) has been accomplished starting from 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ (**1**), and their partial deboronation reaction leading to the structurally chiral [7-(2′-pyridyl)-8-SR-7,8-*nido*-$C_2B_9H_{10}$]$^-$ derivatives (R = Et, [**4**]$^-$; R = ^{i}Pr, [**5**]$^-$) has been studied. Capillary electrophoresis combined with the chiral selector α-cyclodextrin has permitted the separation of the electrophoretically pure racemic [7-(2′-pyridyl)-8-SR-7,8-*nido*-$C_2B_9H_{11}$]$^-$ ions into two peaks each one corresponding to the interaction of one enantiomer with the α-cyclodextrin. The N,S-heterodisubstituted *o*-carborane containing a mercapto group, 1-(2′-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$, **1**, is one of the two examples of a rigid bidentate chelating (*pyridine*)N-C-C-C-S(*H*) motif having been structurally fully characterized. To study the potential of such a binding site, **1** has been tested as a ligand with metal ions requiring different coordination numbers, two (Au^+) and four (Pd^{2+} and Rh^+). The crystal structures of the Pd(II) and Au(I) complexes are reported. For the Pd(II) complex, **1** acts as a bidentate ligand whereas for Au(I), **1** acts as a monodentate ligand through the thiolate.

Introduction

Derivatives of *o*-carborane 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ bearing a nitrogen-containing substituent R attached to the cage carbon atom (C_c), have attracted attention as potential medicinal agents for use in boron neutron capture therapy (BNCT) and as potentially-chelating carboranyl ligand precursors.[1]

Cyclodextrins are chiral selectors of first choice in chromatography and electrophoresis.[2] α-Cyclodextrin and its derivatives proved to be powerful selectors in chiral liquid chromatography separations and preparations of zwitterionic boron cluster compounds.[3] Surprisingly, α-cyclodextrin has been shown to be an effective chiral selector for a set of randomly chosen boron cluster anions if capillary electrophoresis was the separation technique.[4]

Our group has been concerned with the synthesis of dithioether 1,2-$(SR)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[5] monothioether 1-SR-2-R′-1,2-*closo*-$C_2B_{10}H_{10}$,[6] diphosphino 1,2-$(PR)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[7] monophosphino 1-PR_2-2-R′-1,2-*closo*-$C_2B_{10}H_{10}$[8,7d] and S,P-heterodisubstituted 1-PR_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ compounds.[9] Recently, the synthesis, partial deboronation and crystal structures of 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ and [7-(2′-pyridyl)-7,8-*nido*-$C_2B_9H_{11}$]$^-$ have been reported.[10] The first full characterization of an *o*-carborane containing a mercapto group, 1-(2′-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$, **1**, has been recently communicated.[11] Compound **1** represents a potential ligand for metal complexation acting as a bidentate chelating N,S-ligand. There are only two molecules reported with the bidentate chelating (*pyridine*)N-C-C-C-S(*H*) moiety whose crystal structures have been determined. One corresponds to **1** shown in Fig. 1C, and the second to the thiofenchone derivative shown in Fig. 1A.[12] Of notice is that whereas **1** crystallizes as such, the thiofenchone derivative requires protonation with HCl. In what concerns metal complexes of the bidentate chelating (*pyridine*)N-C-C-C-S(*H*) motif, only one metal

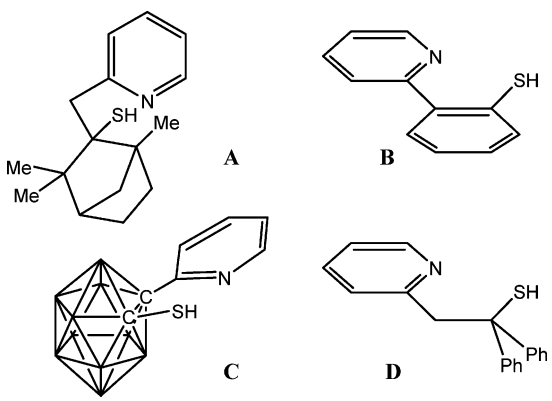

Fig. 1 Examples of bidentate chelating (*pyridine*)N-C-C-C-S(*H*) ligands: B and C rigid and A and D non-rigid.

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† It is a pleasure for the authors to dedicate this paper to Prof. Dr. Ken Wade on the occasion of his 75th birthday, in recognition of his outstanding contribution to the fields of borane clusters and organometallic chemistry.

‡ CCDC reference numbers 663535–663537. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715362g

§ Electronic supplementary information (ESI) available: UV spectra of compounds [NMe_4][**4**], [NMe_4][**5**], [NMe_4][**9**]–[NMe_4][**12**]. Chiral separation of [NMe_4][**5**], [NMe_4][**9**]–[NMe_4][**11**]. See DOI: 10.1039/b715362g

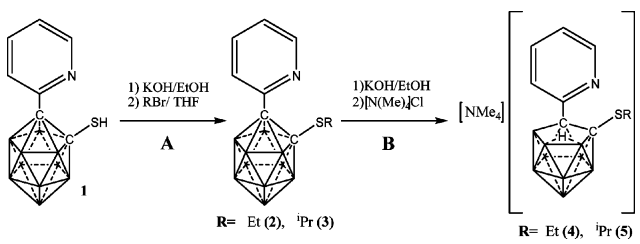
(Ru) complex of a geometrically similar chelating coordination site to that of **1** (see ligand B in Fig. 1) has been published.[13] The lack of information on these bidentate chelating (*pyridine*)N-C-C-C-S(*H*) ligands was even more pronounced when the restriction of rigidity on the moiety linking the pyridine and the –S(*H*) group was removed. This led to ligands with no double bonds between the two denticities of the ligand. For such a situation only one crystal structure of a Ni complex with the bulky ligand shown in Fig. 1D has been described.[14]

This paper describes the synthesis of N,S-heterodisubstituted 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R= Et, **2**; ^{i}Pr, **3**) compounds and their partial degradation which leads to the racemic anionic [7-(2′-pyridyl)-8-SR-7,8-*nido*-$C_2B_9H_{10}]^-$ (R = Et, **[4]**$^-$; ^{i}Pr, **[5]**$^-$) derivatives. Capillary electrophoresis with cyclodextrin in addition to instrumental techniques has been used to separate and identify these racemic mixtures. The absence of metal complexes with bidentate chelating (*pyridine*)N-C-C-C-S(*H*) ligands motivated us to start preliminary coordination studies on **1** with Pd(II), Au(I), and Rh(I) cations. Thus complexes **6–8** with Pd(II), Au(I) and Rh(I) are reported along with the crystal structures of the Pd(II) and Au(I) complexes. The few existing examples of complexes with the bidentate chelating (*pyridine*)N-C-C-C-S(*H*) ligands do not permit one to draw many conclusions on the influence of the carborane cage in such a chelating motif but their complexes may help to fill this important void.

Results and discussion

Reactivity of 1-(2′-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$

1 Synthesis and characterization of 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R = Et, ^{i}Pr) species. Starting from **1** the synthesis of *closo*-C_c-heterodisubstituted 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R = Et, **2**, ^{i}Pr, **3**) compounds has been accomplished after deprotonation with KOH in ethanol followed by alkylation with the appropriate alkyl bromide in 81 and 88% yield respectively (see Scheme 1A). These compounds contain two possible coordinating sites, C_c-C–N and C_c-SR, in the same carborane cluster. This is the first time that bidentate ligands with these functional groups have been reported and is the result of advances in the development of easy routes to alkylate the mercapto group in carborane chemistry. The existence of one available C_c-pyridyl unit in 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ has allowed the introduction of a second and different functional group. These ligands add to the 1,2-$(SR)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[5] 1,2-$(PR_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$[7] and 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$[9b] series and open the way to study the reactivity of chelating S,N-heterodisubstituted [1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}]^-$ thiolate ligand with metal complexes.



Scheme 1 A, synthetic pathway to N,S *closo*-heterodisubstituted *o*-carborane derivatives. B, their partial degradation.

Compounds **2** and **3** have been characterized by elemental analyses, IR and NMR techniques. The IR spectra show typical ν(B–H) absorptions at frequencies above 2550 cm^{-1}, characteristic for 1,2-*closo*-$C_2B_{10}H_{10}$ derivatives.[15] The $^{11}B\{^1H\}$-NMR of **2** and **3** present spectral data in the typical −2.0 to −10.5 ppm range for a *closo*-C_2B_{10} cluster. This is even more compressed than the spectral range observed for 1-SR-1,2-*closo*-$C_2B_{10}H_{11}$ and 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ compounds that appear in the range 0 to −10.5 and −1 to −13 ppm, respectively. The nature of the R alkyl group does not greatly influence the $^{11}B\{^1H\}$-NMR spectrum. In this way a 1 : 1 : 2 : 2 : 4 pattern for **2** and 1 : 1 : 2 : 6 pattern for **3** are observed as was expected for C_c non-equivalently substituted carborane. The resonances of intensity 4 and 6 shall be attributed to the coincidental overlap of two and three resonances of intensity two, respectively.

2 Partial deboronation of 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R = Et, ^{i}Pr). Partial deboronation or the formal removal of a B^+ from 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R = Et, **2**; ^{i}Pr, **3**) derivatives to yield the corresponding anionic species [7-(2′-pyridyl)-8-SEt-7,8-*nido*-$C_2B_9H_{10}]^-$ **[4]**$^-$ and [7-(2′-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}]^-$ **[5]**$^-$ was readily accomplished using KOH in ethanol (see Scheme 1B).[16] These species were isolated as the tetramethylammonium salts in analytically stoichiometric but not in isomeric purity (see Fig. 2). This is explained by considering that two equivalent boron atoms exist in 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ that are susceptible to the deboronation process. These are the boron atoms adjacent to both cluster carbon atoms. Upon nucleophilic attack to remove only one boron in the cluster, it is expected that the anion generated will be obtained as a

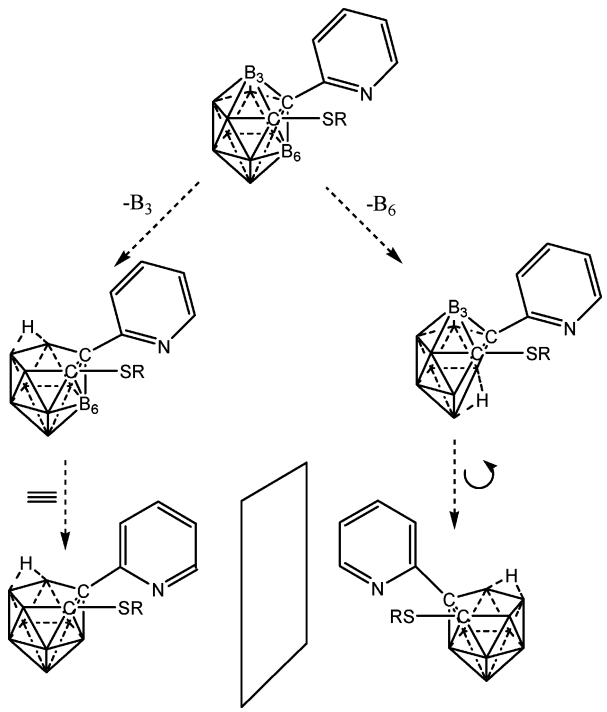


Fig. 2 Formation of a racemic mixture of the [7-(2′-pyridyl)-8-SR-7,8-*nido*-$C_2B_9H_{10}]^-$ anions upon deboronation of 1-(2′-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$.

racemic mixture. The heterodisubstituted *closo* compounds show a similar reactivity towards nucleophilic attack by EtO^- as that reported for 1-SR-1,2-*closo*-$C_2B_{10}H_{11}$ compounds. The existence of the pyridyl group does not alter the stability of the C_c–S bond towards EtO^-.

The *nido* species have been characterized by elemental analyses, MALDI-TOF-MS, IR and NMR techniques. Both **[4]**$^-$ and **[5]**$^-$, show strong IR ν(B–H) resonances near 2520 cm^{-1}, in agreement with a *nido* $[C_2B_9]^-$ cluster.[15] The $^{11}B\{^1H\}$-NMR resonances for **[4]**$^-$ and **[5]**$^-$ appear in the range −8 to −36 ppm with patterns 2 : 1 : 1 : 2 : 1 : 1 : 1 and 2 : 1 : 2 : 1 : 1: 1 : 1, respectively, in agreement with an asymmetric *nido* $[C_2B_9H_{10}]^-$ cluster. The $^1H\{^{11}B\}$ NMR spectra of **[4]**$^-$ and **[5]**$^-$ shows the resonances that correspond to the Et- and ^{i}Pr-groups and the three common ones: i) resonances between 8.37 and 7.00 ppm corresponding to the pyridyl group, ii) resonances between 2.51–0.24 ppm corresponding to the hydrogen atoms bonded to boron and iii) a resonance at high field −2.05 ppm characteristic of the B–H–B hydrogen bridge.

The anionic *nido* compounds were also analyzed by MALDI-TOF-MS analysis. As an example, the highest peak for **[5]**$^-$ displays a signal with isotopic distribution centred at m/z 284.4 corresponding to the expected anionic fragment $^{12}C_{10}{}^1H_{21}{}^{11}B_9{}^{14}N^{32}S$ and two peaks at 238.3 and 208.3. The experimental peak position and isotopic distribution match the theoretical calculations that correspond to the molecular peak and the -^{i}Pr and -S^{i}Pr cleavage products respectively.

Crystal structure of [NMe$_4$][7-(2′-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$]

Crystallization by slow evaporation of [NMe$_4$][**5**] in acetone at a controlled temperature (4 °C), afforded air and moisture insensitive yellow single crystals suitable for X-ray analysis. The ORTEP plot of the structure of the anion **[5]**$^-$ is presented in Fig. 3 and selected bond lengths (Å), angles and torsion angles (°) for **[5]**$^-$ in Table 1. Although it has different substituents on the cluster carbon atoms, the molecular structure of [NMe$_4$][**5**] is similar to that of [NMe$_4$][7-PPh$_2$-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$].[9b] The S–C_c and C_c–C_c bond lengths are comparable in both compounds despite large differences in the C_c-substituents. In this regard,

Table 1 Selected bond lengths (Å), angles (°) and torsion angles (°) of [NMe$_4$][**5**]

S–C8	1.786(3)	C7–B11	1.613(4)
S–C19	1.834(3)	C8–B9	1.648(4)
C7–C8	1.603(3)	B9–B10	1.832(5)
C7–C13	1.510(3)	B10–B11	1.802(4)
C8–S–C19	103.05(12)	S–C8–C7	118.51(18)
C8–C7–C13	118.0(2)		
C8–C7–C13–N14	97.9(3)		

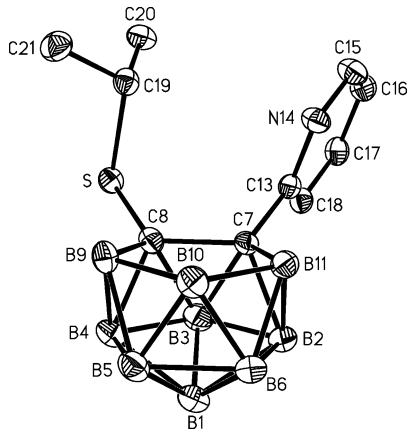


Fig. 3 The structure of the anion **[5]**$^-$ in [NMe$_4$][**5**]. Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

the C_c–$C_{pyridyl}$ distance 1.510(3) Å in [NMe$_4$][7-(2′-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$], is appreciably smaller than the C_c–P distance of 1.855(3) Å in [NMe$_4$][7-PPh$_2$-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$].[9b] The packing of the anions and cations does not show any abnormal features: the cation has six anion neighbours and the anion has six cation ones. Both heteroatoms form very weak H-bonds with CH hydrogens. The shortest N···H distance is 2.68 Å.

Spectral study of [NMe$_4$][4] and [NMe$_4$][5]

UV electrospectrophotometry is a simple accessible detection technique for anionic boron clusters.[10b] To optimize the photometric detection, UV spectra of the anions **[4]**$^-$, **[5]**$^-$ and several reported thioether and pyridyl derivatives, [7-R′-8-SR-7,8-*nido*-$C_2B_9H_{10}$]$^-$ (R′ = H, R = Et, **[9]**$^-$; R′ = R = Ph, **[10]**$^-$; R′ = Me, R = Ph, **[11]**$^-$ and [NMe$_4$][7-(2′-pyridyl)-7,8-*nido*-$C_2B_9H_{11}$]; **[12]**$^-$, were measured before running electrophoretic experiments in order to determine the influence of the *exo*-substituents (Table 2). The investigated anions have low molar extinction coefficients at wavelengths between 200 and 210 nm that can be used for detection. The weakest UV-light absorption was for the species **[9]**$^-$ and monotonously decreased up to 235 nm. The phenyl group bonded to C_c extend the light absorption to higher wavelengths and provoked formation of absorption maxima above 200 nm. The pyridine ring shifts the absorption cut-off to slightly higher wavelengths than the phenyl and thiophenyl groups.

Capillary electrophoresis

The simplest variant of the technique, capillary electrophoresis in free solution, is dominant in electrophoretic methods developed

Table 2 Light absorption characteristics of studied monothioethers of the type [7-R-8-SR′-7,8-*nido*-$C_2B_9H_{10}$]$^-$

Compound	UV cut-off/nm	λ_{200}/nm	ε_{200}/L mol^{-1} cm^{-1}	λ_1/nm	ε_1/L mol^{-1} cm^{-1}	λ_2/nm	ε_2/L mol^{-1} cm^{-1}
[4]$^-$	317	200	1.31×10^4	209	1.26×10^4	260	4.18×10^3
[5]$^-$	317	200	1.07×10^4	211	1.03×10^4	259	3.00×10^3
[9]$^-$	268	200	6.68×10^3	—	—	—	—
[10]$^-$	308	200	4.06×10^4	260	6.68×10^3	—	—
[11]$^-$	308	200	1.84×10^4	258	1.05×10^4	—	—
[12]$^-$	400	204	5.99×10^3	263	2.87×10^3	339	2.95×10^3

for both achiral and chiral analysis of charged organic compounds of low molecular mass.[2] Application of capillary electrophoresis to the analysis of electrophoretically charged cluster species has been reported.[4] In this work capillary zone electrophoresis was used with the aim of determining the chemical purity and chirality of the anions $[4]^-$, $[5]^-$, $[9]^-$–$[12]^-$.

Chemical purity

The background electrolyte at pH 7.3 (see Experimental section) was selected to check the chemical purity of these monothioether anions. Electrophoretic analysis revealed that all the anions are electrophoretically pure.

Chirality

Separation of a racemic compound or ion, which is electrophoretically pure, into two peaks by action of a chiral selector is evidence for its chirality.[17,2] The tetramethylammonium salts of the investigated racemic boron cluster anions are practically insoluble in water but they easily dissolve in polar organic solvents like methanol, ethanol, acetonitrile or acetone, which, however, do not dissolve native cyclodextrins. Water–organic solvents must be therefore used for chiral separations. The organic constituent of the background electrolyte (BGE) dissolves boron cluster anions and adjusts the strength of their interaction with the cavity of the used cyclodextrin, which is excessively strong in aqueous solution. The chirality of the anionic species was verified by using α-cyclodextrin as the chiral selector.

A voltage of −20 kV was applied to the polyacrylamide coated fused silica capillary[18] of a 53 cm separation length. BGE containing α-cyclodextrin was prepared daily by dissolution of the proper amount from the stock aqueous TRIS buffer adjusted with methylsulfonic acid at pH 7.3. After dissolving α-cyclodextrin, the buffer was mixed with methanol in 7 : 3 (v/v) ratio.

Chiral discrimination of any compound with a proper chiral selector depends on the chiral selector concentration in the background electrolyte and passes through a maximum.[2b] A wide range of α-cyclodextrin concentrations had to be used for the generation of a measurable separation selectivity for these ions. The influence of the α-cyclodextrin concentration on the difference of migration speed of atropoisomers of the investigated chiral anions separated with α-cyclodextrin, $\Delta\mu$, was therefore measured up to an 18 mmol L^{-1} concentration of α-cyclodextrin. This concentration approaches the solubility limit of α-cyclodetrin in the water–methanol 7 : 3 (v/v) mixture. Measurable $\Delta\mu$ values evidence electrophoretic separation of the studied compounds into two zones with clearly developed maxima. In Fig. 4 the separation of $[4]^-$ into its enantiomers is shown. For chiral separations of other investigated anions see ESI.§ Table 3 shows that chirality was safely evidenced for any stable compound using more than one α-cyclodextrin concentration.

3 Metal complexation studies of 1-(2′-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$. The chelating properties of 1,2-$(PR_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[7d,10,19] 1,2-$(SR)_2$-1,2-*closo*-$C_2B_{10}H_{10}$, 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$[9a] have already been studied. As we have demonstrated earlier[19g,20] the reaction of *exo*-heterodisubstituted carborane derivatives with transition metal complexes, $[MCl(PPh_3)_n]$ in methanol or ethanol, leads to deboronation of the *closo* cluster producing an 11-vertex monoanionic *nido* species.[9a] A nucleophilic attack by ethanol at the more positive boron atoms, either B(3) or B(6), takes place producing a mononegative chelating ligand as a result of removal of one boron atom. Therefore special care, avoiding possible nucleophiles, needs to be taken in attempting the synthesis of transition metal complexes in which the *closo* C_2B_{10} fragment is retained. Preserving the *closo* nature of the cluster is not a simple task[19c,g,20] but [1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}]^-$ offered a unique chance to study a S^-/pyridine 6-membered chelating bidentate ligand. To this aim coordination was addressed towards transition metals Pd(II), Au(I) and Rh(I) that demand different coordinating sites.

Diethyl ether was the solvent of choice to avoid competing reactions caused by nucleophiles. The requirement for the absence of any nucleophile was even applied in the purification process. These restrictions were applied in the synthesis of [PdCl(1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh_3)] (**6**); [Au (1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh_3)] (**7**) and [Rh(1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh_3)$_2$] (**8**). The syntheses of these complexes was achieved by reacting $[RhCl(PPh_3)_3]$, $[PdCl_2(PPh_3)_2]$, $[AuClPPh_3]$ with the "*in situ*" prepared [1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}]^-$ in diethyl ether (Scheme 2).

The IR spectra of **6–8** show ν(B–H) resonances near 2560 cm^{-1} that agree with a retention of the *closo* structure in the complexes. The ^{11}B-NMR spectrum in the range −1.9 to −13.3 ppm points

Table 3 Influence of the α-cyclodextrin concentration on the difference in migration speed of atropoisomers of investigated chiral anions, $\Delta\mu$, in the background electrolyte obtained by mixing of aqueous buffer, which was prepared by adjusting 14.4 mmol L^{-1} methylsulfonic acid to pH 7.3 with TRIS, and methanol in 7 : 3 (v/v) ratio

	α-Cyclodextrin concentration/mmol L^{-1}						
Compound	0.3	1.6	3.0	6.0	9.0	14.0	18.0
$[4]^-$	[a]	0.07	0.13	0.19	0.22	0.23	0.20
$[5]^-$	[a]	0.09	[a]	0.23	0.25	[a]	[a]
$[9]^-$	0.12	1.40	1.61	[a]	[a]	[a]	[a]
$[10]^-$	[a]	0	0	0.07	0.07	0.08	0.05
$[11]^-$	[a]	0	0.06	0.09	0.09	0.08	[a]

[a] Not measured.

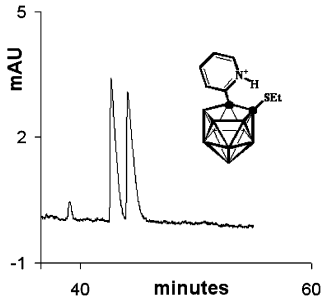
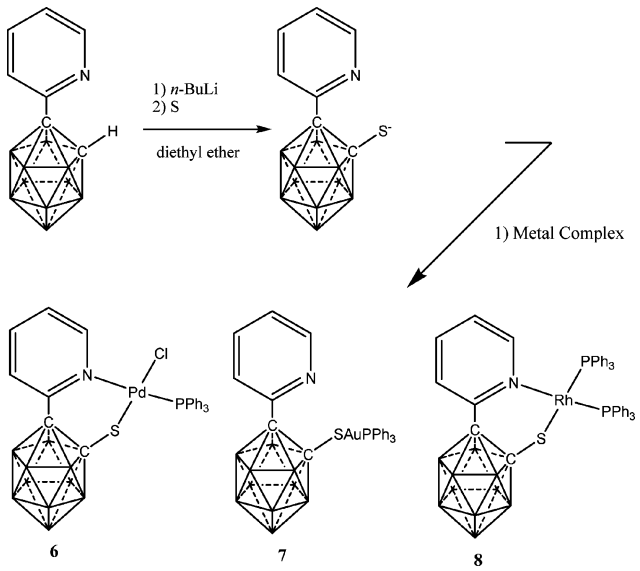


Fig. 4 Chiral separation of $[4]^-$ in BGE containing 11 mmol L^{-1} of α-cyclodextrin. The BGE was prepared by mixing aqueous methylsulfonic acid–TRIS buffer of pH 7.3 with methanol 7 : 3 (v/v) ratio. The difference in mobilities of the atropoisomers of $[4]^-$, $\Delta\mu$, was 0.25 mobility units when a voltage of −20 kV was applied on the polyacrylamide coated fused silica capillary of 75 μm inner diameter and 53 cm separation length.



Scheme 2 Complexation reaction between the "*in situ*" prepared [1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$]$^-$ ligand with transition metals that demand different coordinating sites.

to the same conclusion, with a pattern 2 : 2 : 2 : 2 : 2 for **6**, 1 : 4 : 5 for **7** and 1 : 1 : 2 : 2 : 2 : 2 for **8**.

Unambiguous determination of the molecular structures of **6** and **7**, was possible after good crystals of these complexes were obtained from acetone–*n*-hexane and acetone–chloroform, respectively. Perspective views of the complex units are presented in Fig. 5 and 6, and selected bond distances and angles are gathered in Tables 4 and 5. The X-ray analyses of **6** and **7** confirmed the *closo* nature of the resulting palladium and gold complexes but with a different coordination behavior of the ligand originated by the different coordination requirements of the metals. In **6** the carborane cage is co-ordinated bidentately through the N and S atoms to the Pd(II) ion thus forming a 6-membered C_3NPdS chelate ring. In **6**, the Cl atom and the PPh_3 group in *cis* positions complete the distorted square-planar coordination around the metal. In **7**, the ligand is monodentately coordinated through

Table 4 Selected bond lengths (Å), angles (°) and torsion angles (°) for **6**

Pd–Cl	2.3339(8)	S–C2	1.778(3)
Pd–S	2.3041(8)	C1–C2	1.703(4)
Pd–P	2.2314(9)	C1–C13	1.516(5)
Pd–N14	2.143(3)		
Cl–Pd–S	175.44(3)	Pd–N14–C13	129.3(2)
S–Pd–N14	87.23(7)	C2–C1–C13	117.8(3)
P–Pd–N14	175.31(7)	S–C2–C1	120.1(2)
Pd–S–C2	98.32(10)		
C2–C1–C13–N14	−44.1(4)		

Table 5 Selected bond lengths (Å) and angles (°) and torsion angles (°) for **7**

Au–S	2.3052(10)	C1–C2	1.725(6)
Au–P	2.2616(10)	C1–C13	1.501(6)
S–C2	1.774(4)		
S–Au–P	174.86(4)	C2–C1–C13	119.5(3)
Au–S–C2	108.48(14)	S–C2–C1	121.3(3)
C2–C1–C13–N14	−78.2(5)		

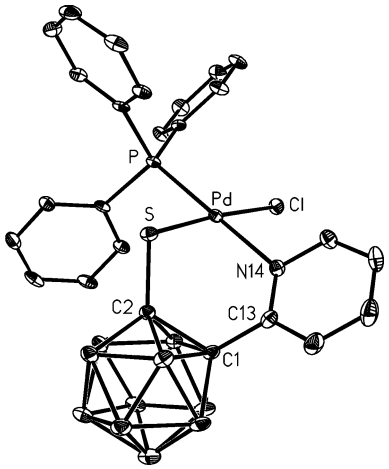


Fig. 5 Molecular structure of **6**. Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

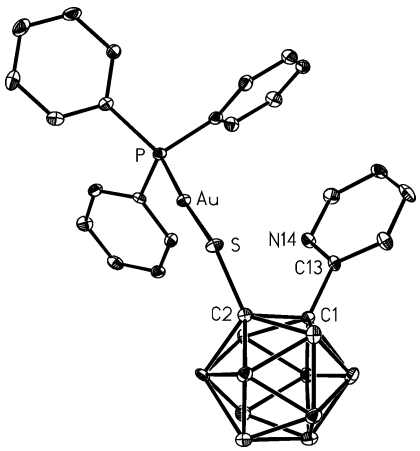


Fig. 6 Molecular structure of **7**. Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

the S atom (S is a softer Lewis base than N_{Pyr}) to Au(I) with no participation of the pyridyl group in the coordination. Nearly linear coordination of Au(I) is completed by the P atom of the PPh_3 group.

Comparison of the conformation of the carborane ligand in **6** and **7** with the free (1-(2′-pyridyl)-2-SH-1,2-$C_2B_{10}H_{10}$) ligand reveals noticeable differences in the orientation of the pyridyl group. For the free ligand the N–C_{pyr}–C_c–C_c torsion angle is 96.4(2)°.[11] Monodentate coordination of the ligand in **7** does not change the angle very much (N–C_{pyr}–C_c–C_c = −78.2(5)°), but in **6**, bidentate coordination of the ligand to Pd (II) changes the orientation of the pyridyl group markedly (N–C_{pyr}–C_c–C_c = −44.1(4)°). In addition, minor differences in the C_c–C_c distances can be seen between the free ligand and complexes **6** and **7**. The C_c–C_c distance of 1.730(3) Å in the free ligand is comparable with the distance of 1.725(6) Å in **7**, but in the bidentately coordinated ligand of **6** the distance is shortened to 1.703(4) Å.

The crystal packing of the neutral complex units in **6** and **7** is controlled by very weak van der Waals contacts. In both complexes there are only weak charges on the heteroatoms and on the other hand the compounds contain very weakly acidic H-atoms.

Conclusions

The synthesis of *closo* and *nido* C_c heterodisubstituted 1-(2′-pyridyl)-2-SR-1,2-$C_2B_{10}H_{10}$ (R = Et, ^{i}Pr) and [7-(2′-pyridyl)-8-SR-7,8-*nido*-$C_2B_9H_{10}]^-$ (R = Et, ^{i}Pr) derivatives has been conducted starting from 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ (**1**). They contain the C_c–C_5H_4N and C_c–S groups in the same carborane cluster. Analytical separation of the racemic mixture has been accomplished using capillary electrophoresis assisted with α-cyclodextrin. Two well defined bands have been observed due to the non-equal interaction of the two enantiomers with α-cyclodextrin. The heterodisubstituted 1-(2′-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$ ligand is able to coordinate to metals producing pure samples of complexes with *closo* cluster retention by using dry non-nucleophilic solvents to perform the reaction. The two coordinating moieties C_c–C_5H_4N and C_c–S are non-equivalent, as has been demonstrated upon reaction with Au(I), where the C_c–S moiety is the only one reactive. With metals requiring a higher coordination number than two, such as Pd(II) and Rh(I), both the C_c–C_5H_4N and C_c–S moieties coordinate to the metal. The Pd(II) complex is one of only two structurally characterized complexes of the bidentated chelating (*pyridine*)N-C-C-C-S(*H*) rigid motif.

Experimental

Materials

1-Pyridyl-2-SH-1,2-*closo*-carborane was synthesized according to the literature.[11] A 1.6 M solution of *n*-butyllithium in *n*-hexane was used as purchased. [8-SEt-7,8-*nido*-$C_2B_9H_{10}]^-$, [**9**]$^-$; [7-Ph-8-SPh-7,8-*nido*-$C_2B_9H_{10}]^-$, [**10**]$^-$; [7-Me-8-SPh-7,8-*nido*-$C_2B_9H_{10}]^-$, [**11**]$^-$; [NMe_4][7-(2′-pyridyl)-7,8-*nido*-$C_2B_9H_{11}$], [**12**]$^-$ were synthesized according to reported methods.[21,10b] [$RhCl(PPh_3)_3$],[22] [$PdCl_2(PPh_3)_2$],[23] [$AuClPPh_3$][24] were synthesized as described elsewhere. All organic compounds and inorganic salts were analytical reagent grade and were used as received. The solvents for the synthesis were reagent grade. All reactions were carried out under a dinitrogen atmosphere using standard Schlenk techniques.

Mesityloxide, α-cyclodextrin, acetonitrile and methanol were from Sigma-Aldrich, the solvents being of HPLC grade. Mesityloxide, which migrates through the capillary with the speed of electroosmotic flow due to the absence of its own charge, served as the electroosmosis marker. It was a constituent of injected samples in experiments utilizing the uncoated capillary. Methylsulfonic acid, of 99% purity, was from Fluka. Tris(hydroxymethyl)-aminomethane (TRIS) of analytical grade purity was from Lachema. All other chemicals were of analytical grade purity. Distilled and boiled water was used for the preparation of the water solutions. The spectra are mean values from three subsequent measurements corrected for the background UV-light absorption of the used acetonitrile.

Instrumentation

Microanalyses were performed on a Carlo Erba EA1108 microanalyzer. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H-NMR (300.0 MHz), ^{11}B-NMR (96.3 MHz), $^{13}C\{^1H\}$-NMR (75.0 MHz) and $^{31}P\{^1H\}$-NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shift values for ^{1}H-NMR, $^{13}C\{^1H\}$-NMR, ^{11}B-NMR and $^{31}P\{^1H\}$-NMR were referenced relative to external $SiMe_4$, $BF_3{\cdot}OEt_2$ and 85% H_3PO_4 respectively. Chemical shifts are reported in units of parts per million, and all coupling constants are reported in Hz.

Spectra of [NMe_4][7-(2′-pyridyl)-8-SEt-7,8-*nido*-$C_2B_9H_{10}$], [NMe_4][**4**]; [NMe_4][7-(2′-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$], [NMe_4][**5**]; [NMe_4][8-SEt-7,8-*nido*-$C_2B_9H_{10}$], [NMe_4][**9**]; [NMe_4][7-Ph-8-SPh-7,8-*nido*-$C_2B_9H_{10}$], [NMe_4][**10**]; [NMe_4][7-Me-8-SPh-7,8-*nido*-$C_2B_9H_{10}$], [NMe_4][**11**] were measured using the double-beam UV-VIS spectrophotometer UNICAM UV 500 (Thermo Spectronic, Cambridge, UK) equipped with a fused quartz cuvette of 1 cm optical path length and with the Vision 3.5 software (Unicam Limited, Cambridge, UK). The latter contains routines for automatic correction of the light absorption of the used solvent. Acetonitrile was utilized for dissolution of milligram quantities of solid tetramethylammonium salts of [**4**]$^-$, [**5**]$^-$, [**9**]$^-$-[**11**]$^-$ to 1 mmol L^{-1} concentration. These primary solutions were further diluted with acetonitrile by the trial-and-error method to concentrations at which the tetramethylammonium dissolved salts of [**4**]$^-$, [**5**]$^-$, [**9**]$^-$-[**11**]$^-$ exhibited the highest absorbances close to 1 AU. The UV spectrum [NMe_4][7-(2′-pyridyl)-7,8-*nido*-$C_2B_9H_{11}$], [NMe_4][**12**] was measured in the radially illuminated fused silica capillary of inner diameter 75 μm placed in the spectrophotometer JASCO 875 specified below. Software for this spectrophotometer supply optical spectra of the dissolved species after correction for the solvent. The concentration of [NMe_4][**12**] in acetonitrile was 1×10^{-3} mol L^{-1}. The spectra of the tetramethylammonium salts of anions [**4**]$^-$, [**5**]$^-$, [**9**]$^-$–[**12**]$^-$ are given as ESI.§

The main parts of the laboratory electrophoretic set-up were the switchable high voltage power supply Spellman CZE 1000 R (Plainview, NY, USA) and the UV-VIS spectrophotometer JASCO 875 (Tokyo, Japan). The spectrophotometer constructed for liquid chromatography was adapted for experiments with fused silica capillaries whose outer wall was thermostated by circulating liquid with precision better than ±0.1 °C. Joule heat input into the separation capillary up to 0.2 W at the applied −20 kV driving voltage guaranteed a very low difference between the temperature of the outer capillary wall thermostated to 25 °C and the temperature in the capillary centre. The electrode compartments and paths for filling the compartments, for injecting samples and for flushing of the separation capillary were drilled in a polyetheretherketon (PEEK) block (DSM Engineering Plastic Products, Tielt, Belgium).[4] The polyacrylamide coated[18] fused silica capillary of 75 μm inner diameter, 53 cm separation length and 64.5 cm total length, free of electroosmotic flow, was used for the experiments. 0.8 mm of the capillary radially illuminated by the UV light of 200 nm worked as the photometric detection cell. Stock aqueous buffer was prepared from 14.4 mmol L^{-1} methylsulfonic acid adjusted to pH 7.3 with solid TRIS; approximately 1 mol L^{-1} TRIS solution was used in the last step of the pH adjustment. Injected samples were prepared from known milligram amounts of solid tetramethylammonium salts dissolved in a few drops of acetonitrile and then diluted to concentrations close to 1 mmol L^{-1} using the 1 : 1 : 2 (v/v/v) mixture of water with aqueous stock buffer and acetonitrile. Concentrations of measured compounds are given in spectra (see ESI§). Background electrolyte was

prepared by mixing the stock aqueous buffer with methanol in a 7 : 3 (v/v) ratio. The CSW 1.7 (Data Apex, Prague, Czech Republic) data station served for the measurement of migration times of detected zones and for calculation of peak characteristics common in chromatography. Migration times were converted to mobilites given in 10^{-9} m^2 V^{-1} s^{-1} units using the definition equation given elsewhere.[2]

Synthesis of 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ (1)

This compound synthesis was first reported by Wade *et al.*[10a,25] The synthetic procedure described here is different to the one reported.

A total of 0.747 g (6 mmol) of decaborane and 1.56 ml of dimethylaniline dissolved in 20 ml of toluene was refluxed for 2 h under nitrogen. After cooling, 0.41 ml (4 mmol) of ethynylpiridine, was added and the reaction mixture was heated under reflux for 18 h more. The solvents were removed under vacuum, and the residue was treated with 5 ml of methanol for 30 min under stirring. Upon evaporation of the solvent, the product was treated with petroleum ether (boiling range = 35–70 °C). The insoluble solid was sublimed and the petroleum ether was evaporated to dryness to afford in total 0.36 g (1.6 mmol) of **1** (40%). Anal. calcd for $C_7H_{15}B_{10}N$: N, 6.33; C, 37.99; H, 6.83; S, 11.4; Found: N, 6.08; C, 38.57; H, 6.82%. IR: ν/cm^{-1} 3067 (C_{aryl}–H); 2958, 2924, 2854 (C_{aryl}–H); 2643, 2631, 2605, 2590, 2567 (B–H); 1574 (C=N); 1464, 1434 (C–N); 1019, 1011 (C–N–C). $^1H\{^{11}B\}$-NMR (CD_3COCD_3): δ 8.51 (d, $^3J_{HH}$ = 4.4, C_{pyr}–H_6, 1H), 7.92 (td, $^3J_{HH}$ = 7.8, ^4J(H,H) = 1.6 C_{pyr}–H_4, 1H), 7.71 (d, $^3J_{HH}$ = 7.8, C_{pyr}–H_3, 1H), 7.51 (ddd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 4.4, $^5J_{HH}$ = 0.6, C_{pyr}–H_5, 1H), 5.42 (s, C_c–H, 1H), 2.49 (s, B–H), 2.35 (s, B–H), 2.27 (s, B–H). ^{11}B-NMR (CD_3COCD_3): δ −2.7 (d, $^1J_{BH}$ = 152, 1B), −3.5 (d, $^1J_{BH}$ = 150, 1B), −7.9 (d, $^1J_{BH}$ = 153, 2B), −9.8 (d, 2B), −10.5 (d, $^1J_{BH}$ = 167, 2B), −12.4 (d, $^1J_{BH}$ = 158, 2B). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 148.8 (s, C_{2pyr}), 152.0 (s, C_{2pyr}), 150.6 (s, C_{6pyr}), 139.6 (s, C_{4pyr}), 126.4 (s, C_{3pyr}), 123.1 (s, C_{5pyr}), 77.6 (s, C_c–Py), 59.6 (s, C_c–H).

Synthesis of 1-(2′-pyridyl)-2-SEt-1,2-*closo*-$C_2B_{10}H_{10}$ (2)

To a two necked round bottom flask (50 ml), containing a solution of KOH (25 mg, 0.45 mmol) in deoxygenated ethanol (10 ml), was added (1-(2′-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$) (115 mg, 0.45 mmol). After stirring for 1 h at room temperature the solvent was evaporated and the residue redissolved in dry THF (10 ml). Bromoethane (0.013 ml, 0.90 mmol) was added and the mixture was refluxed for 2 h. All volatiles were evaporated under vacuum, and the residue was treated with diethyl ether (10 ml) and water 10 ml, the organic layer was separated and washed with KOH (3 × 10 ml, 0.5 M), dried over anhydrous $MgSO_4$ and evaporated under vacuum resulting a yellow solid. Yield: 112 mg (88%). Anal. calcd for $C_9H_{19}B_{10}NS$: N, 4.97; C, 38.41; H, 6.8; S, 11.4; Found: N, 4.95; C, 38.20; H, 6.50; S, 11.15%. IR: ν/cm^{-1} 2965, 2924 (C_{aryl}–H/C_{alkyl}–H); 2569 (B–H); 2364, 2338 (S–R); 1584 (C=N); 1463, 1433 (C–N); 1081, 1014 (C–N–C); 811 (CH_3); 774, 740 (C_{aryl}–H). $^1H\{^{11}B\}$-NMR (CD_3COCD_3): δ 8.67 (d, $^3J_{HH}$ = 4.7, C_{pyr}–H_6, 1H), 7.95 (ddd, $^3J_{HH}$ = 7.6, ^4J(H,H) = 7.7, $^5J_{HH}$ = 1.5, C_{pyr}–H_4, 1H), 7.89 (ddd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 4.7, C_{pyr}–H_5, 1H), 7.5 (ddd, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 4.6, $^5J_{HH}$ = 0.6, C_{pyr}–H_3, 1H), 2.77 (q, $^3J_{HH}$ = 7.5, S–CH_2CH_3, 2H), 3.00 (s, B–H, 1H), 2.53 (s, B–H, 1H), 2.45 (s, B–H, 4H), 2.37 (s, B–H, 2H), 2.22 (s, B–H, 2H), 0.90 (t, $^3J_{HH}$ = 7.5, CH_3, 3H). ^{11}B-NMR (CD_3COCD_3): δ −2.0 (d, $^1J_{BH}$ = 196, 1B), −2.9 (d, $^1J_{BH}$ = 144, 1B), −7.6 (d, $^1J_{BH}$ = 172, 2B), −9.1 (2B), −9.8 (d, $^1J_{BH}$ = 132, 4B). $^{13}C\{^1H\}$-NMR (CD_3COCD_3): δ 148.8 (s, C_{2pyr}), 148.1 (s, C_{6pyr}), 139.1 (s, C_{4pyr}), 125.5 (s, C_{3pyr}), 124.9 (s, C_{5pyr}), 87.51 (s, C_c–Py), 85.2 (s, C_c–SEt), 30.0 (s, C_{CH2}), 11.9 (s, C_{CH3}).

Synthesis of 1-(2′-pyridyl)-2-S^{i}Pr-1,2-*closo*-$C_2B_{10}H_{10}$ (3)

In the same manner as for compound **2**, to a solution of KOH (6 mg, 0.11 mmol) in deoxygenated ethanol (5 ml), was added (1-(2′-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$) (28 mg, 0.11 mmol). After stirring for 1 h at room temperature the solvent was evaporated and the residue redissolved in dry THF (5 ml). Bromoisopropyl (0.02 ml, 0.22 mmol) was added and the mixture was refluxed for 2 h. All volatiles were evaporated under vacuum, and the residue was treated with diethyl ether (10 ml) and water (10 ml), the organic layer was separated and washed with KOH (3 × 10 ml, 0.5 M), dried over anhydrous $MgSO_4$ and evaporated under vacuum resulting a yellow oil. Yield: 29 mg (81%). Anal. calcd for $C_{10}H_{21}B_9NS$: N, 4.92; C, 42.20; H, 7.44; S, 11.27. Found: N, 4.64; C, 42.2; H, 7.70; S, 10.91%. IR: ν/cm^{-1} 2932 (C_{aryl}–H/C_{alkyl}–H); 2577 (B–H); 2352, 2361 (S–R); 1464, 1434 (C–N); 1081, 1012 (C–N–C). $^1H\{^{11}B\}$-NMR ($CDCl_3$): δ 8.65 (d, $^3J_{HH}$ = 4.5, C_{pyr}–H, 1H), 7.75 (m, C_{pyr}–H, 2H), 7.39 (ddd, $^3J_{HH}$ = 5.3, $^4J_{HH}$ = 1.8, C_{pyr}–H, 1H), 3.25 (h, $^3J_{HH}$ = 6.9, CH, 1H), 2.95 (s, B–H, 2H), 2.57 (s, B–H, 2H), 2.47 (s, B–H, 4H), 2.27 (s, B–H, 2H), 1.12 (d, $^3J_{HH}$ = 6.9, CH_3, 6H). ^{11}B-NMR ($CDCl_3$): δ −2.4 (d, $^1J_{BH}$ = 156, 1B), −3.6 (d, $^1J_{BH}$ = 138, 1B), −8.5 (d, $^1J_{BH}$ = 159, 2B), −10.4 (d, $^1J_{BH}$ = 126, 6B). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 149.1 (s, C_{pyr}), 136.9 (s, C_{pyr}), 126.1 (s, C_{pyr}), 124.7 (s, C_{pyr}), 121.5 (s, C_{pyr}), 87.5 (s, C_c–pyr), 85.7 (s, C_c–S^{i}Pr), 42.6 (s, S–CH), 23.8 (s, CH–CH_3).

Synthesis of [NMe_4][7-(2′-pyridyl)-8-SEt-7,8-*nido*-$C_2B_9H_{10}$], [NMe_4][4]

To a Schlenk flask containing a solution of KOH (70 mg, 1.2 mmol) in deoxygenated ethanol (5 ml), was added 1-(2′-pyridyl)-2-SEt-1,2-*closo*-$C_2B_{10}H_{10}$ (71 mg, 0.25 mmol). The mixture was refluxed for 3 h, cooled to room temperature and the solvent evaporated. The residue was dissolved in water (2 ml) and treated with a solution of tetramethylammonium chloride. The white solid was filtered off and washed with water and diethyl ether. Yield: 61 mg, 0.17 mmol (70%). Anal. calcd for $C_{13}H_{31}B_9N_2S$: N, 8.13; C, 45.29; H, 9.06; S, 9.30. Found: N, 8.01; C, 45.41; H,9.17, S, 9.51%. IR: ν/cm^{-1} 2937 (C_{aryl}–H); 2534 (B–H), 2362, (S–R); 1472 (C–N); 1026 (C–N–C). ^1H-$\{^{11}B\}$NMR (CD_3COCD_3): δ 8.37 (d, $^3J_{HH}$ = 4, C_{pyr}–H, 1H), 7.48 (t, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, C_{pyr}–H, 1H), 7.26 (d, $^3J_{HH}$ = 8, C_{pyr}–H, 1H), 7.00 (t, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, C_{pyr}–H, 1H), 3.44 (s, $N(CH_3)_4$, 12H), 2.92 (q, $^3J_{HH}$ = 7.5, CH_2–CH_3, 1H), 2.65 (q, $^3J_{HH}$ = 7.5, CH_2–CH_3, 1H), 2.47 (s, B–H, 1H), 2.23 (s, B–H, 1H), 2.20 (s, B–H, 1H), 1.73 (s, B–H, 2H), 1.48 (s, B–H, 1H), 1.38 (s, B–H, 1H), 0.83 (t, $^3J_{HH}$ = 7.5, CH_2–CH_3, 3H), 0.73 (s, B–H, 1H), 0.24 (s, B–H, 1H), −2.05 (s, BHB, 1H). ^{11}B-NMR (CD_3COCD_3): δ −7.1 (d, $^1J_{BH}$ = 138, 2B), −12.1 (d, $^1J_{BH}$ = 158, 1B), −15.9 (d, $^1J_{BH}$ = 142, 3B), −18.48 (d, $^1J_{BH}$ = 145, 1B), −32.6 (dd, $^1J_{BH}$ = 132, $^1J_{BH}$ = 29, B(10)), −35.1 (d, $^1J_{BH}$ = 138, B(1)). $^{13}C\{^1H\}$-NMR (CD_3COCD_3): δ 155.9 (s, C_{py}), 147.4 (s, C_{pyr}), 135.2 (s, C_{4pyr}), 125.2 (s, C_{3pyr}), 120.4 (s, C_{5pyr}), 62.7 (s, C_c), 55.1 (s, $N(CH_3)_4$), 22.2 (s, CH_2), 13.4 (s, CH_3). MALDI-TOF-MS: 270.36 (47.5%, M), 208.27 (100%, M − SEt).

Synthesis of [NMe$_4$][7-(2′-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$], [NMe$_4$][5]

To a Schlenk flask containing a solution of KOH (11 mg, 0.20 mmol) in deoxygenated ethanol (5 ml), was added 1-(2′-pyridyl)-2-S^{i}Pr-1,2-*closo*-$C_2B_{10}H_{10}$ (12 mg, 0.04 mmol). The mixture was refluxed for 3 h, cooled to room temperature and evaporated. The residue was dissolved in water (2 ml) and treated with a solution of tetramethylammonium chloride. The white solid was filtered off and washed with water and diethyl ether. Yield: 9 mg, 0.025 mmol, (64%). Anal. calcd for $C_{14}H_{33}B_9N_2S$: N, 7.83; C, 47.00; H, 9.02, S, 8.96. Found: N, 7.65; C, 47.12; H 9.14, S, 8.80%. IR: ν/cm^{-1} 3035, 2970, 2922, 2866 (C_{aryl}–H); 2528 (B–H), 1587 (C=N); 1481, 1471 (C_{alkyl}). ^{1}H-{^{11}B}NMR (CD_3COCD_3): δ 8.37 (d, $^3J_{HH}$ = 4, C_{pyr}–H, 1H), 7.49 (td, $^3J_{HH}$ = 8, ^4J(H,H)= 2, C_{pyr}–H, 1H), 7.31 (d, $^3J_{HH}$ = 8, C_{pyr}–H, 1H), 7.01 (td, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, C_{pyr}–H, 1H), 3.44 (s, N(CH_3)$_4$, 12H), 3.07 (h, $^3J_{HH}$ = 7, CH, 1H), 2.51 (s, B–H, 1H), 2.28 (s, B–H, 1H), 1.65 (s, B–H, 1H), 1.50 (s, B–H, 1H), 1.29 (s, B–H, 1H), 1.03 (d, $^3J_{HH}$ = 7, CH–CH_3, 3H), 0.85 (d, $^3J_{HH}$ = 7, CH–CH_3, 3H), 0.75 (s, B–H, 1H), 0.24 (s, B–H, 1H), −2.04 (s, BHB, 1H). ^{11}B-NMR (CD_3COCD_3): δ −8.3 (d, $^1J_{BH}$ = 137, 2B), −13.4 (d, $^1J_{BH}$ = 154, 1B), −15.7 (d, $^1J_{BH}$ = 152, 1B), −17.7 (d, $^1J_{BH}$ = 131, 2B), −18.8 (d, $^1J_{BH}$ = 162,1B), −33.6 (d, $^1J_{BH}$ = 169, 1B), −36.0 (d, $^1J_{BH}$ = 141, 1B). ^{13}C{^{1}H}-NMR (CD_3COCD_3): δ 161.2 (s,C_{2py}), 147.4 (s, C_{6pyr}), 134.4 (s, C_{4pyr}), 125.9 (s, C_{3pyr}), 120.3 (s, C_{5pyr}), 69.8 (s, C_c), 55.1 (s, N(CH_3)$_4$), 38.7 (s, CH), 24.4 (s, CH_3), 23.1 (s, CH_3). MALDI-TOF-MS: 284.4 (100%, M), 238.3 (75.4%, M − ^{i}Pr), 208.3 (55.2%, M − S^{i}Pr).

Synthesis of [PdCl(1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh_3)] (6)

To a Schlenk flask containing a solution of 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ (41 mg, 0.18 mmol) in dried diethyl ether (5 ml), was added *n*-BuLi (0.12 ml, 0.18 mmol) at 0 °C. Stirring was maintained for 30 min at room temperature. S powder was added (6 mg, 0.18 mmol) at 0 °C during 10 min. Stirring was maintained for 30 min at 0 °C and 30 min at RT. [$PdCl_2(PPh_3)_2$] (129 mg, 0.18 mmol) was added and stirred during 1 h at RT. A brown solid, that does not contain boron, precipitated. The orange solution was filtered and taken to dryness. Yield: 97 mg (80%). Anal. calcd for $C_{25}H_{29}B_{10}NSClPPd$: N, 2.13; C, 45.74; H, 4.45; S, 4.88. Found: N, 2.03; C, 45.88; H, 4.56, S, 5.01%. IR: ν/cm^{-1} 2930 (C_{aryl}–H); 2607, 2592, 2567 (B–H), 1433, 1101, 1018, 690, 515 (PPh_3). ^{1}H-{^{11}B}-NMR ($CDCl_3$): δ 8.41 (s, C_{pyr}–H, 1H), 7.71–7.32 (m, 18H), 2.48–2.23 (m, B–H). ^{11}B-NMR ($CDCl_3$): δ 0.4 (d, $^1J_{BH}$ = 158, 1B), −0.3 (d, $^1J_{BH}$ = 158, 1B), −4.8 (d, $^1J_{BH}$ = 140, 2B), −7.0 (d, $^1J_{BH}$ = 123, 2B), −7.8 (d, $^1J_{BH}$ = 191, 2B), −9.6 (d, $^1J_{BH}$ = 174, 2B). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 150.9 (s, C_{pyr}), 148.7 (s, C_{pyr}), 137.4 (s, C_{pyr}), 132.2 (d, ^1J(C,P) = 11, C_{PPh3}), 131.6 (s, C_{PPh3}), 128.5 (d, ^1J(C,P) = 12.4, C_{PPh3}), 124.3 (s, C_{pyr}), 121.5 (s, C_{pyr}), 75.3 (s, C_c), 65.9 (s, C_c). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 44.7 (s, PPh_3).

Synthesis of [Au(1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh_3)] (7)

The process was as for **6** taking 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ (37 mg, 0.16 mmol), dry diethyl ether (4 ml), *n*-BuLi (0.1 ml, 0.16 mmol) at 0 °C and S powder (5 mg, 0.16 mmol). [$AuClPPh_3$] (78 mg, 0.16 mmol) was added and stirred during 2 h at RT. A brown solid was generated and filtered off and not identified. To the organic fraction was added hexane (2 ml) and a pale brown solid precipitated that was washed with hexane. Yield: 112 mg (62%). Anal. calcd for $C_{25}H_{29}B_{10}AuNSP$ + 0.1C_6H_{14}: N, 1.86; C, 41.66; H, 4.46; S, 4.52. Found: N, 1.86; C, 41.73; H, 4.03, S, 3.95%. IR: ν/cm^{-1} 3052 (C_{aryl}–H); 2597, 2578, 2561 (B–H), 2363 (S–R); 1583 (C=N); 1434, 1101, 752, 690, 540 (PPh_3). ^{1}H-{^{11}B}-NMR ($CDCl_3$): δ 8.40 (d, $^3J_{HH}$ = 3, C_{pyr}–H_6, 1H), 7.73 (d, $^3J_{HH}$ = 8, C_{pyr}–H_3, 1H), 7.59 (t, $^3J_{HH}$ = 8, C_{pyr}–H_4, 1H), 7.42 (m, PPh_3, 15H), 7.19 (m, C_{pyr}–H, 1H), 3.49 (s, B–H, 2H), 2.88 (s, B–H, 2H), 2.45 (s, B–H, 3H), 2.22 (s, B–H, 3H). ^{11}B-NMR ($CDCl_3$): δ −1.9 (d, $^1J_{BH}$ = 152, 1B), −5.9 (d, $^1J_{BH}$ = 134, 4B), −9.6 (d, $^1J_{BH}$ = 153, 5B). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 150.34 (s, C_{py}), 149.11 (s, C_{pyr}), 136.50 (s, C_{pyr}), 134.13 (d, $^1J_{CP}$ = 14, C_{Ph}), 131.90 (s, C_{Ph}), 129.31 (d, $^1J_{CP}$ = 11, C_{Ph}), 128.61 (s, C_{Ph}), 126.22 (s, C_{pyr}), 124.20 (s, C_{pyr}), 88.95 (s, C_c), 86.52 (s, C_c). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 38.13 (s, PPh_3). MALDI-TOF-MS: 251.25 (100%, M − $AuPPh_3$).

Synthesis of [Rh(1-(2′-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh_3)$_2$] (8)

The procedure was as for **6** taking 1-(2′-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$ (37 mg, 0.16 mmol) in dry diethyl ether (4 ml), *n*-BuLi (0.1 ml, 0.16 mmol) and S powder (5 mg, 0.16 mmol). [$RhCl(PPh_3)_3$] (152 mg, 0.16 mmol) was added and stirred during 20 h at RT. The solution was concentrated and after the addition of hexane, a brown solid precipitated that did not contain boron. The solution was taken to dryness and a brown solid was obtained. Yield: 54 mg (50%). Anal. calcd for $C_{43}H_{44}B_{10}NSRhP_2$: N, 1.59; C, 58.70; H, 5.04; S, 3.64. Found: N, 1.70; C, 58.66; H, 5.33, S, 3.73%. IR: ν/cm^{-1} 3059, 2962 (C_{aryl}–H); 2569 (B–H), 1435, 1118, 692, 542 (PPh_3). ^{1}H-{^{11}B}-NMR ($CDCl_3$): δ 8.39 (d, $^3J_{HH}$ = 4, C_{pyr}–H, 1H), 7.74–7.1 (m, 30H), 2.46 (s, B–H, 1H), 2.33 (s, B–H, 8H), 2.25 (s, B–H, 1H). ^{11}B-NMR ($CDCl_3$): δ −2.5 (d, $^1J_{BH}$ = 147, 1B), −3.1 (d, $^1J_{BH}$ = 151, 1B), −7.6 (d, $^1J_{BH}$ = 151, 2B), −9.9 (d, $^1J_{BH}$ = 129, 2B), −10.6 (d, $^1J_{BH}$ = 182, 2B), −12.5 (d, $^1J_{BH}$ = 160, 2B). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 148.7 (s, C_{py}), 137.4 (s, C_{pyr}), 132.9 (s, C_{pyr}), 131.6 (s, C_{Ph}), 128.6 (s, C_{Ph}), 124.3 (s, C_{pyr}), 121.4 (s, C_{pyr}). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 42.0 (br s, PPh_3).

X-Ray crystallography

Single-crystal data collections for [NMe$_4$][**5**], **6** and **7** were performed at −100 °C with an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo-Kα radiation. Crystallographic parameters for [NMe$_4$][**5**], **6** and **7** are gathered in Table 6.

The structures were solved by direct methods and refined on F^2 using the SHELX97 program.[26] For each compound, non-hydrogen atoms were refined with anisotropic displacement parameters. For [NMe$_4$][**5**], the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters or positional parameters of the atoms were refined, while for **6** and **7**, all hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. [NMe$_4$][**5**] crystallizes in a non-centrosymmetric space group, and the absolute configuration of [NMe$_4$][**5**] was determined by refinement of the Flack *x* parameter.

Table 6 Crystallographic data and refinement parameters of $[NMe_4]$**[5]**, **6** and **7** at −100 °C

	$[NMe_4]$**[5]**	**6**	**7**
Formula	$C_{14}H_{33}B_9N_2S$	$C_{25}H_{29}B_{10}ClNPPdS$	$C_{25}H_{29}AuB_{10}NPS$
M_r/g mol^{-1}	358.77	656.50	711.59
Crystal system	Orthorhombic	Triclinic	Monoclinic
Crystal habit, color	Prism, colourless	Block, yellow	Plate, colourless
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	9.0020(9)	9.3314(4)	12.8012(2)
b/Å	14.9136(14)	11.9503(6)	13.3513(4)
c/Å	15.8719(15)	15.2810(4)	17.1365(5)
α/°	90	104.695(2)	90
β/°	90	98.904(2)	103.541(2)
γ/°	90	111.702(2)	90
V/V^3	2130.8(4)	1471.71(10)	2847.43(13)
Z	4	2	4
λ/Å	0.71073	0.71073	0.71073
ρ_{calcd}/g cm^{-3}	1.118	1.482	1.660
μ/mm^{-1}	0.152	0.866	5.315
R_{int}	0.300	0.0426	0.0665
Data/restraints/parameters	4147/0/254	4805/0/361	5260/0/353
Goodness-of-fit[a] on F^2	1.027	1.027	1.019
R^b $[I > 2\sigma(I)]$	0.0478	0.0316	0.0285
$R_w{}^c$ $[I > 2\sigma(I)]$	0.1156	0.0650	0.0547
Flack parameter x	0.08(9)	—	—

[a] $S = [\sum(w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$. [b] $R = \sum\|F_o\| - |F_c\|/\sum|F_o|$. [c] $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Acknowledgements

The authors are grateful to the MCyT for financial support (project MAT06–05339 and CTQ2006–26257-E/PPQ) and Generalitat de Catalunya for 2005/SGR/00709.

References

1 (*a*) M. G. H. Vicente, A. Wickramasinghe, D. J. Nurco, H. J. H. Wang, M. M. Nawrocky, M. S. Makar and M. Miura, *Bioorg. Med. Chem.*, 2003, **11**, 3101; (*b*) P. Basak and T. L. Lowary, *Can. J. Chem.*, 2002, **80**, 943; (*c*) A. Cappelli, G. L. Mohr, A. Gallelli, G. Giuliani, A. M. Anzini, S. Vomero, M. Fresta, P. Porcu, E. Maciocco, A. Concas, G. Biggio and A. Donati, *J. Med. Chem.*, 2003, **46**, 3568; (*d*) C. Frixa, M. F. Mahon, A. S. Thompson and M. D. Threadgill, *Org. Biomol. Chem.*, 2003, **1**, 306; (*e*) Y. J. Lee, J. D. Lee, J. J. Ko, S. H. Kim and S. O. Kang, *Chem. Commun.*, 2003, 1364; (*f*) A. Maderna, R. Huertas, M. F. Hawthorne, R. Luguya and M. G. H. Vicente, *Chem. Commun.*, 2002, 1784; (*g*) G. Rana, K. Vyakaranam, S. C. Ledger, S. L. Delaney, J. A. Maguire and N. S. Hosmane, *Appl. Organomet. Chem.*, 2003, **17**, 361; (*h*) A. H. Soloway, W. Tjarks, B. A. Barnum, F. G. Rong, R. F. Barth, I. M. Codogni and J. G. Wilson, *Chem. Rev.*, 1998, **98**, 1515; (*i*) J. F. Valliant and P. Schaffer, *J. Inorg. Biochem.*, 2001, **85**, 43; (*j*) L. I. Zakharkin, G. G. Zhigareva, V. A. Ol'shevskaya and L. E. Vinogradova, *Russ. J. Gen. Chem.*, 1997, **67**, 770.

2 (*a*) B. Chankvetadze, *Capillary Electrophoresis in Chiral Analysis*, John Wiley & Sons, Chichester, 1997; (*b*) R. Vespalec and P. Bocek, *Chem. Rev.*, 2000, **100**, 3715.

3 (*a*) J. Plesek, *Inorg. Chim. Acta*, 1999, **287**, 45; (*b*) B. Grüner and Z. Plzák, *J. Chromatogr., A*, 1997, **789**, 497.

4 V. Slavícek, B. Grüner and R. Vespalec, *J. Chromatogr., A*, 2003, **984**, 121.

5 (*a*) F. Teixidor, A. M. Romerosa, J. Rius, C. Miravitlles, J. Casabó, C. Viñas and E. Sanchez, *J. Chem. Soc., Dalton Trans.*, 1990, 525; (*b*) F. Teixidor and R. W. Rudolph, *J. Organomet. Chem.*, 1983, **241**, 301; (*c*) F. Teixidor, C. Viñas, J. Rius, C. Miravitlles and J. Casabó, *Inorg. Chem.*, 1990, **29**, 149; (*d*) C. Viñas, W. M. Butler, F. Teixidor and R. W. Rudolph, *Inorg. Chem.*, 1986, **25**, 4369; (*e*) F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs and J. Casabó, *Inorg. Chem.*, 1994, **33**, 2645.

6 F. Teixidor, C. Viñas, J. Casabó, A. M. Romerosa, J. Rius and C. Miravitlles, *Organometallics*, 1994, **13**, 914.

7 (*a*) R. P. Alexander and H. A. Schroder, *Inorg. Chem.*, 1963, **2**, 1107; (*b*) N. N. Godovikov, A. N. Degtyarev, V. Bregadze and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 2369; (*c*) R. Rohrsheid and R. H. Holm, *J. Organomet. Chem.*, 1965, **4**, 335; (*d*) F. Teixidor, C. Viñas, M. M. Abad, R. Núñez, R. Kivekäs and R. Sillanpää, *J. Organomet. Chem.*, 1995, **503**, 193; (*e*) L. I. Zakharkin, V. Bregadze and O. Y. Okhlobystin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, **4**, 211; (*f*) L. I. Zakharkin, V. I. Bregadze and O. Y. Okhlobystin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 1539; (*g*) V. P. Balema, S. Blaurock and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1237; (*h*) V. P. Balema, S. Blaurock and E. Hey-Hawkins, *Eur. J. Inorg. Chem.*, 1998, 651.

8 (*a*) N. N. Godovikov, A. N. Degtyarev and V. Bregadze, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, **11**, 2568; (*b*) W. E. Hill and L. M. Silva-Triviño, *Inorg. Chem.*, 1979, **18**, 361; (*c*) L. I. Zakharkin, M. N. Zhubekova and A. V. Kazantsev, *Zh. Obshch. Khim.*, 1972, **42**, 1024.

9 (*a*) F. Teixidor, R. Benakki, C. Viñas, R. Kivekäs and R. Sillanpää, *Inorg. Chem.*, 1999, **38**, 5916; (*b*) F. Teixidor, C. Viñas, R. Benakki, R. Kivekäs and R. Sillanpää, *Inorg. Chem.*, 1997, **36**, 1719.

10 (*a*) 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; (*b*) C. Viñas, A. Laromaine, F. Teixidor, H. Horáková, A. Langauf, R. Vespalec, I. Mata and E. Molins, *Dalton Trans.*, 2007, 3369.

11 S. Batsanov, M. A. Fox, T. G. Hibbert, J. A. K. Howard, R. Kivekäs, A. Laromaine, R. Sillanpää, C. Viñas and K. Wade, *Dalton Trans.*, 2004, 3822.

12 B. Koning, A. Meetsma and R. M. Kellogg, *J. Org. Chem.*, 1998, **63**, 5533.

13 M. W. C. Thompson, D. A. Bardwell, J. C. Jeffery, L. H. Rees and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1997, 721.

14 T. Yamamura, H. Watanabe, Y. Niino, K. Fujisawa and Y. Morooka, *Inorg. Chim. Acta*, 1997, **263**, 415.

15 L. A. Leites, *Chem. Rev.*, 1992, **92**, 279.

16 (*a*) P. M. Garrett, F. N. Tebbe and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 5016; (*b*) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642; (*c*) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862.

17 O. B. Ramsay, *Stereochemistry*, Eastern Michigan University, Ypsilanti, MI, 1981.

18 M. Vespalcová and D. Gregorová, *Sep. Sci. Technol.*, 2003, **26**, 727.
19 (*a*) R. Núñez, C. Viñas, F. Teixidor and M. M. Abad, *Appl. Organomet. Chem.*, 2003, **17**, 509; (*b*) F. Simal, S. Sebille, A. Demonceau, A. F. Noels, R. Núñez, M. Abad, F. Teixidor and C. Viñas, *Tetrahedron Lett.*, 2000, **41**, 5347; (*c*) C. Viñas, M. M. Abad, F. Teixidor, R. Sillanpää and R. Kivekäs, *J. Organomet. Chem.*, 1998, **555**, 17; (*d*) R. Kivekäs, R. Sillanpää, F. Teixidor, C. Viñas and M. M. Abad, *Acta Chem. Scand.*, 1996, **50**, 499; (*e*) F. Teixidor, C. Viñas, M. M. Abad, R. Núñez, R. Kivekäs and R. Sillanpää, *J. Organomet. Chem.*, 1995, **503**, 193; (*f*) R. Kivekäs, R. Sillanpää, F. Teixidor, C. Viñas, R. Núñez and M. Abad, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 1864; (*g*) F. Teixidor, C. Viñas, M. M. Abad, M. Lopez and J. Casabó, *Organometallics*, 1993, **12**, 3766; (*h*) B. Wrackmeyer, Z. G. Hernandez, R. Kempe and M. Herberhold, *Eur. J. Inorg. Chem.*, 2007, 239; (*i*) A. S. King, G. Ferguson, J. F. Britten and J. F. Valliant, *Inorg. Chem.*, 2004, **43**, 3507; (*j*) A. Richel, S. Delfosse, A. Demonceau, A. F. Noels, S. Paavola, R. Kivekas, C. Viñas and F. Teixidor, *Abstracts of Papers of the American Chemical Society*, 224:453-POLY Part 2, Aug 18 2002; (*k*) S. Paavola, F. Teixidor, C. Viñas and R. Kivekas, *J. Organomet. Chem.*, 2002, **657**, 187; (*l*) S. Paavola, F. Teixidor, C. Viñas and R. Kivekäs, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2002, **58**, M237; (*m*) S. Paavola, F. Teixidor, C. Viñas and R. Kivekas, *J. Organomet. Chem.*, 2002, **645**, 39.
20 F. Teixidor, C. Viñas, M. M. Abad, C. Whitaker and J. Rius, *Organometallics*, 1996, **15**, 3154.
21 (*a*) F. Teixidor, C. Viñas, R. Benakki, R. Kivekäs and R. Sillanpää, *Inorg. Chem.*, 1997, **36**, 1719; (*b*) F. Teixidor and C. Viñas, *Science of Synthesis*, Georg Thieme, Stuttgart, 2005, vol. 6, p. 1235 and references therein.
22 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 214.
23 J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge and M. M. Jones, *Inorg. Chem.*, 1970, **9**, 2374.
24 R. Uson, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.
25 R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride and K. Wade, *J. Organomet. Chem.*, 1993, **462**, 19.
26 G. M. Sheldrick, *SHELX,97*, University of Göttingen, Germany, 1997.

