DALTON
FULL PAPER

Coordinating properties of mixed pyrrolyl/dicarbollide cobalt metallocene-type complexes

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Mixed-sandwich Co(III) complexes incorporating an η^5 pyrrolyl unit $[\eta^5\text{-NC}_4\text{H}_4]^-$ are very stable when the second η^5 moiety is a dicarbollide $[\eta^5\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$. The existence of a lone pair on N in the neutral *closo*-$[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$ (**1**) has allowed for the first time a study of the N-σ bonding capacity of a pyrrolyl ligand η^5 bonded to a metal in an oxidation state higher than two. This capacity has been proven by reacting *closo*-$[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$ with Lewis acids (BH_3, BF_3 and Ag^+) and a Co(III) macrocycle. In all cases the reaction went to completion proving the strength of the σ bond generated. The stability of the $[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$ complexes *vs.* oxidation state Co(III)/Co(II) was studied by cyclic voltammetry. It was found that $[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]^-$ is not as stable as $[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$; however, when coordinated to cobalt(III), both $[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]^-$ and $[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$ are of comparable stability. The stability of the reduced form Co(II) in the mixed pyrrolyl/dicarbollide is enhanced when an electron withdrawing group is bonded to the cluster carbon atom in the dicarbollide.

Introduction

The first cobalt sandwich complex incorporating one pyrrolyl and one dicarbollide unit was reported in 1996.[1] Since this early work, a number of synthetic strategies have been developed to obtain mixed-sandwich complexes of this type.[2] Formally, the three positive charged cobalt compensates the dinegative dicarbollide and the mononegative pyrrolyl. Therefore, the complex is neutral, with an electron lone pair on the nitrogen atom of the pyrrolyl unit. The result is a complex which is isoelectronic to pyridine, imidazole or azaferrocene, among other nitrogen bases. The question is whether the η^5 coordination of the pyrrolyl unit to a highly electron-density demanding metal, Co(III), will not diminish the coordinating capacity of the pyrrolyl nitrogen. The number of readily available η^5 similar systems is practically restricted to azaferrocene,[3] or, less related, to the semi-sandwich pyrrolyltricarbonyl manganese.[4] Kuhn *et al.*[5] have demonstrated that the coordination reaction of $S(CH_3)_2 \rightarrow BH_3$ with permethylated 1,1′-diazaferrocene yields the corresponding stable diadduct. Other examples involving N-σ coordination to metal complexes can be found, although the data available is restricted to low valent metals.[6]

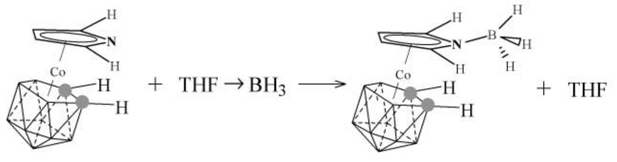
The similarity of *closo*-$[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$ to azaferrocene provided a new system with a metal in +3 oxidation state able to evaluate the N-σ coordinating properties in sandwich η^5 coordinated azaheterocycles. This pyrrolyl/dicarbollide cobalt system offers interesting possibilities mostly derived from its stability to air, easy preparation and purification and high yield. Furthermore, use of dicarbollide has permitted the synthesis of dicarbollide/pyrrolyl complexes where there are no substituents on the α positions of the pyrrolyl group. The absence of electron-donating groups on the pyrrolyl ligands allows one to probe the influence of η^5 bonding on the coordinating character of this heterocycle.

From among the mixed dicarbollide/pyrrolyl complexes described in the literature,[1,2] we have chosen *closo*-$[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$ (**1**) for study due to its geometrical simplicity. It does not contain substituents on the cluster carbon (C_c) atoms or at the α positions of the pyrrolyl unit. For comparing purposes, however, *closo*-$[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10}]$ (**2**) which contains a phenyl ring near the N-coordinating site, therefore hindering N coordination, was examined in parallel.

Results and discussion

Reaction with Lewis acids: formation of 1→BH_3 (3), 1→BF_3 (4) and 2→BF_3 (5)

It is well known that BH_3 and BF_3 form stable adducts with THF, $(CH_3)_2S$ and, in general, any molecule containing lone pairs (*i.e.*, Lewis bases). To prove that nitrogen σ-coordination is feasible with *closo*-$[3\text{-Co}(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11}]$, this was allowed to react with increasing amounts of THF→BH_3 (see Scheme 1) ranging from 1 : 0.1 to 1 : 1 in the absence of coordinating solvent. For compound **1**, sequential adduct formation is illustrated in Fig. 1. The $^{11}B\{^1H\}$ NMR spectrum of **1** shows, in toluene, six resonances with a 1 : 1 : 2 : 2 : 2 : 1 pattern in the range +7.3 to −22.2 ppm (Fig. 1a). Upon the addition of THF→BH_3 seven new peaks appear (Figs 1b and 1c), which coexist with those for pure **1**. When the stoichiometric amount of THF→BH_3 is added (Fig. 1d), all resonances corresponding to "free" complex **1** dissappear and only the new pattern 1 : 1 : 2 : 2 : 2 : 1 : 1 is observed in the range +8.7 to −20.8 ppm. This corresponds to pure compound **3**. The resonance at −20.8 ppm becomes a quartet in the ^{11}B spectrum, and is assigned to the BH_3 boron atom.



Scheme 1 Reaction of formation of **1**→BH_3 (**3**).

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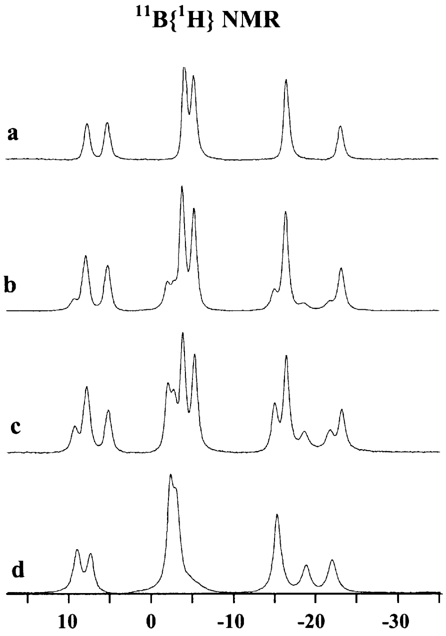

Fig. 1 $^{11}B\{^1H\}$ NMR spectra of the reaction of compound **1** with THF⟶BH_3 at different **1** : THF⟶BH_3 ratios: (a) 1 : 0, (b) 1 : 0.25, (c) 1 : 0.50, (d) 1 : 1.

Although the formation of the adduct was complete at the ratio 1 : 1, excess of THF⟶BH_3 was added. Under these reducing conditions the mixed-sandwich complex was not stable. Most probably Co(III) ⟶ Co(II) reduction takes place, leading to an unstable complex. To prove this hypothesis, the same set of experiments were done with the non-reducing $(C_2H_5)_2O$⟶BF_3. In this case, $CDCl_3$ was used as non-coordinating solvent. **1** was mixed with increasing amounts of $(C_2H_5)_2O$⟶BF_3 covering the range 1 : 0.1 to 1 : 1, and the results, illustrated in Fig. 2, are comparable to those found for THF⟶BH_3. Fig. 2a corresponds to compound **1**. As before, seven new signals are observed upon successive additions of $(C_2H_5)_2O$⟶BF_3 (Figs 2b and 2c). Fig. 2d corresponds to the stoichiometric 1 : 1 relation or to **1**⟶BF_3 (**4**). The resonance at 0.6 ppm that is a singlet in the ^{11}B spectrum, is assigned to the coordinated BF_3. The ^1H NMR spectrum of **1**⟶BF_3 displays two resonances in the pyrrolyl region with chemical shift positions at 7.1 (2H) and 6.6 (2H) ppm slightly displaced to low field with regard to **1**. As expected, an excess of $(C_2H_5)_2O$⟶BF_3 left unaltered the spectrum of **1**⟶BF_3 (1 : 1), indicating that our former interpretation concerning the instability of the reduced form of **1** was correct. This will later be seen with the cyclic voltammogram studies reported.

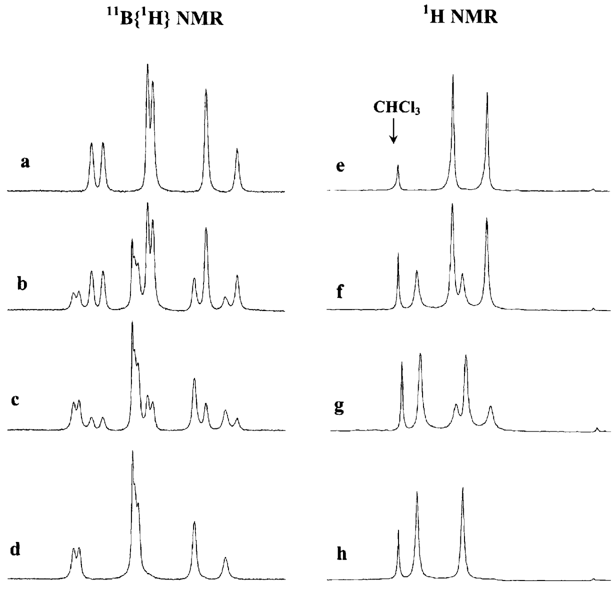

Fig. 2 $^{11}B\{^1H\}$ NMR and $^1H\{^{11}B\}$ NMR spectra of the reaction of compound **1** with $(C_2H_5)_2O$⟶BF_3 at different **1** : $(C_2H_5)_2O$⟶BF_3 ratios: (a) 1 : 0, (b) 1 : 0.33, (c) 1 : 0.66, (d) 1 : 1.

We have observed by X-ray diffraction that the pyrrolyl nitrogen atom is placed bisecting the C–C bond of the dicarbollide (see Fig. 3). Considering that the presence of a bulky group bonded to the dicarbollide carbon atom could difficult the σ coordination to BF_3, we decided to study the reaction of *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**2**) with $(C_2H_5)_2$-O⟶ BF_3 as it could provide a clear view of the strength of such a bond. Experiments were conducted for **2** in equal way as for **1**, thus **2** was mixed with $(C_2H_5)_2O$⟶BF_3 in different ratios and their $^{11}B\{^1H\}$ NMR spectra recorded. The starting 1 : 1 : 4 : 1 : 2 pattern in the range +8.3 to −15.5 ppm for **2** changed to 1 : 1 : 1 : 2 : 2 : 1 : 1 : 1 : 1 in the range +14.4 to −14.2 ppm when the ratio **2** : $(C_2H_5)_2O$⟶BF_3 was 1 : 1. The singlet at 0.6 ppm was assigned to the BF_3 unit. As for the non-sterically crowded **1** the reaction was fully shifted to the formation of the adduct. The coexistence of the species in excess in solution and the adduct, *e.g.* **1** and **1**⟶BF_3; **2** and **2**⟶BF_3 or **1** and **1**⟶BH_3 indicate the great stability of the adduct not reverting to the free species in the NMR time scale.

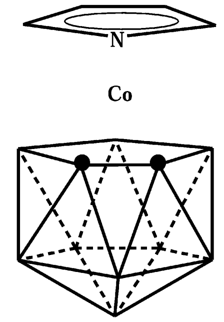

Fig. 3 The nitrogen atom of the pyrrolyl unit in mixed cobalt complexes incorporating one pyrrolyl and one dicarbollide unit is placed bisecting the C–C bond of the dicarbollide.

Reaction with Ag^+. Formation of [(3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$)$_2$-Ag][BF_4] (6) and [(3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$)$_2$Ag]-[BF_4] (7)

The reaction of **1** and **2** with Ag[BF_4] in ratio 3 : 1 led to the formation, in CH_2Cl_2, of reasonably light- and air-stable complexes (**6** and **7**, respectively), which were characterized by NMR and MALDI-TOF mass spectroscopies. The proposed structure for compound **6** is illustrated in Fig. 4. The species is a

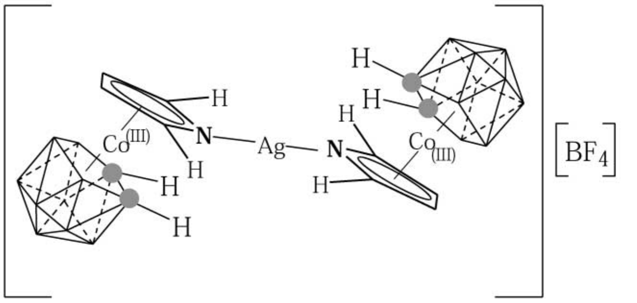

Fig. 4 Proposed structure of compound **6**.

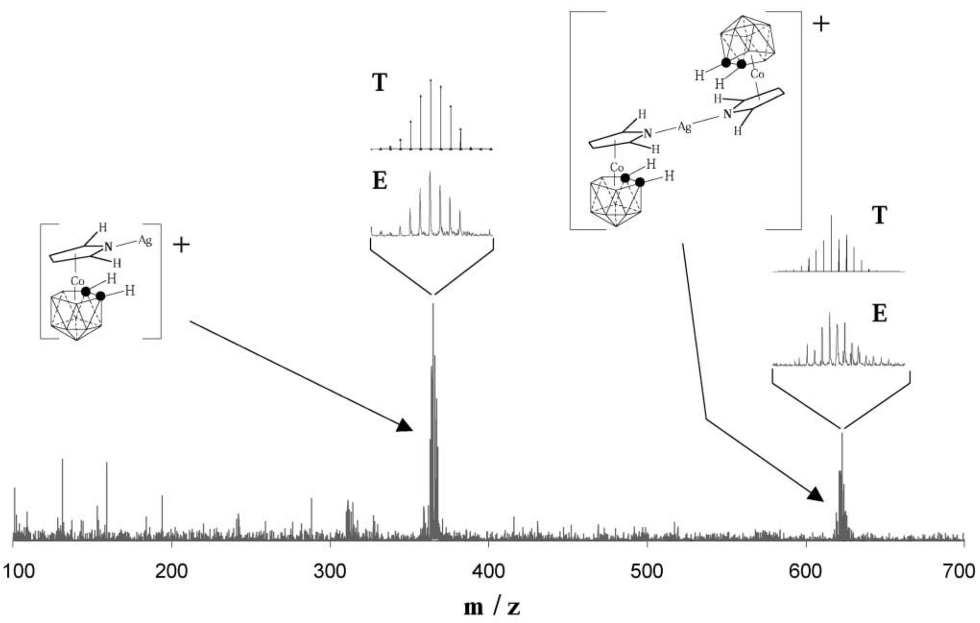

Fig. 5 MALDI-TOF mass spectrum obtained for compound **6** (T = calculated, E = experimental).

cation compensated by the $[BF_4]^-$ as evidenced by $^{11}B\{^1H\}$ NMR. The $^{11}B\{^1H\}$ NMR spectrum of **6** displays six resonances with a 2 : 2 : 1 : 8 : 4 : 2 pattern. The resonance at −0.5 ppm is a singlet in the ^{11}B NMR spectrum, and is assigned to $[BF_4]^-$. As a result of coordination, the pyrrolyl hydrogen atoms are slightly shifted to low field relative to those found for **1** in the ^1H NMR spectrum. The MALDI-TOF mass spectrum of **6** is shown in Fig. 5. Typical patterns associated to boron clusters are observed with the highest peaks, being at *m*/*z* = 623 and *m*/*z* = 365 which are assigned to $[Ag(\mathbf{1})_2]^+$ and $[Ag(\mathbf{1})]^+$, respectively. A comparison of the experimental (E) and theoretical (T) distributions for the two peaks is included in Fig. 5. The peak at *m*/*z* = 365 can be interpreted as a fragment of the peak at *m*/*z* = 623.

Compound **7**, which has lower symmetry than **6**, displays three resonances in the $^1H\{^{11}B\}$ NMR pyrrolyl region. This diminished symmetry does not influence the $^{11}B\{^1H\}$ NMR that is comparable to that for **6** with a 2 : 2 : 1 : 8 : 2 : 4 pattern, the resonance at −0.5 ppm being assigned to $[BF_4]^-$.

As for **6**, the MALDI-TOF also displayed peaks for $[Ag(\mathbf{2})_2]^+$ and $[Ag(\mathbf{2})]^+$, respectively, further supporting the trimetallic nature of compound **7**.

Formation of 1⟶mcox (8) and 2⟶mcox (9)

Cobaloximes (**cox**) are readily available compounds[7] much easier to synthesize than porphyrines. Thus, they are suitable to be studied in coordination reactions and their results are expected to be comparable with those of phthalocyanines and porphyrins.

The reactions of **1** and **2** with methylaquocobaloxime (**mcox**) in an anhydrous non-coordinating solvent (methylene chloride) lead to the isolation of solids upon the addition of the same volume of hexane. Fig. 6 illustrates the reaction of formation and the proposed structure for complex **8**. Crystallization was used as a purification method, and red needles were obtained from saturated methylene chloride–hexane (1 : 1) solutions for both **8** and **9**. The ^1H NMR spectrum is consistent with a modified methylcobaloxime whose water molecule has been substituted. Therefore, the ^1H NMR spectrum of **8** shows an acidic hydrogen at 18.1 ppm and the axial CH_3 at 2.2 ppm. In addition, two resonances were found in the pyrrolyl region slightly displaced to high field relative to those of **1**. The fact that only one resonance is found for the in-plane methyl groups suggests that there is no preferential orientation of **1**, interacting in the same way the four methyl groups of the macrocycle. The $^{11}B\{^1H\}$ NMR spectrum pattern and frequency closely resembles that for **1**.

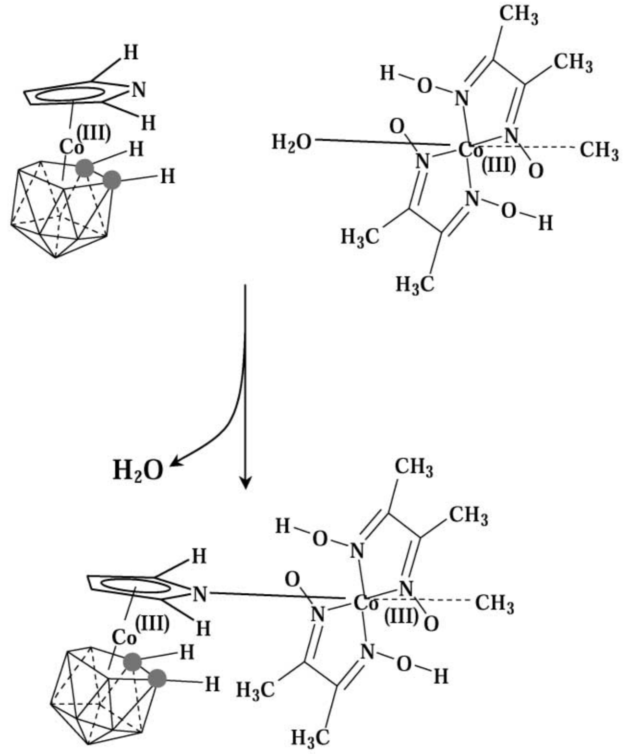

Fig. 6 Proposed structure and reaction of formation for compound **8**.

The easiness of complexation between **1** and methylaquocobaloxime was monitored by ^1H NMR spectroscopy. An initial solution of methylaquocobaloxime in $CDCl_3$ was allowed to react with increasing amounts of **1**. Fig. 7 shows the ^1H NMR spectra at different ratios. As with $(C_2H_5)_2O \longrightarrow BF_3$ or $THF \longrightarrow BH_3$ the reaction was very quick. Therefore, total coexistence of resonances attributed to independent mcox and **1⟶mcox** was observed at any ratio. A similar behavior is found for **9**, however the existence of the phenyl group breaks the possible C_s symmetry of the complex and leads to the two equal-intensity signals (6 : 6 pattern) corresponding to the

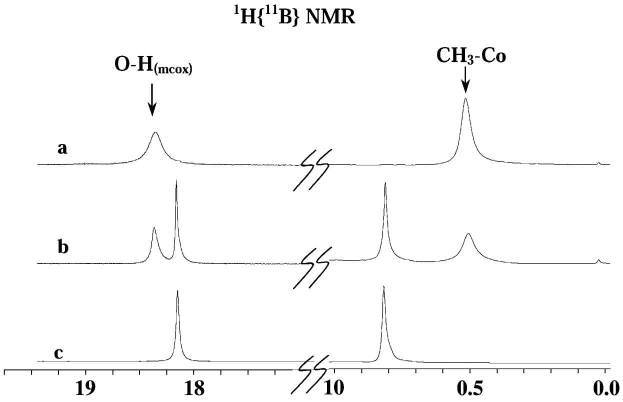

Fig. 7 $^{1}H\{^{11}B\}$ NMR spectra of the reaction of compound **1** with **mcox** at different **1** : **mcox** ratios: (a) 0 : 1, (b) 0.5 : 1, (c) 1 : 1.

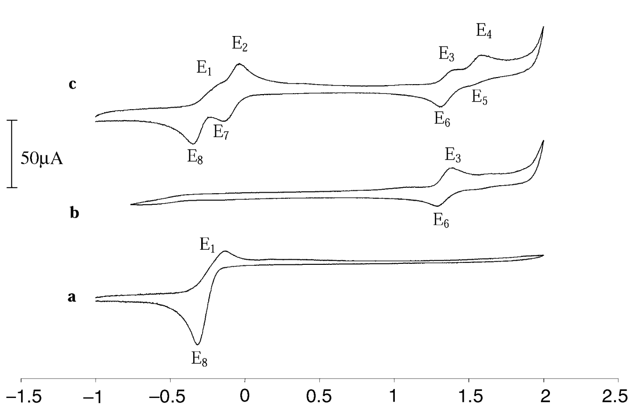

Fig. 8 Voltamperograms corresponding to compound **1** (curve a), methylaquocobaloxime (curve b) and a mixture of the compounds in 1 : 1 ratio (curve c) in chloroform as a solvent.

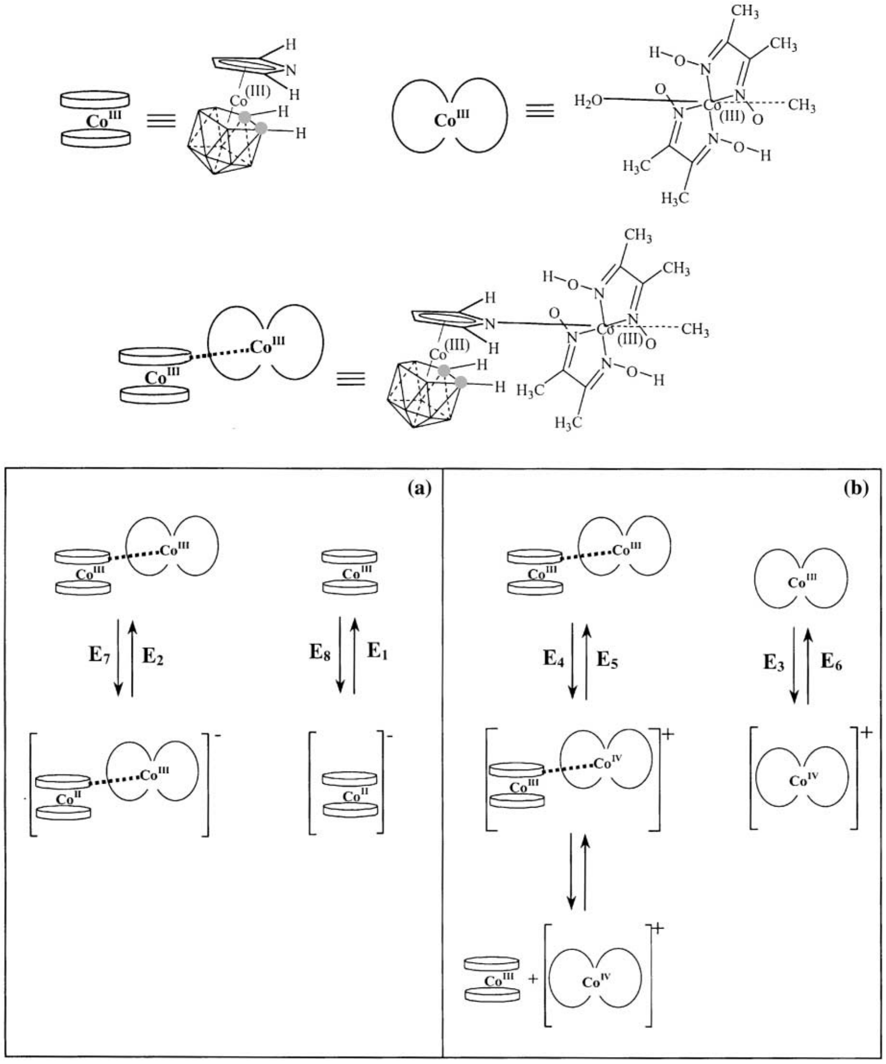

Fig. 9 Schematic representation of the oxidation and reduction processes presented in Fig. 8.

methyl groups of the cobaloxime. This is the first indication that an axial orientation can be obtained, although the number of signals corresponding to methyl groups is too low to indicate a fixed conformation at room temperature.

Electrochemical characterization

The NMR studies have shown that a fast reaction takes place between **1** or **2** with THF⟶BH_3, $(C_2H_5)_2O$⟶BF_3, Ag^+ or **mcox**. Indeed, only the starting compound in excess and the generated compounds, *e.g.* **1** and **1**⟶BH_3, were present according to NMR study. We can indicate that a 100% conversion takes place when the stoichiometric amount of THF⟶BH_3 is added as a consequence of the high stability of pure **1**⟶BH_3 adduct. Notwithstanding this, for ratios of **1** : THF⟶BH_3 <1 we noticed that the generated adduct **1**⟶BH_3 did decompose. BH_3 is a reducing agent and we interpreted that **1**⟶BH_3 was not stable when the oxidation state of Co was II. The question was whether **1** itself was unstable under reducing conditions or if the adduct was the unstable species.

For this purpose, we considered that complex **1⟶mcox** (**8**)

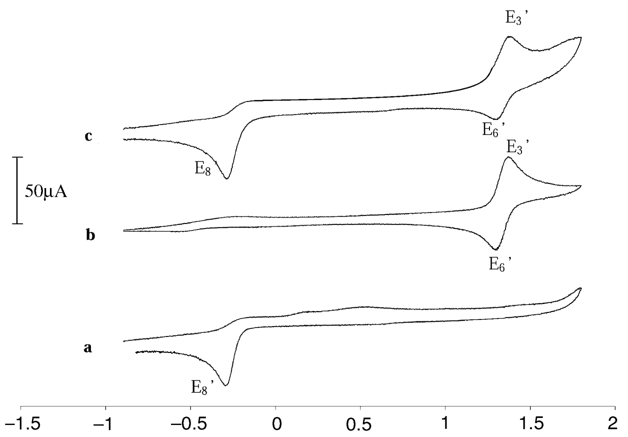

Fig. 10 Voltamperograms corresponding to compound **1** (curve a), methylaquocobaloxime (curve b) and a mixture of the compounds in 1 : 1 ratio (curve c) in acetonitrile as a solvent.

and **2**⟶**mcox** (**9**) would bring important information concerning the stability of N-σ coordinated [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] upon oxidation/reduction. This stability was tested in both non-coordinating and coordinating media by using cyclic voltammetry (CV).

(a) Stability in a non-coordinating medium. Complexes **8** and **9** contain two metallic centers suitable to undergo redox processes. The Co(III) in the cobaloxime unit can be oxidized to the IV formal oxidation state, while the Co(III) in the mixed cobaltacarborane unit can be reduced to its II formal oxidation state. Thus, three pairs of oxidation states, II/III, III/III, and III/IV, are possible.

The cyclic voltammetry response of **1** in chloroform is shown in Fig. 8a. Two well-defined peaks assigned to the couple [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$]/[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$]$^-$ are observed. We observe that the oxidation peak (E_1) is less intense than the reduction peak (E_8); that is in agreement with the **1**⟶BH_3 results indicated above concerning the unstability of the mixed cobalt complex under reducing conditions. The CV for methylaquocobaloxime (**mcox**) in $CHCl_3$ (Fig. 8b) shows two well-defined peaks corresponding to the Co(III)/Co(IV) process of the central atom, with a half-wave potential of 1.34 V. Fig. 8c displays the CV obtained when equimolar quantities of **1** and **mcox** were mixed together. At this stage, the three species corresponding to **1**, **mcox** and **8** coexist. Therefore, eight peaks are observed, four corresponding to oxidation processes and four to reduction ones, or four corresponding to starting materials and four to the **1**⟶**mcox**. Fig. 9a summarizes our interpretation of the processes associated with the cobalt atom at the carborane unit and Fig. 9b the processes associated with the cobalt atom in the cobaloxime unit. A main difference is found between the CV and the NMR of **1**⟶**mcox**. The NMR has shown that there is only one species upon mixing equimolar amounts of **1** and **mcox**. The CV shows that **1**, **mcox** and **1**⟶**mcox** coexist under the same reaction conditions. Our interpretation, consistent with the CV, is that by using this technique we generate *in situ* **1** and **mcox** from **1**⟶**mcox**.

The peaks at E_1 and E_8 in Fig. 8c correspond, respectively, to oxidation and reduction of the cobalt atom in the mixed ligand **1**. Similarly, E_2 and E_7 correspond to the same process in **1**, this time coordinated *via* the pyrrolyl to the cobaloxime. Comparing the two equivalent redox processes on **1** and **1**⟶**mcox**, an $E_{1/2}$ shift of 300 mV to higher voltage values and an enlargement of the oxidation peak E_2 *vs.* E_1 is observed, in such a way that the height of $E_2 \sim E_7$. These changes indicate a higher stability of the Co(II) in **1**⟶**mcox** than in free **1**, essentially induced by σ-coordination of the nitrogen atom. Peaks E_3 and E_6 in curve c correspond, respectively, to oxidation and reduction processes associated with the cobalt atom of the methylaquocobaloxime. Two peaks, E_4 and E_5, are observed about 230 mV to higher values with respect to E_3 and E_6. The E_4 and E_5 peaks correspond to the **mcox** cobalt redox process in **1**⟶**mcox**. The shift of the peaks to higher values indicates stabilization of the **mcox** Co(III), in **1**⟶**mcox** caused by substitution of the hard water by the softer nitrogen. Decomplexation of **1**⟶**mcox** to **1** and **mcox** takes place at high oxidation potentials. This is proven by the unequal reduction (E_5) and oxidation (E_4) peaks of **1**⟶**mcox**, see Fig. 8c. The oxidation peak is more intense that the reduction one, indicating that a fraction of the oxidized form is not reduced due to decomposition of the complex and formation of pure **1** and **mcox** species.

Similar results were obtained studying **2**⟶**mcox**; however two points deserve special mention. Peaks E_1 and E_8 have the same height; this was not true for **1**, which means that **2** has better reversibility than **1**. Besides, a shift in $E_{1/2}$ for **2** of about 100 mV to more positive values relative to **1** is found, indicating that the +2 formal oxidation state in **2** is more stable than in **1**. Both phenomena, peaks height and shift, are interpreted by the presence of the phenyl ring which allows dissipation of the excess of charge from the cobalt atom through the aromatic ring.

(b) Stability in a coordinating medium. These CV studies were carried out in CH_3CN (Fig. 10). Immediate differences with regard to the non-coordinating solvent are observed in the CV for **1** where the peak associated with the oxidation process has virtually disappeared. As expected, the CV for **mcox**, Fig. 10b, is similar in appearance to the curve obtained in chloroform (Fig. 8b). The greatest difference with the non-coordinating solvent was found upon mixing equal ratios of **1** and **mcox** (Fig. 10c). The resulting voltammogram is the simple addition of curves (a) and (b), indicating that no complex formation has taken place. The σ-coordinating capacity of [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] was not sufficient to compete with a large excess of acetonitrile preventing the formation of the Co–pyrrolyl bond. This result was confirmed by means of ^{1}H NMR and ^{11}B NMR spectroscopy carried out in CD_3CN. The resonances corresponding to the pyrrolyl unit (^{1}H NMR) and the boron cage atoms (^{11}B NMR) of the sandwich complex match these for the reagents. A completely parallel behavior was found upon mixing compound **2** and **mcox** in CH_3CN.

Conclusions

Mixed-sandwich Co(III) complexes ([3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$]) incorporating one unsubstituted pyrrolyl and one dicarbollide units present good N-σ coordinating properties through the electron pair on the nitrogen atom of the pyrrolyl unit. They are the first examples of N-σ coordination by a pyrrolyl η^5-coordinated to a metal in an oxidation state higher than 2. N-σ bond formation was observed when *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] was mixed with Lewis acids (($(C_2H_5)_2O$⟶BH_3, THF⟶BF_3 and Ag^+) and a Co(III) macrocycle. In all cases the reaction went to completion, proving the strength of the σ-bond generated. The presence of a bulky group (phenyl) on one of the cluster carbon atoms of the dicarbollide unit did not inhibit the coordinating ability of the mixed complex; however, it altered the electrochemical properties of the two cobalt nuclei in the resulting dinuclear complexes. This phenyl group also stabilized the Co(II) state in the mixed complex, as a result of its electron-withdrawing capacity. Therefore the Co(III)/Co(II) redox process for **2** is more reversible than for **1** in non-coordinating solvent media.

Experimental

Instrumentation

IR spectra were recorded with KBr pellets on a FTIR-8300 Shimadzu spectrophotometer. ^{1}H and ^{1}H{^{11}B} NMR (300.13

MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz) and ^{11}B and $^{11}B\{^1H\}$ NMR (96.29 MHz) spectra were recorded at room temperature with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^1H, $^1H\{^{11}B\}$ and $^{13}C\{^1H\}$ NMR spectra were referenced to $Si(CH_3)_4$, and those for ^{11}B and $^{11}B\{^1H\}$ NMR spectra were referenced to $(C_2H_5)_2O{\longrightarrow}BF_3$. Chemical shifts are reported in ppm downfield from $Si(CH_3)_4$ and coupling constants in Hz. Cyclic voltammograms were recorded using an EG&G PAR 273 A potentiostat/galvanostat. MS spectra were recorded using a Bruker Biflex MALDI-TOF mass spectrometer.

Materials

closo-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_9$][1] and methylaquocobaloxime[7] were prepared according to literature methods. $(C_2H_5)_2O{\longrightarrow}BF_3$, THF$\longrightarrow BH_3$ and tetrabutylammonium hexafluorophosphate (Fluka), and Ag[BF_4] and tetrabutylammonium chloride (Aldrich) were used as received without further purification. Diethyl ether and toluene were freshly distilled from sodium benzophenone. Other solvents were of reagent grade purity and were used without further purification and stored over molecular sieves. Experiments were carried out under dry, oxygen-free dinitrogen atmosphere, using standard Schlenk techniques, with some subsequent manipulation in the open laboratory.

Electrochemical measurements

Electrochemical measurements were performed in a standard double-compartment three-electrode cell. Ag/AgCl/[$N(C_4H_9)_4$]-Cl (0.1 M in CH_3CN) was used as a reference electrode. A 4-mm^2 platinum plate and a platinum wire were used as working and counter electrode, respectively. All measurements were performed both in acetonitrile and in chloroform with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Cyclic voltammograms were recorded with a scan rate of 80 mV s^{-1}.

Preparations

Synthesis of 1$\longrightarrow BH_3$ (3). THF$\longrightarrow BH_3$ (0.1 mL g, 0.100 mmol) was added to **1** (0.026 g, 0.100 mmol) in dry toluene (1 ml) at room temperature, resulting a bright orange solution. δ_B 8.7 [1B, d, ^1J(B,H) = 138], 7.4 [1B, d, ^1J(B,H) = 149], −2.0 (2B), −2.7 (2B), −14.4 [2B, d, ^1J(B,H) = 153], −17.9 [1B, d, ^1J(B,H) = 149], −20.8 [1B, q, ^1J(B,H) = 142].

Synthesis of 1$\longrightarrow BF_3$ (4). $(C_2H_5)_2O{\longrightarrow}BF_3$ (0.016 g, 0.100 mmol) was added to **1** (0.026 g, 0.100 mmol) in CD_3Cl (1 ml) at room temperature, producing a bright orange solution. δ_H 7.1 (2H, s, N–C_{pyr}–H), 6.6 (2H, s, C_{pyr}–C_{pyr}–H), 4.9 (2H, s, C_c–H); $\delta_{C\{H\}}$ 104.8 (s, N–C_{pyr}), 92.5 (s, C_{pyr}–C_{pyr}), 59.1 (s, C_c); δ_B 11.8 [1B, d, ^1J(B,H) = 129], 10.7 [1B, d, ^1J(B,H) = 126], 0.6 (s, 1B), −0.5 (2B), −1.2 (2B), −12.5 [2B, d, ^1J(B,H) = 163], −18.8 [1B, d, ^1J(B,H) = 174].

Synthesis of 2$\longrightarrow BF_3$ (5). $(C_2H_5)_2O{\longrightarrow}BF_3$ (0.016 g, 0.100 mmol) was added to **2** (0.033 g, 0.100 mmol) in CD_3Cl (1 ml) producing a bright orange solution. δ_H 7.6–7.3 (5H, m, –C_6H_5), 7.2 (1H, s, N–C_{pyr}–H), 6.7 (1H, s, N–C_{pyr}–H), 6.0 (2H, s, C_{pyr}–C_{pyr}–H), 4.9 (1H, s, C_c–H); $\delta_{C\{H\}}$ = 135.1, 129.3, 125.2, 125.0 (s, –C_6H_5), 113.9 (s, N–C_{pyr}), 101.1 (s, N–C_{pyr}), 94.1 (s, C_{pyr}–C_{pyr}), 93.2 (s, C_{pyr}–C_{pyr}), 62.0 (s, C_c–H); δ_B 14.4 [1B, d, ^1J(B,H) = 138], 12.1 [1B, d, ^1J(B,H) = 166], 0.6 (s, 1B), 0.1 (2B), −1.7 (2B), −6.1 [1B, d, ^1J(B,H) = 165], −11.6 [1B, d, ^1J(B,H) = 166], −14.2 [1B, d, ^1J(B,H) = 171].

Synthesis of 6. Compound **1** (0.054 g, 0.206 mmol) was dissolved in CH_2Cl_2 (5 ml) and Ag[BF_4] (0.020 g, 0.103 mmol) added. The solution was stirred for 30 min and the dark orange solid which precipitated was collected. The mixture was filtered off, washed with cold methylene chloride (2 mL) and vacuum-dried. (0.030 g, 68%). (Found: C, 20.52; H, 4.15; N, 3.72. $C_{12}B_{19}H_{30}Co_2N_2F_4Ag$ requires: C, 20.31; H, 4.26; N, 3.95%); ν/cm^{-1}: (C_c–H) 3120, 3055, (B–H) 2617, 2590, 2567, 2536, (B–F) 1089, 1060 (KBr pellet); δ_H 7.2 (4H, s, N–C_{pyr}–H), 6.7 (4H, s, C_{pyr}–C_{pyr}–H), 4.9 (4H, s, C_c–H); $\delta_{H\{B\}}$ 7.2 (4H, s, N–C_{pyr}–H), 6.7 (4H, s, C_{pyr}–C_{pyr}–H), 4.9 (4H, s, C_c–H), 3.1 (6H, br s, B–H), 1.9 (4H, br s, B–H), 1.7 (8H, br s, B–H); $\delta_{C\{H\}}$ 111.1 (s, N–C_{pyr}), 94.0 (s, C_{pyr}–C_{pyr}), 55.7 (s, C_c); δ_B 7.7 [2B, d, ^1J(B,H) = 151], 4.4 [2B, d, ^1J(B,H) = 145], −0.5 (s, 1B), −4.2 [8B, d, ^1J(B,H) = 149], −15.3 [4B, d, ^1J(B,H) = 157], −21.6 [2B, d, ^1J(B,H) = 176]. MS-MALDI-TOF: m/z = 622 [Ag(**1**)$_2$]$^+$ and 365 [Ag(**1**)]$^+$.

Synthesis of 7. The procedure was the same as for **6** but using compound **2** (0.102 g, 0.31 mmol) and Ag[BF_4] (0.030 g, 0.15 mmol) as starting materials (0.035 g, 63%) (Found: C, 33.71; H, 4.33; N, 3.23. $C_{24}B_{19}H_{38}Co_2N_2F_4Ag$ requires C, 33.45; H, 4.44; N, 3.25%); ν/cm^{-1}: (C_c–H) 3118, 3045, (B–H) 2593, 2565, 2555, (B–F) 1076, 1051 (KBr pellets); δ_H 7.7–7.3 (10H, m, C_{ar}–H), 6.9 (2H, s, N–C_{pyr}–H), 6.5 (4H, s, C_{pyr}–C_{pyr}–H), 6.1 (2H, s, N–C_{pyr}–H), 5.9 (2H, s, C_c–H); $\delta_{H\{B\}}$ = 7.7–7.3 (10H, m, C_{ar}–H), 6.9 (2H, s, N–C_{pyr}–H), 6.5 (4H, s, C_{pyr}–C_{pyr}–H), 6.1 (2H, s, N–C_{pyr}–H), 5.9 (2H, s, C_c–H), 3.9 (2H, br s, B–H), 3.3 (6H, br s, B–H), 1.8 (4H, br s, B–H), 1.7 (6H, br s, B–H); $\delta_{C\{H\}}$ = 143.2, 136.7, 128.2, 125.6 (s, C_6H_5), 115.1, 112.8 (s, N–C_{pyr}), 93.7, 92.1 (s, C_{pyr}–C_{pyr}), 54.7 (s, C_c); $\delta_{B\{H\}}$ = 8.3 [2B, d, ^1J(B,H) = 149], 5.6 [2B, d, ^1J(B,H) = 150], −0.5 (s, 1B), −4.0 (br s, 8B), −11.3 [2B, d, ^1J(B,H) = 159], −15.9 [4B, d, ^1J(B,H) = 158]; MS-MALDI-TOF: m/z = 774 [Ag(**2**)$_2$]$^+$ and 441 [Ag(**2**)]$^+$.

Synthesis of 8. To a solution of methylaquocobaloxime (0.065 g, 0.201 mmol) in 5 mL of methylene chloride, compound **1** (0.104 g, 0.402 mmol) was added. After 5 min of stirring at room temperature, the orange solution was vacuum-dried. The red residue was washed twice with 5 mL of ice-cold methylene chloride–hexane (1 : 1). The solid was dried under vacuum overnight. Recrystallization from CH_2Cl_2–C_6H_{14} (1 : 1) gave red needles. (100 mg, 88%) (Found: C, 32.23; H, 5.54; N, 12.32. $C_{15}B_9O_4H_{32}Co_2N_5$ requires: C, 32.08; H, 5.74; N, 12.47); ν/cm^{-1}: (C_{ar}–H) 3035, 3006, (C–H) 2910, (B–H) 2597, 2576, 2553, 2528, (C–H) 1564, (C=N) 1236 (KBr pellets); δ_H 18.1 (2H, s, OH), 6.6 (2H, s, N–C_{pyr}–H), 6.4 (2H, s, C_{pyr}–C_{pyr}–H), 4.4 (2H, s, C_c–H), 2.2 (12H, s, –CH_3), 0.8 (3H, s, Co–CH_3); $\delta_{H\{B\}}$ = 18.1 (2H, s, OH), 6.6 (2H, s, N–C_{pyr}–H), 6.4 (2H, s, C_{pyr}–C_{pyr}–H), 4.4 (2H, s, C_c–H), 3.4 (1H, br s, B–H), 3.1 (3H, br s, B–H), 2.2 (12H, s, –CH_3), 1.8 (5H, br s, B–H), 0.8 (3H, s, Co–CH_3); $\delta_{C\{H\}}$ = 150.0 (s, CH_3–Co), 109.5 (s, N–C_{pyr}), 92.7 (s, C_{pyr}–C_{pyr}), 54.3 (s, C_c), 12.1 (s, C–CH_3); δ_B 9.9 (1B), 7.8 (1B), −2.2 (2B), −3.7 (2B), −13.8 [2B, d, ^1J(B,H) = 162], −20.5 [1B, d, ^1J(B,H) = 169].

Synthesis of 9. The procedure was as for **8** but with compound **2** (0.134, 0.402 mmol) as starting material (92 mg, 70%) (found: C, 39.50; H, 5.84; N, 10.62. $C_{21}B_9O_4H_{36}Co_2N_5$ requires: C, 39.55; H, 5.69; N, 10.98); ν/cm^{-1} (C_{ar}–H) 3097, (C_c–H) 3016, (C–H) 2896, (B–H) 2599, 2559, 2530, 2516, (C–H) 1554, (C=N) 1234 (KBr pellets); δ_H 18.3 (2H, s, OH), 7.6–7.3 (5H, m, C_{ar}–H), 6.8 (1H, N–C_{pyr}–H), 6.6 (1H, N–C_{pyr}–H), 5.7 (1H, s, C_{pyr}–C_{pyr}–H), 5.5 (1H, s, C_{pyr}–C_{pyr}–H), 4.3 (1H, s, C_c–H), 2.2 (6H, s, –CH_3), 2.1 (6H, s, –CH_3), 0.9 (3H, s, Co–CH_3); $\delta_{H\{B\}}$ 18.3 (2H, s, OH), 7.6–7.3 (5H, m, C_{ar}–H), 6.8 (1H, N–C_{pyr}–H), 6.6 (1H, N–C_{pyr}–H), 5.7 (1H, s, C_{pyr}–C_{pyr}–H), 5.5 (1H, s, C_{pyr}–C_{pyr}–H), 4.3 (1H, s, C_c–H), 3.6 (2H, br s, B–H), 3.4 (1H, br s, B–H), 2.9 (1H, br s, B–H), 2.2 (6H, s, –CH_3), 2.1 (6H, s, –CH_3), 1.9 (3H, br s, B–H), 1.8 (2H, br s, B–H), 0.9 (3H, s, Co–CH_3); $\delta_{C\{H\}}$ 151.0 (s, CH_3–Co), 149.5, 144.5, 129.1, 128.4 (s, C_{ar}), 105.8 (s, N–C_{pyr}), 117.8 (s, N–C_{pyr}), 95.2 (s, C_{pyr}–C_{pyr}), 94.9 (s, C_{pyr}–C_{pyr}), 57.6 (s, C_c–H), 12.2 (s, C–CH_3), 12.0 (s, C–CH_3); δ_B 11.5 [1B, d, ^1J(B,H)

= 153], 8.9 [1B, d, ^1J(B,H) = 159], −2.6 (4B), −8.0 [1B, d, ^1J(B,H) = 177], −13.4 [1B, d, ^1J(B,H) = 145], −15.1 [1B, d, ^1J(B,H) = 153].

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