

ANNEX

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Methylation and de-methylation in cobaltabisdicarbollide derivatives.

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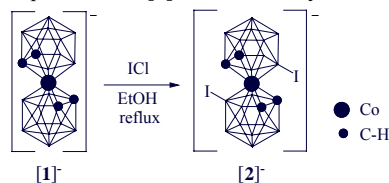
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Introduction

Since its discovery,¹ the chemistry of cobaltabisdicarbollide anion, $[3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{-}$, **[1]**, has been prevalent within the boron cluster literature, and it continues to be a subject of intense study.² Halogen substituted derivatives such as $[8,8^{\prime},9,9^{\prime},12,12^{\prime}\text{-X}_6\text{-}3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]^{-}$, (X= Cl, Br, I), $[8,8^{\prime}\text{-X}_2\text{-}3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^{-}$, (X= Cl, Br, I), have been synthesized but, with some exceptions, they have not been considered suitable starting materials³ to produce derivatives of **[1]**. Recently Hawthorne et al.⁴ have reported the synthesis of $[3,3^{\prime}\text{-Co}(8,9,12\text{-}(\text{CH}_3)_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_8)_2]^{-}$ starting from $[8,8^{\prime},9,9^{\prime},12,12^{\prime}\text{-I}_6\text{-}3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]^{-}$, which opens a route to hexasubstituted derivatives of **[1]**. Also, B(8)-O derivatives of $[3,3^{\prime}\text{-Co}(\text{C}_2\text{B}_9\text{R}_3\text{H}_8)_2]^{-}$ are available through $[8\text{-C}_4\text{H}_8\text{O}_2\text{-}3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1^{\prime},2^{\prime}\text{-C}_2\text{B}_9\text{H}_{11})]^{-}$ which was reported in 1996.⁵ This dioxanate compound is susceptible to nucleophilic attack on the positively charged oxygen atom, e.g. by pyrrolol,⁶ imide, cyanide or amines,⁷ phenolate, dialkyl or diarylphosphite⁸ and N-alkylcarbamoyldiphenylphosphine oxides⁹ resulting in one anionic species as a consequence of the opening of the dioxane ring. But mono or di B(8)-R (R= alkyl) substituted derivatives of **[1]** have not yet been reported. In this work we report on the application of a modified Kumada reaction¹⁰ to produce B-C bonds for the di-substituted cobaltabisdicarbollide derivatives. Molecules containing B-C and B-O bonds are also generated and, interestingly, a high yield oxo-de-methylation is observed for the first time in cluster boron chemistry.

Results and Discussion

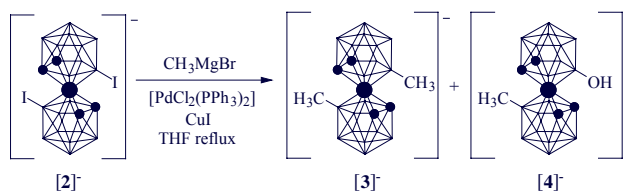
Caesium 8,8'-diiodocobaltabisdicarbollide, Cs**[2]**, was prepared by a modification of the original synthesis by Mátel et al.^{3a} employing ICl instead of I₂. The procedure is much more simple and permits the isolation of Cs**[2]** with an easy purification step (Scheme 1). This method provides a rapid and reliable synthesis of multigram quantities of **[2]** in an overall yield of 98%.



Scheme 1. Preparation of caesium 8,8'-diiodocobaltabisdicarbollide, Cs**[2]**.

The reaction involves refluxing a mixture of Cs**[1]** and ICl in ethanol (10 h) to obtain a solution containing Cs**[2]** and the excess of ICl. After destroying the latter with Na₂SO₃, pure Cs**[2]** is obtained concentrating the solution from which a crystalline orange solid separates.

Dimethyl substitution of **[1]** at the 8, 8' positions was achieved by B-C cross coupling reaction employing a modified Kumada reaction (Scheme 2). Addition of 5 equivalents of methylmagnesium bromide to a cooled (0°C) solution of Cs**[2]** in THF, followed by a catalytic amount of [PdCl₂(PPh₃)₂] and CuI and reflux for 5 h gave a mixture of compounds according to ¹¹B-NMR. Following evaporation of the THF, the residue was extracted with acidic water and diethyl ether. After chromatography on silica with AcOEt, four different bands were separated. Two of these accounted for more than 90% of the collected masses, and have been the ones studied. These bands correspond to Cs[8,8'-(CH₃)₂-3,3'-Co(1,2-C₂B₉H₁₀)₂], Cs**[3]**, and to Cs[8-CH₃-8'-OH-3,3'-Co(1,2-C₂B₉H₁₀)₂], Cs**[4]**. For the specific conditions utilized in this preparation, the ratio of Cs**[3]**/Cs**[4]** is 2/1. This coupling reaction was repeated for 2, 15 and 30 hours refluxing time. Although minor variations in the ratio of Cs**[3]**/Cs**[4]** were observed, these were attributed to differences in the working up method and not to the transformation of **[3]** into **[4]**. The chemical stability of Cs**[3]** towards Grignard derivatives was further proven by adding methylmagnesium bromide to a cooled (0°C) solution of Cs**[3]** in THF (ratio 5:1), followed by a catalytic amount of [PdCl₂(PPh₃)₂] and CuI and reflux for 5 h. The ¹¹B-NMR of the reaction crude indicated that **[3]** remained unaltered.



Scheme 2. 8,8'-dimethyl substitution of **[1]** by B-C cross coupling reaction.

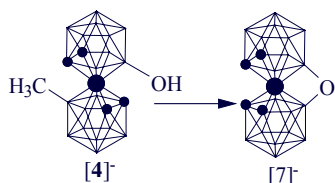
Similarly, the chemical stability of **[3]** towards iodine was proven by adding the latter to a solution of Cs**[3]** in EtOH (ratio 2:1) and reflux for 2h. Again the ¹¹B-NMR of the reaction crude confirmed that **[3]** remained unaltered.

The same coupling procedure has been utilized to produce Cs[8,8'-(CH₃CH₂)₂-3,3'-Co(1,2-C₂B₉H₁₀)₂], Cs**[5]**, and Cs[8-CH₃CH₂-8'-OH-3,3'-Co(1,2-C₂B₉H₁₀)₂], Cs**[6]**, with ethyl magnesium bromide instead of methylmagnesium bromide. The dependence of the Cs**[5]**/Cs**[6]** ratio is comparable to the **[3]** and **[4]** analogues.

Reaction of Cs**[4]** with I₂ in refluxing ethanol (2 h) leads through an unprecedented oxo-de-methylation process to a solution containing $[8,8^{\prime}\text{-}\mu\text{-O-}3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^{-}$ **[7]** (Scheme 3). Pure Cs**[7]** is obtained in 47% yield after concentrating the solution, and eluting the residue with AcOEt in a SiO₂ column.

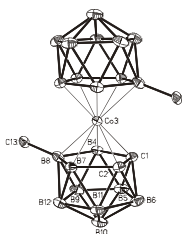
¹ Isabel Rojo is enrolled in the PhD program of the UAB.

The necessity of I₂ was proven by refluxing Cs[4] in EtOH for 2h. In these experimental conditions unaltered Cs[4] was obtained. The relevance of the alkyl group in the oxo-de-alkylation reaction was studied by reacting Cs[6] with I₂ in the same experimental conditions as for Cs[4]. For R=Et no reaction was observed.



Scheme 3. Schematic representation of the oxo-de-methylation process.

Full structural elucidation of [3] was obtained with an X-ray diffraction study of [PPN][3], (PPN= bis(triphenylphosphoranylidene)ammonium) (Figure 1, Table 1). [PPN][3] was produced dissolving the orange solid Cs[3] in the minimum amount of EtOH and a solution of [PPN]Cl in EtOH/water was added, resulting in the precipitation of [PPN][3]. This was filtered off, washed with water and petroleum ether and dried in vacuum. Crystals suitable single-crystal data collection were obtained by slow evaporation of an ethanol/ acetone solution



of the compound.

Figure 1. Schematic drawing of [3] with 20% thermal displacement ellipsoids.

Table 1. Crystallographic Parameters for [PPN][3].

empirical formula	C ₄₂ H ₅₆ B ₁₈ CoNP ₂	
fw	890.33	
cryst. syst.	monoclinic	
cryst. habit, color	block, red	
space group	C2/c	
a (Å)	30.9930(7)	
b (Å)	8.9763(2)	
c (Å)	18.5724(5)	
β (deg)	115.9374(11)	
V (Å ³)	4646.44(19)	
Z	4	
T (°C)	-100	
λ (Å)	0.71073	
ρ (g cm ⁻³)	1.273	
μ (cm ⁻¹)	4.72	
goodness-of-fit ^a on F ²		1.039
R ^b [I>2σ(I)]	0.0478	
wR ^c [I>2σ(I)]	0.1027	
^a S = [Σw(F _o ² - F _c ²) ²]/(n - p) ^{1/2} , ^b R = Σ F _o - F _c /Σ F _o , ^c wR = [Σ[w(F _o ² - F _c ²) ²]/Σ[w(F _o ²) ²] ^{1/2}		

Asymmetric unit of [PPN][3] consists of half of [8,8'-(CH₃)₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ or [3]⁻ complex unit, with the metal occupying at inversion center, and half of [PPN]⁺ ion, with the nitrogen atom at 2-fold axis. Thus the methyl groups of the centrosymmetric [3]⁻ moiety as well as the cage carbons lie on opposite sides of the complex moiety. Crystallographic parameters for [PPN][3] are presented in Table 1, and selected bond lengths and angles are listed in Table 2. A drawing of [3]⁻ is shown in Figure 1.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [PPN][3].

Co(3)-C(1)	2.017(3)	P-N	1.5787(12)
Co(3)-C(2)	2.017(3)	C(13)-B(8)-Co(3)	117.5(3)
Co(3)-B(4)	2.087(3)	C(13)-B(8)-B(4)	124.9(3)
Co(3)-B(7)	2.101(4)	C(13)-B(8)-B(7)	124.3(3)
Co(3)-B(8)	2.159(4)	P-N-P ^d	146.9(2)
C(1)-C(2)	1.645(4)	^d Equivalent position -x, y, -z+1/2	
B(8)-C(13)	1.488(6)		

The clusters for [PPN][3] have the expected near-icosahedral geometry with the lengths of the differing types of connectivities standing in the expected sequence C-C < C-B < B-B, the magnitude of these connectivities being comparable to these determined for [1]⁻.^{6,8,9} A notable exception is the short B-C bond of the B(8)-Me *exo*-cluster group, which is 1.488(6) Å. For ex. in [8,8',9,9',12,12'-(CH₃)₆-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻,⁴ the shortest B-Me bond length in a similar chemical environment is 1.679(12) Å.

Characterization of the remaining synthesized compounds has been done mostly with ¹¹B-NMR and MALDI-TOF mass spectra. The ¹¹B-NMR spectrum of derivatives of Cs[1] is the result of the addition of the two individual halves, as schematised in Figure 2.¹¹ As an example, the ¹¹B{¹H}-NMR of Cs[8-CH₃-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] is the addition of the ¹¹B{¹H}-NMR of Cs[1] plus Cs[3]. The spectrum of the first displays resonances at ppm, 6.5(1), 1.4(1), -6.0(4), -17.2(2) and -22.7(1) and the spectrum of Cs[3] at ppm 14.9(1), 1.0(1), -4.0(4), -17.4(2) and -24.2(1). The spectrum of Cs[8-CH₃-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] should then be very close to 14.9(1), 6.5(1), 1.4(1), 1.0(1), -4.0(4), -6.0(4), -17.2(2), -17.4(2), -22.7(1), and -24.2(1). The experimental spectrum of Cs[8-CH₃-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]¹² consists of bands at 16.6(1), 7.6(1), 0.6(2), -3.5(2), -4.7(2), -5.2(2), -6.2(2), -17.3(2), -17.8(2), -22.4(1) and -25.3(1). We have tested this method with other available examples and it works extremely well. It is therefore a remarkable tool to assist in the structural elucidation of derivatives of [1] mainly when other techniques like COSY, GIAO are not applicable. The ¹¹B-NMR of Cs[4] displays resonances at 23.7(1), 13.1(1), 0.3(1), -2.5(1), -4.2(4), -5.7(2), -6.9(2), -17.6(2), -19.8(2), -24.1(1), -28.4(1). If resonances attributable to the expected participant component Cs[3] are removed, the spectrum is left with the resonances of the unknown fragment, 23.7(1), -2.5(1), -5.7(2), -6.9(2), -19.8(2) and -28.4(1). The 1:1:2:2:2:1 pattern is consistent with a C_s fragment symmetry, and the high chemical shift value at 23.7 strongly supports assignment to B(8)-OH. The synthesis of Cs[8,8'-(OH)₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] had been produced by the reductive acetoxylation of Cs[1].¹³ The reported NMR displays resonances at 25.8(1), -4.6(1), -5.6(2), -8.6(2), -19.8(2), and -29.6(1). The matching with the non-methyl moiety of Cs[4] is excellent, proving the Cs[8-CH₃-8'-OH-3,3'-Co(1,2-C₂B₉H₁₀)₂] nature of Cs[4]. Its atomic composition was elucidated by comparison of the highest mass peak envelop found near 354 m/z in the MALDI-TOF mass spectrum with the simulated peak for B₁₈CoC₅OH₂₄ corresponding to the formula of [4]⁻. A similar reasoning was applied for the structural elucidation of Cs[5] and Cs[6].

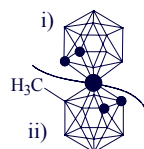


Figure 2. The ¹¹B-NMR spectrum of [8-(CH₃)-3,3'-Co(1,2-C₂B₉H₁₀)(1,2-C₂B₉H₁₁)]⁻ is the result of the addition of the two individual halves: i) + ii).

Compound [7] was characterized by MALDI-TOF mass spectrometry, and by comparison of the ^{11}B -NMR spectrum with reported data.¹⁴ Compound Cs[7] had been earlier synthesized by reaction of Cs[1] with paraformaldehyde and H_2SO_4 in acetic anhydride (19.7 % yield). The structure had been initially¹⁴ reported to correspond to $[8,8'\text{-}\mu\text{-OCH}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ but a later X-ray diffraction¹⁵ analysis confirmed it to be Cs $[8,8'\text{-}\mu\text{-O-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$.

Conclusions

The synthesis of [3]-[6] has shown that the modified Kumada reaction can be applied to produce B-C bonds for di-substituted cobaltabisdicarbollide metallocarboranes. For the reaction to proceed and avoid unreacted di-iodo starting material a high ratio (2.5:1) of the Grignard reagent per iodine in [2] has to be used. When the ratio is lowered to 1.25:1 a large proportion of unreacted starting material is recovered. This suggests that other reactions consuming CH_3MgBr or $\text{CH}_3\text{CH}_2\text{MgBr}$ take place besides the formation of the B-CH₃ or B-CH₂CH₃ moieties. The syntheses of [4] and [6] are explained through unknown intermediates shown as ["4"] in Figure 3 that upon hydrolysis produce the hydroxy derivative. The ["4"] intermediate does not derive from [3] as was proven earlier when discussing the stability of [3] towards Grignard reagents. It must be formed in parallel to [3]. It is remarkable the unprecedented de-methylation process found for [4] to yield [7], and the fact that a de-ethylation did not happen with [6].

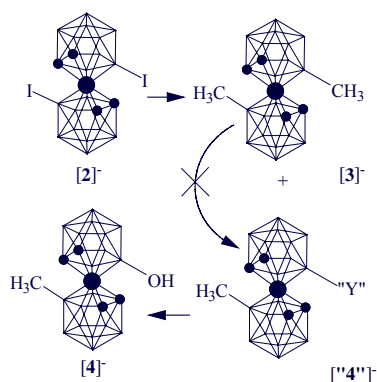


Figure 3. From diiodide to hydroxymethyl showing the intermediate precursor of the latter. The crossed arrow indicates that ["4"] does not have its origin in [3].

Experimental Section

General Considerations. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. 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)]. ^1H and $^1\text{H}\{^{11}\text{B}\}$ NMR (300.13 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz), and ^{11}B NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were recorded from CD_3COCD_3 solutions at 25 °C. Chemical shift values for ^{11}B NMR spectra were referenced to external $\text{BF}_3\cdot\text{OEt}_2$, and those for ^1H , $^1\text{H}\{^{11}\text{B}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to $\text{Si}(\text{CH}_3)_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz.

All reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques. Column chromatography was performed on Matrix silica 60 (0.040-0.063 mm). Methylmagnesium bromide and ethylmagnesium bromide were obtained from Aldrich as 3.0 M solution in diethyl ether. THF was distilled from sodium benzophenone prior to use. EtOH was dried over molecular sieves and deoxygenated prior to use. Cesium salt of compound 1 was supplied by Katchem Ltd. (Prague) and used as received. All other reagents were obtained from commercial sources and used as purchased. Bis-(triphenylphosphine)palladium dichloride¹⁶ was synthesized according to the literature.

Synthesis of Cs $[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ (Cs[2]). Iodine monochloride (3.0 g, 18.48 mmol) was added to a solution of Cs $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ (3.92 g, 8.58 mmol) in 80 mL of EtOH. The reaction mixture was refluxed for 10 hours. The excess of iodine monochloride was decomposed by addition of 1.68 g (13.34 mmol) of Na_2SO_3 in 40 mL of water and the whole solution was boiled for 5 min. The solvent was concentrated until the precipitation of an orange solid. This was filtered off and washed with water and petroleum ether. The solid was dried in vacuo. Yield: 5.99 g (98 %). Anal. Calcd for $\text{C}_4\text{H}_{20}\text{B}_{18}\text{CoCsI}_2$: C: 6.78, H: 2.85 %. Found: C: 7.00, H: 2.83 %. IR ν (cm^{-1}): 3039 ($\text{C}_c\text{-H}$), 2592, 2563, 2530 (B-H), 978, 772. ^1H -NMR δ : 4.40 (br s, 4H, $\text{C}_c\text{-H}$), 3.22-1.82 (br m, 16H, B-H). $^1\text{H}\{^{11}\text{B}\}$ -NMR δ : 4.40 (br s, 4H, $\text{C}_c\text{-H}$), 3.22 (br s, 4H, B-H), 3.06 (br s, 2H, B-H), 2.59 (br s, 4H, B-H), 2.12 (br s, 2H, B-H), 1.82 (br s, 4H, B-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR δ : 60.07 (s, $\text{C}_c\text{-H}$). ^{11}B -NMR δ : 3.6 (d, $^1\text{J}(\text{B,H})=144$, 2B), -2.5 (d, $^1\text{J}(\text{B,H})=144$, 8B), -4.4 (s, 2B, B(8,8')), -16.2 (d, $^1\text{J}(\text{B,H})=159$, 4B), -21.7 (d, $^1\text{J}(\text{B,H})=171$, 2B). MALDI-TOF-MS: (m/z) = 575.4 (M), 449.5 (M-1), 322.5 (M-21).

Synthesis of Cs $[8,8'\text{-(CH}_3)_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ (Cs[3]) and Cs $[8\text{-CH}_3\text{-}8'\text{-OH-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ (Cs[4]). A solution of Cs $[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ (200 mg, 0.28 mmol) in THF (12 mL) was treated with methylmagnesium bromide (0.47 mL, 1.4 mmol) (3.0 M in diethyl ether) at 0 °C, forming a brown precipitate. The mixture was left to room temperature for 30 min and then $[\text{PdCl}_2(\text{PPh}_3)_2]$ (7.9 mg, 0.01 mmol) and CuI (2.2 mg, 0.01 mmol) were added in a single portion. The brown solution was refluxed for 5 hours. The grey solid was discarded by filtration. After removal of the solvent, 20 mL of diethyl ether was added. This was extracted three times with 20 mL of dilute HCl (60 mL of water containing 0.15 mL of concentrated HCl). The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was flash-chromatographed over silica gel using as eluent ethyl acetate. Two main bands were separated: [3] ($R_f = 0.15$) and [4] ($R_f = 0.26$). The yield were for Cs[3] 67 %, 91 mg, and for Cs[4] 33 %, 45.3 mg.

Cs[3]: Anal. Calcd for $\text{C}_6\text{H}_{26}\text{B}_{18}\text{CoCs}$: C: 14.87, H: 5.41 %. Found: C: 14.80, H: 5.38 %. IR ν (cm^{-1}): 3048 ($\text{C}_c\text{-H}$), 2922, 2831 ($\text{C}_{\text{alkyl}}\text{-H}$), 2535 (B-H), 747 (B-C), 1373, 1307, 1101, 976. ^1H -NMR δ : 4.17 (br s, 4H, $\text{C}_c\text{-H}$), 0.31 (br s, 6H, CH_3), 2.56-1.60 (br m, 16H, B-H). $^1\text{H}\{^{11}\text{B}\}$ -NMR δ : 4.17 (br s, 4H, $\text{C}_c\text{-H}$), 2.56 (br s, 4H, B-H), 1.85 (br s, 4H, B-H), 1.60 (br s, 8H, B-H), 0.31 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR δ : 51.23 (s, $\text{C}_c\text{-H}$) 9.17, 8.40, 7.65, 6.86 (br q, B- CH_3). ^{11}B -NMR δ : 14.9 (s, 2B, B(8,8')), 1.0 (d, $^1\text{J}(\text{B,H})=141$, 2B, B(10,10')), -4.0 (d, $^1\text{J}(\text{B,H})=141$, 8B, B(4,4',7,7',9,9',12,12')), -17.4 (d, $^1\text{J}(\text{B,H})=153$, 4B, B(5,5',11,11')), -24.2 (d, $^1\text{J}(\text{B,H})=167$, 2B, B(6,6')). MALDI-TOF-MS: (m/z) = 352.7 (M).

Cs[4]: Anal. Calcd for $\text{C}_5\text{H}_{24}\text{B}_{18}\text{CoCsO}$: C: 12.34, H: 4.97 %. Found: C: 12.31, H: 4.95 %. IR ν (cm^{-1}): 3047 (BO-H), 3039 ($\text{C}_c\text{-H}$), 2922, 2834 ($\text{C}_{\text{alkyl}}\text{-H}$), 2573, 2528 (B-H), 747, 725 (B-C), 1077, 973. ^1H -NMR δ : 4.27 (br s, 2H, $\text{C}_c\text{-H}$), 4.00 (br s, 2H, $\text{C}_c\text{-H}$), 0.26 (br s, 3H, CH_3), 2.83-1.41 (br m, 16H, B-H). $^1\text{H}\{^{11}\text{B}\}$ -

NMR δ : 4.27 (br s, 2H, C_c-H), 4.00 (br s, 2H, C_c-H), 2.83 (br s, 1H, B-H), 2.75 (br s, 2H, B-H), 2.59 (br s, 4H, B-H), 1.95 (br s, 2H, B-H), 1.79 (br s, 2H, B-H), 1.57, 1.53 (br s, 4H, B-H), 1.41 (br s, 1H, B-H), 0.26 (br s, 3H, CH₃). ¹³C{¹H}-NMR δ : 53.01 (s, C_c-H), 48.27 (s, C_c-H), 8.49, 7.87, 6.82, 6.16 (br q, B-CH₃). ¹¹B-NMR δ : 23.7 (s, 1B, B(8)), 13.1 (s, 1B, B(8')), 0.3 (d, ¹J(B,H)=146, 1B, B(10')), -2.5 (d, ¹J(B,H)=157, 1B, B(10)), -4.2 (d, ¹J(B,H)=144, 4B, B(4',7',9',12')), -5.7 (d, ¹J(B,H)=135, 2B, B(9,12)), -6.9 (d, ¹J(B,H)=121, 2B, B(4,7)), -17.6 (d, ¹J(B,H)=163, 2B, B(5',11')), -19.8 (d, ¹J(B,H)=167, 2B, B(5,11)), -24.1 (d, ¹J(B,H)=167, 1B, B(6')), -28.4 (d, ¹J(B,H)=171, 1B, B(6)). MALDI-TOF-MS: (m/z) = 354.5 (M).

Synthesis of Cs[8,8'-(CH₃CH₂)₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (Cs[5]) and Cs[8-CH₃CH₂-8'-OH-3,3'-Co(1,2-C₂B₉H₁₀)₂] (Cs[6]). A solution of Cs[8,8'-I₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (200 mg, 0.28 mmol) in THF (12 mL) was treated with ethylmagnesium bromide (0.47 mL, 1.4 mmol) (3.0 M in diethyl ether) at 0°C, forming a brown precipitate. The mixture was left to room temperature for 30 min and then [PdCl₂(PPh₃)₂] (7.9 mg, 0.01 mmol) and CuI (2.2 mg, 0.01 mmol) were added in a single portion. The brown solution was refluxed for 6 hours. The grey solid was discarded by filtration. After removal of the solvent, 20 mL of diethyl ether was added. This was extracted three times with 20 mL of dilute HCl (60 mL of water containing 0.15 mL of concentrated HCl). The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was flash-chromatographed over silica gel using as eluent ethyl acetate. Two main bands were separated: [5] (R_f = 0.11) and [6] (R_f = 0.22). The yield were for Cs[5] 62 %, 90 mg, and for Cs[6] 31 %, 45 mg.

Cs[5]: Anal. Calcd for C₈H₃₀B₁₈CoCs: C: 18.74, H: 5.90 %. Found: C: 18.52, H: 5.80 %. IR ν (cm⁻¹): 3039 (C_c-H), 2961, 2922, 2854 (C_{alkyl}-H), 2562 (B-H), 747 (B-C), 1378, 1299, 1139, 980. ¹H-NMR δ : 4.23 (br s, 4H, C_c-H), 1.31 (br m, 4H, CH₂), 0.85 (br m, 6H, CH₃), 2.60-1.61 (br m, 16H, B-H). ¹H{¹¹B}-NMR δ : 4.23 (br s, 4H, C_c-H), 2.78 (br s, 2H, B-H), 2.62 (br s, 4H, B-H), 1.95 (br s, 2H, B-H), 1.80 (br s, 2H, B-H), 1.61 (br s, 4H, B-H), 1.51 (br s, 2H, B-H), 1.31 (br m, 4H, CH₂), 0.85 (br m, 6H, CH₃). ¹³C{¹H}-NMR δ : 51.14 (s, C_c-H), 18.90 (s, CH₂CH₃). ¹¹B-NMR δ : 16.8 (s, 2B, B(8,8')), 1.0 (d, ¹J(B,H)=133, 2B), -4.4 (d, ¹J(B,H)=111, 4B), -5.5 (d, ¹J(B,H)=118, 4B), -17.2 (d, ¹J(B,H)=148, 4B), -24.0 (d, ¹J(B,H)=177, 2B). MALDI-TOF-MS: (m/z) = 380.7 (M).

Cs[6]: Anal. Calcd for C₆H₂₆B₁₈CoCsO: C: 14.39, H: 5.23 %. Found: C: 14.30, H: 5.19 %. IR ν (cm⁻¹): 3039 (C_c-H), 2961, 2922, 2867 (C_{alkyl}-H), 2560 (B-H), 743, 724 (B-C), 1099, 979. ¹H-NMR δ : 4.35 (br s, 2H, C_c-H), 4.04 (br s, 2H, C_c-H), 1.34 (br m, 2H, CH₂), 0.93 (br m, 3H, CH₃), 2.78-1.51 (br m, 16H, B-H). ¹³C{¹H}-NMR δ : 53.36 (s, C_c-H), 47.90 (s, C_c-H). ¹¹B-NMR δ : 23.4 (s, 1B), 14.3 (s, 1B), 0.3 (d, ¹J(B,H)=141, 1B), -2.3 (d, ¹J(B,H)=157, 1B), -4.1 (d, ¹J(B,H)=179, 2B), -5.8 (d, ¹J(B,H)=137, 4B), -6.7 (d, ¹J(B,H)=100, 2B), -17.5 (d, ¹J(B,H)=155, 2B), -20.0 (d, ¹J(B,H)=157, 2B), -23.7 (d, ¹J(B,H)=166, 1B), -28.3 (d, ¹J(B,H)=166, 1B). MALDI-TOF-MS: (m/z) = 367.6 (M).

Synthesis of Cs[8,8'- μ -O-3,3'-Co(1,2-C₂B₉H₁₀)₂], Cs[7]. To a solution of Cs[8-CH₃-8'-OH-3,3'-Co(1,2-C₂B₉H₁₀)₂] (76 mg, 0.16 mmol) in EtOH (5 mL) was added 80 mg (0.31 mmol) of iodine. The orange solution was refluxed for 2 hours. The solvent was removed and the residue was purified over silica gel using ethyl acetate as eluent. A red band corresponding to Cs[7] was obtained (R_f = 0.71). Yield: 47 %, 34.5 mg. Anal. Calcd for C₄H₂₀B₁₈CoCsO: C: 10.21, H: 4.28 %. Found: C: 10.01, H: 4.12 %. IR ν (cm⁻¹): 3039 (C_c-H), 2573, 2540 (B-H), 1378, 1261, 1037. ¹H-NMR δ : 3.76 (br s, 4H, C_c-H), 3.99-1.29 (br m, 16H, B-H). ¹H{¹¹B}-NMR δ : 3.99 (br s, 4H, B-H), 3.76 (br s, 4H, C_c-H),

2.13 (br s, 2H, B-H), 1.88 (br s, 4H, B-H), 1.58 (br s, 4H, B-H), 1.29 (br s, 2H, B-H). ¹³C{¹H}-NMR δ : 45.24 (s, C_c-H). ¹¹B-NMR δ : 17.5 (s, 2B, B(8,8')), -1.5 (d, ¹J(B,H)=149, 2B, B(10,10')), -8.0 (s, ¹J(B,H)=143, 4B, B(4,4',7,7')), -9.4 (d, ¹J(B,H)=137, 4B, B(9,9',12,12')), -14.2 (d, ¹J(B,H)=160, 4B, B(5,5',11,11')), -25.9 (d, ¹J(B,H)=163, 2B, B(6,6')). MALDI-TOF-MS: (m/z) = 338.6 (M).

X-ray diffraction studies.

Single-crystal data collection [PPN][8,8'-(CH₃)₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] or [PPN][3] was performed at -100°C on an Enraf Nonius Kappa CCD diffractometer using graphite monochromatized Mo K α radiation. A total of 7161 reflections were collected giving 4091 unique reflections [*R*_{int} = 0.0521]. The structure were solved by direct methods and refined on *F*² by the SHELXL97 program.¹⁷ Non-hydrogen atoms were refined anisotropic thermal displacement parameters but hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal displacement parameters, and bond lengths and angles for [PPN][8,8'-(CH₃)₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] ([PPN][3]). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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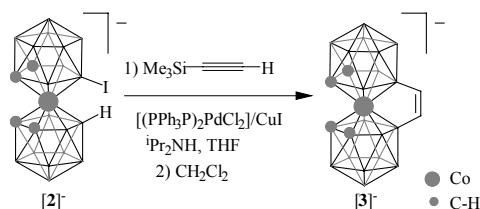
Generation of bridging alkene and conjugated dialkenes on the [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ platform exclusively generated from alkynes. The unique hydroboration role of [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻

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The cobaltabis(dicarbollide) anion, [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻, [1]⁻, first synthesized by Hawthorne and co-workers,¹ has proven to be very valuable in many areas of applied research.² Our group has focused on the synthesis of carbon substituted derivatives³ of [1]⁻ and recently has begun to explore its derivatives on boron.⁴ In this paper we report on the unprecedented metal mediated transformation of an alkyne into a B,B' bridging alkene. The ene formation can be associated with the cooperative effect of a B-I and a B-H geometrically placed on an adequate platform, and to their electronic properties. In addition, the synthesis of a conjugated dialkene derivative of [1]⁻ is described. Although examples of metal mediated dialkene formation exist,⁵ the novelty reported in this paper, in addition of being the first announced in a (hetero)borane cluster, is that it is generated only from an alkyne (trimethylsilylacetylene), contrarily to the usual case where an alkyne and an alkene are needed. This has been possible through the singular capacity of a B-H to produce hydroboration.



Scheme 1. Preparation of the alkene-linked cobaltabisdicarbollide, [3].

The 8-monoiodinated derivative, Cs[3,3'-Co(8-I-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], Cs[2],^{4,6} is obtained from Cs[1] and is used as the starting material for the preparation of the alkene-linked cobaltabis(dicarbollide). Reaction of Cs[2] with trimethylsilylacetylene in the presence of [PdCl₂(PPh₃)₂]/CuI and diisopropylamine in refluxing THF leaves, after removing the solvent and stirring with CH₂Cl₂, an insoluble red solid, Cs[3] (Scheme 1). ¹H-NMR of Cs[3] indicates the absence of the -SiMe₃ group. This was unexpected as removal of -SiMe₃ requires the use of specific reagents, e.g. Bu₄NF.⁷ The ¹¹B-NMR displays a pattern 1:3:2:2:1 ranging from +26.0 to -25.4 ppm, which suggests that in Cs[3] both dicarbollide moieties are symmetry related if the resonance of intensity 3 is due to the coincidental overlap of two resonances (1+2). The two moieties could have been equivalent if

two alkynyl groups, one in each moiety, had been introduced. This was not the case although Grimes and co-workers have recently reported that the reaction of [Cp*Co(5-I-1,2-Et₂-1,2-C₂B₃H₄)]⁸ with trimethylsilylacetylene using similar catalyst set as the one for Cs[3] and diethylamine as solvent led to a mixture of trimethylsilylalkynyl mono and disubstituted metallacarboranes, the latter being produced in 58% yield. In Grimes example the disubstitution had taken place in contiguous boron atoms at the same carborane ligand moiety. Relevant information about the structure of [3]⁻ was obtained from the Matrix Assisted Laser Desorption Ionization mass spectrum (MALDI-TOF) in the negative mode. An envelop was observed near 348.6 m/z which precisely corresponds to the calculated envelop for [μ-8,8'-C₂H₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻, [3]⁻. This formula would be in agreement with the NMR spectroscopic data. The formation of Cs[3] can be described considering that an ethylene group generated from an alkyne bridges two equivalent sites of the precursor leaving the original structure practically unaffected. An X-ray diffraction study of Cs[3] confirmed the formulation (Figure 1).⁹ The ethene bridge with a C13-C13' distance of 1.325(5) Å strongly determines the mutual orientation of the carborane moieties. Consequently, the C₂B₃ faces coordinated to Co are tilted by 7.1(2)° from parallel orientation and B8 and B8' are closer, deviating 11° from ideal eclipsed conformation.

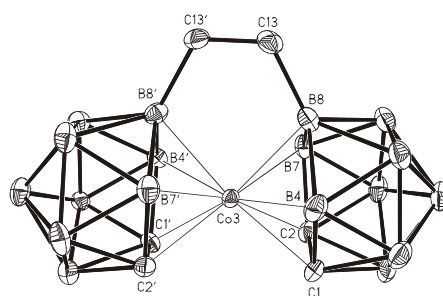


Figure 1. Structure of the anion of Cs[3]. Thermal ellipsoids are drawn at the 50% probability level.

In an attempt to learn on the required reacting sites on [1]⁻ for the ethene bridging reaction to proceed, two reactions were conducted: i) Cs[3,3'-Co(8-I-1,2-C₂B₉H₁₀)₂], Cs[4] having two B(8)-I units, was reacted with trimethylsilylacetylene, ii) Cs[1] with two B(8)-H was also reacted with the alkyne. In both cases

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the reaction conditions were the same as for the synthesis of Cs[3]. No reaction was observed in either case. This implies that the two non-equivalent groups B(8)-I and B(8')-H are complementary and necessary for the alkyne insertion. Likewise the role of the trimethylsilyl group was assessed performing the reaction of [2] with acetylene, phenylacetylene, methyl propargyl ether and propargyltrimethylsilane and no reaction was observed. Why does this reaction then take place? We interpret the reaction as shown in Figure 2. Initially a B-C coupling takes place, which is shifted to the reagents side (step i). This could explain the absence of dicarbollide alkyne derivatives with any of the alkynes tested. For the particular case of trimethylsilylacetylene the polarizable C-Si bond should facilitate hydroboration by the B(8)-H (step ii). Upon the formation of the alkene, the =CBSi carbon becomes electron-rich and susceptible to electrophilic attack. This fact plus the bulkyness of the -SiMe₃ groups and the electropositive character of Si provide a pathway for a hydrosilylation process leading to the bridging alkene (step iii).

This reaction finds no parallel in alkyne organic or organometallic chemistry but some similarities can be found in the enyne metathesis first described by Katz.¹⁰ In Katz's original example a conjugated dialkene is generated, in which one of the two ene groups bridges the 2,2' positions in biphenyl to yield 9-vinylphenantrene. Conceptually phenantrene and [3] are alike. They are formally generated from biphenyl and [1] respectively, upon the addition of a C=C moiety. This could have been just a geometrical curiosity but it provided some hints about the reactivity of iodococene, [2], as we describe next.

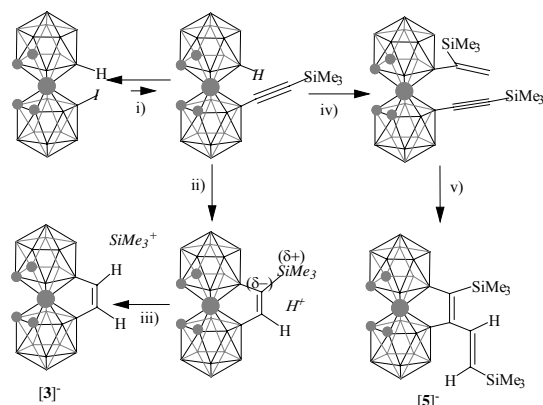


Figure 2. Possible paths of the reaction between [2] and trimethylsilylacetylene.

The reaction leading to Cs[3] was not quantitative. After removal of Cs[3] and evaporation of H₂CCl₂, the MALDI-TOF analysis of the solid revealed several peak envelopes proving that its composition was complex. The two largest envelopes corresponded one to unreacted [1] and the second to a derivative of [1] that is the result of fusing two trimethylsilyl moieties, [5] (Figure 2). An optimization of the reaction conditions has been done to improve the yield of the latter. In this way proton sponge, triethylamine, diethylamine, diisopropylamine and butyllithium have been used as base, and diisopropylamine and THF as solvent. Room temperature and refluxing conditions or a combination of both have also been tested. Finally, different ratios of the alkyne vs. [2] have been studied. The nature of the final products do not vary much with the different conditions, but the reaction at room temperature in which diisopropylamine is used both as a base and as solvent produces [5] in largest quantity. We consider that the pathway proposed for [3] is also

valid for [5]. Once the boron-carbon bond formation has taken place, step i) in Figure 2, an alternative route to step ii) is possible that is indicated as step iv). Both ii) and iv) steps are based on a hydroboration. For ii) the hydroboration on the triple bond is intramolecular while for iv) the hydroboration is intermolecular. It has been known that hydroboration of alkynylsilanes proceed with opposite regiochemistry to put the boron on the carbon bonded to silicon.¹¹ We have not found exception to this observation; both steps ii) and iv) are in agreement with this observation. Following step iv) an alkene group is generated in the molecule which adds to the already present alkyne. In the presence of the "Pd" catalyst an enyne metathesis¹² catalytic cycle leading to the formation of the cobaltabisdicarbollide conjugated dialkene takes place, which is a reasonable product of enyne metathesis.¹³ The spectroscopic data are in agreement with this formulation. The MALDI-TOF simulation of the peak corresponding to [5] matches the experimental one observed at 518.5 m/z. The ¹H-NMR of [5] shows in addition to other resonances two doublets at 6.68 and 5.95 ppm with J(H,H)= 21 Hz which are indicative of alkene protons in a *trans* disposition. The non-equivalency of the two dicarbollide moieties in [5] is clear from the 1:1:1:1:4:2:2:4:2 ¹¹B-NMR pattern spectra.

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Supporting Information Available. Synthetic and characterization details for Cs[3] and Cs[5]; and X-ray structure details (pdf) and crystallographic data (CIF) for Cs[3]. This material is available free of charge via the Internet <http://pubs.acs.org>.

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Polypyrrole Overoxidation Resistance Improvement with Weakly Coordinating Cobaltabisdicarbollide Doping Complexes.

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The overoxidation resistance of electropolymerized polypyrroles doped with $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ derivatives bearing different substituents was studied. The investigations were performed using Low Scan Voltammetry techniques, and SEM images were recorded for selected samples. Results show that modifications of the nude cobaltabisdicarbollide peanut shape leading to bulkier derivatives cause a faster overoxidation of the material. Introduction of bulky groups on the dicarbollide moieties of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ lowers the good three-dimensional packing possibility of the PPy threads and the capacity of the $\text{B}_{\text{cluster}}\text{-H}$ bonds to compensate positive charges of PPy bipolarons. Additionally, overoxidation resistance improvement is also attributable to the redistribution of electron density in the doping agent. This is achieved by incorporating electron-withdrawing groups in the $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ cluster. In this way, polypyrrole doped with $[3,3'\text{-Co}(8\text{-(CH}_2\text{CH}_2\text{O)}_3\text{-CH}_3\text{-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ is more resistant to overoxidation than PPy doped with $[8,8'\text{-}\mu(1'',2''\text{-C}_6\text{H}_4)\text{-3,3'\text{-Co}(-1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ or $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$.

1. Introduction

In the past decades, intensive investigations have been carried out on intrinsic conducting polymers because of the large practical application possibilities of these promising materials in many fields.^{1,2} Among those conjugated double bond polymers, polypyrroles (PPy) have attracted much attention and have been recognized for their interesting applications as sensors,³⁻¹¹ coatings,^{12,13} fuel cells^{14,15} among others. It is well established that for conventional uses, PPy stability at a definite potential or a long-term stability for repetitive oxidation-reduction cycling are needed. Rapid degradation in water or air at high oxidative potential¹⁶⁻²¹ or reversibility losses when oxidation-reduction sequences are applied to the material²²⁻²⁴ are the major limitations of PPy for commercial and industrial developments. PPy chemical stability limit is known to be the overoxidation limit of the material, beyond which conducting material properties are definitely lost. The overoxidation stability highly depends on the PPy doping anion nature²⁵⁻²⁷ and in the experimental conditions applied to the material. Therefore, during overoxidation, nucleophiles like OH⁻ attack the polymer cationic sites, generating hydroxyl groups.²⁸ This process is subsequently followed by the carbonyl-bond formation, the disruption of the conjugated double-bond system^{18,28-33} and polymer doping anion losses. Such degradation processes have been characterized by *in-situ* FTIR studies,^{28,30-34} impedance spectroscopy,³⁵ UV/vis experiments^{28,29} and microcalorimetric measurements.¹⁹

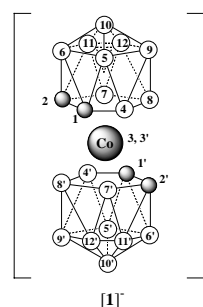


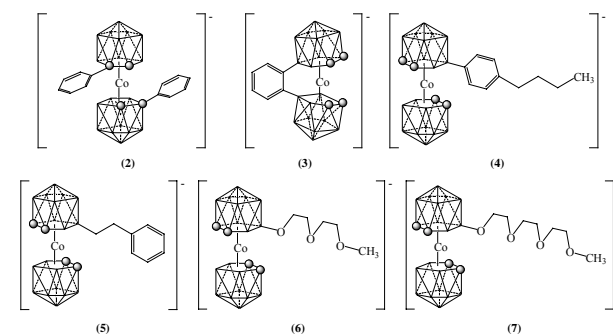
Chart 1

In recent publications of our group, we have reported the use of the high chemically resistant, weakly coordinating cobaltabisdicarbollide $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ [1]⁻ anion as a doping agent (chart 1).^{27,36} It gives a much

better overoxidation capacity than, as far as we are aware, any other anions studied to date. Overoxidation threshold resistance is determined to be at 1270 mV for polypyrrole doped with [1]⁻ (PPy/[1])²⁷ while overoxidation thresholds in the 800 to 1000 mV range are reported for PPy synthesized in the same experimental conditions, but with common doping anions such as perchlorate $[\text{ClO}_4]^-$, hexafluorophosphate $[\text{PF}_6]^-$, or dodecylbenzene sulfonate [DBS].^{27,29} The PPy/[1] overoxidation resistance is also better than with $[\text{CB}_{11}\text{H}_{12}]^-$ and $[\text{B}_{10}\text{Cl}_{10}]^{2-}$ doped polypyrroles. The $[\text{CB}_{11}\text{H}_{12}]^-$ and $[\text{B}_{10}\text{Cl}_{10}]^{2-}$ anions, in similarity to [1]⁻, also have a cluster structure with the negative charge delocalised through the whole molecule. The PPy/ $[\text{CB}_{11}\text{H}_{12}]^-$ and PPy/ $[\text{B}_{10}\text{Cl}_{10}]^{2-}$ materials are stable up to 1090 and 890 mV, respectively.³⁷ To date, no derivative compounds of [1]⁻ had produced an overoxidation resistance better than the parent compound. Halogen substitutions at the B(8), B(9) and B(12) positions of [1]⁻ (Chart 1) yield the hexachloro $[3,3'\text{-Co}(8,9,12\text{-Cl}_3\text{-1,2-C}_2\text{B}_9\text{H}_8)_2]^-$ or hexabromo $[3,3'\text{-Co}(8,9,12\text{-Br}_3\text{-1,2-C}_2\text{B}_9\text{H}_8)_2]^-$ derivatives that reduce the overoxidation potential threshold from 1270 mV to 1180 mV and 1100 mV, respectively.³⁷

Chart 2

We have hypothesized that the high degradation resistance generated by [1]⁻ had to be related to the anion shape, to the



availability of BH's, and their orientations and interactions with the polypyrrole strands. To support this, we have studied in the present work, the overoxidation of PPy doped with different derivatives of [1] represented in Chart 2. [3,3'-Co(1-C₆H₅-1,2-C₂B₉H₁₀)₂] [2] was selected as an example of cluster carbon substituted compound, and [8,8'-μ(1'',2''-C₆H₄)-3,3'-Co(-1,2-C₂B₉H₁₀)₂] [3] for its rigidity and its more voluminous shape. [3,3'-Co(8-(1''-(4''-C₄H₉)-C₆H₄)-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] [4], [3,3'-Co(8-(1''-(4''-C₆H₅)-C₂H₄)-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] [5] were chosen for their similar volume but opposite electronic effects, and [3,3'-Co(8-(CH₂CH₂O)₂-CH₃-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] [6] and [3,3'-Co(8-(CH₂CH₂O)₃-CH₃-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] [7] for their capacity to trap protons from the solution or to coordinate alkaline and other hard metal ions, hence to compensate positive charges.³⁸ PPy electrochemical polymerization and overoxidation threshold potentials with compounds [1]-[7] are reported and discussed in the paper.

2. Experimental Section

Solvents and Reagents. Acetonitrile was purchased from Aldrich and distilled prior to its use. Pyrrole was purified by distillation and stored under nitrogen at 0°C in dark. The cobaltabisdicarbollide cesium salt, Cs[Co(C₂B₉H₁₁)₂], Cs[1] was obtained from Katchem and used as received. The cobaltabisdicarbollide derivatives NMe₄[3,3'-Co(1-C₆H₅-1,2-C₂B₉H₁₀)₂], NMe₄[2],³⁹ NMe₄[8,8'-μ(1'',2''-C₆H₄)-3,3'-Co(-1,2-C₂B₉H₁₀)₂], NMe₄[3],⁴⁰ Cs[3,3'-Co(8-(1''-(4''-C₄H₉)-C₆H₄)-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], Cs[4],⁴¹ Cs[3,3'-Co(8-(1''-(4''-C₆H₅)-C₂H₄)-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], Cs[5],⁴¹ Na[3,3'-Co(8-(CH₂CH₂O)₂-CH₃-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], Na[6],⁴¹ Na[3,3'-Co(8-(CH₂CH₂O)₃-CH₃-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], Na[7],⁴¹ were synthesized as reported in the literature.

Electrochemical Procedures. All electrolyte solutions for polypyrrole (PPy) film preparation were deoxygenated by bubbling nitrogen gas before use. All electrochemical experiments were done using an EG&G Princeton Applied Research model 273A potentiostat-galvanostat. Electropolymerizations were performed in dry CH₃CN in a double-compartment, three electrode cells with a 3 mm diameter glassy carbon plate and a 10 cm platinum wire as working and counter electrodes respectively. Potentials are reported with respect to Ag/AgCl (0.1 M tetrabutyl ammonium chloride in CH₃CN) reference electrode. 0.1 M pyrrole and 3.5*10⁻² M doping anion (1% water) solutions were used. Polypyrrole films were grown using both galvanostatic (with a constant current of 0.5 mA during 225s) and cyclic voltammetry (at 100 mV/s from -1000 to 2000 V, 30 scans) techniques. Overoxidation resistance measurements were carried out in a single-compartment cell on the galvanostatically electropolymerized polypyrroles, by scanning the voltage at a low rate (0.5 mV/s, 0-2000 mV vs. Ag/AgCl 10% KCl H₂O) in a 0.1 M NaCl distilled water solution, after a careful electrode washing with CH₃CN and distilled water.

Electron Microscopy. A Hitachi S530 scanning electron microscope (SEM) was used to examine the PPy morphology.

3. Results and Discussion

3.1. Electrochemical growing properties of the doped polypyrroles.

Doped PPy materials were generated both by galvanostatic and cyclic voltammetry (CV) techniques. During the galvanostatic process, identical behaviour of all PPy/[1]-PPy/[7] doped materials is found. Classical anodic peak and plateau wave with a growth potential value of 1600 mV occur in the chronopotentiograms.

When CV methods are employed for the PPy growth, similar CV shapes that reflect the doped PPy structure properties^{27,42} are registered for the seven doping anions. Differences are found, however, for the intensity data. The PPy/[4] CV growth after thirty sequential scans is shown in Figure 1, as a representative example.

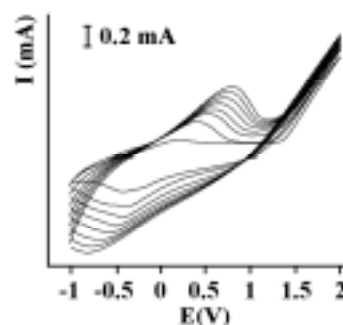


Figure 1. Sequential cyclic voltammetry for the electropolymerization of PPy/[4] in CH₃CN at 100 mV.s⁻¹ from -1000 to 2000 mV. From the 2nd to the 30th scan, every fourth is recorded for a better clarity.

For all PPy/[1]-PPy/[7], the first anodic scan show a strong wave with an onset potential corresponding to the pyrrole ring oxidation. After every new cycle, the continuous growth of reversible oxidation-reduction well-resolved waves indicate the film formation and demonstrate the conducting nature of the formed material. When common doping anions such as [ClO₄]⁻ or [PF₆]⁻ are used, cyclovoltammograms do not present so well-defined semi-cycles. Because of their hydrophobicity, low mobility and large size properties, derivatives of [1] are not expelled from the polymer matrix and reversible redox processes occur. While the number of scans increase, both anodic and cathodic peak positions are shifted to a more positive and negative potential respectively. Usual trace-crossing⁴³⁻⁴⁶ is observed for all scans. After reaching the switching potential at 2000 mV, a higher current is observed in the immediate reverse scan. This intensity trace-crossing has been explained⁴³ by the contribution of free pyrrole monomer molecules present in the newly generated polymer layer.

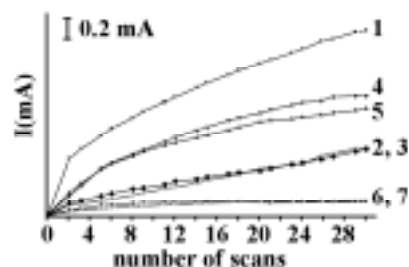


Figure 2. Anodic wave current intensity vs. number of scans for : ■ (1), × (2), ♦ (3), ▼ (4), ▲ (5), + (6), ● (7).

Figure 2 depicts the CV intensity of the anodic peak current vs. the number of scans for PPy/[1]-PPy/[7]. The CV anodic peak current values tend to increase with the number of scans, but as it is seen in figure 2, it is strongly influenced by the ionic size of the dopant, the nature of the side chain on the cluster B(8) atom and by the increasing electrical resistance of the deposit. The more conductive material is obtained with [1]. When the cluster boron B(8) is bonded to an alkyl chain [5] or an aryl one [4], the same growing speed and conductivity behaviour of the PPy film is observed, however, oxidative current values are 33% less than for PPy/[1]. Bulky and rigid anionic compounds [2] and [3] produce intensity values even smaller. Finally, CV intensities for derivatives of [1], B-O bonded compounds [6] and [7], are one order smaller than for PPy/[1]. This last result is in agreement with PPy-[3,3'-Co(8-C₄H₄N-(CH₂)₂-O-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], a self-doped copolypyrrole⁴² whose current intensity was far from the normal [1] doped material.

3.2. Overoxidation Stability, Relationship between the doped PPy overoxidation results and the structure of the doping anions.

Overoxidation measurements were made using a slow linear sweep voltammetry (LSV) technique in NaCl solution at 0.5 mV.s⁻¹ from 0 to 1800 mV with regard to Ag/AgCl and are reported in Figure 3 for the PPy/[1]-PPy/[7]. As it was recently reported, PPy/[1] displays a peak at 1270 mV on the LSV plots, which is consistent to a high overoxidation resistance of the material.^{27,47} This overoxidation threshold is almost 300 mV larger than other values obtained for PPy doped with common anions. Taking into account that PPy electrical properties highly depend on the doping anion properties like charge, anion shape regularity, ionic radius, hydrophobicity or hydrophilicity and on the interaction strength of the anionic species with the polymer matrix,⁴⁸⁻⁵¹ our interpretation of the excellent overoxidation stability of the PPy/[1] material is related to the three-dimensional peanut shape of the doping anion and its capacity to continuously compensate, through the three-dimensional disposition of the BH's, the positive polarons. Simple calculations⁵² show that the distance between the farthest two carbon atoms of the PPy polarons is near 12.3 Å, which is relatively close to the H-B(10)...B(10')-H [Co(C₂B₉H₁₁)₂] axial distance⁵³ (10.2 Å including the two hydrogen atoms). Therefore, the use of [1] gives the possibility of a fully intercalated structure of the polymeric network. On the contrary, the [CB₁₁H₁₂]⁻ anion is spherical (with a diameter of 5.6 Å including the farthest two hydrogen atoms)⁵⁴ and its use can lead to a disruption of the layered space structure arrangement, leading to a lower observed overoxidation resistance. The "spherical" counter-ions such as [ClO₄]⁻ or [PF₆]⁻ testify in favour of such reasoning.

The anion [1]⁻ is also considered to be a weakly coordinating anion, an useful spectator anion in making organometallic compounds to be used in catalysis,⁵⁵⁻⁵⁸ efficient in extracting nuclear wastes,^{39,53,59-62} in supramolecular chemistry⁶³ and in stabilizing cations.^{38,64} For the last property, cluster BH bonds interact freely with the cation. Cation/BH interactions have been described in the literature^{58,64,65} involving principally the B(8), B(9), B(12) sites that are identified as the site of maximum electron density in the cage. Nevertheless, in some examples, B(7)³⁸ and B(10)⁶⁵ were found to interact with the cation positive charge, demonstrating the diverse coordination possibilities of [Co(C₂B₉H₁₁)₂]. It seems therefore that PPy positive charge interactions with cluster BH bonds appear to be a favourable

combination for increasing the overoxidation capacity of the material. Consequently, when B(8), B(9) and B(12) atoms are Br or Cl substituted, cation/BH interactions disappear or are lessened, the typical [Co(C₂B₉H₁₁)₂]⁻ peanut shape is modified, and a drop of overoxidation potential is found.³⁷ The two hexachloro and hexabromo cobaltabisdicarbollide derivatives are thus less protecting. Similar behaviour but more dedicated to metal coordination was already reported by Xie *et al.* for cobaltabisdicarbollide derivatives with silver salts.⁶⁴

In Figure 3, the LSV experiments corresponding to PPy/[1]-PPy/[7] are represented. All display well-defined peaks but major shifts of the peak maximum are observed. The rigid [2]⁻ and [3]⁻ dopants produce less overoxidation resistant materials, displaying LSV peaks at 1210 and 1150 mV, respectively. Compound [4]⁻ produces similar overoxidation resistance than the classical [1] at 1270 mV. Finally, PPy/[5], PPy/[6], PPy/[7], present threshold waves at 1330, 1410, 1450 mV, respectively, which are at more anodic potentials than PPy/[1]. The PPy/[7] potential shift value of 180 mV as compared with PPy/[1] implies that [7]⁻ is the more overoxidation stabilizing anion tested in our experimental conditions and reported so far in the [Co(C₂B₉H₁₁)₂]⁻ family and in the literature.

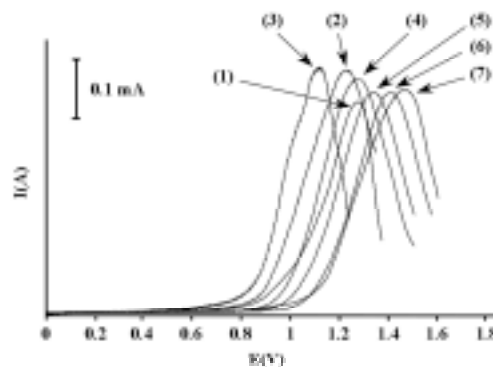


Figure 3. Overoxidation current vs. applied potential for PPy/[1-7].

It also may be observed that compounds [2]⁻-[4]⁻ bearing aryl groups directly bonded to the cluster atoms produce polypyrrole materials with similar or less overoxidation resistance than [1]⁻ whereas other cluster substituents (alkyl or alkoxy) [5]⁻-[7]⁻ improve the overoxidation performance of the materials. This aspect is in agreement with the fact that a low charge density anion can enhance the chemical stability of the PPy.²⁷ Aryl groups withdraw electron density from the cluster but in the same time, compensate the lost of electron density by back-donation.⁶⁶ Other chains, even the alkyl one, only remove electron density from the cluster, therefore producing a lower delocalised charge in the whole carborane cage.

The [3]⁻ doping anion is the one that shows the most defective overoxidation property. In [3]⁻, the phenyl ring bridging both cluster fragments at B(8) and B(8') positions, is perpendicular to the planes of the ligand coordinating C₂B₃ faces. The H-B(8) and H-B(8'), the two sites with more electron density in [1]⁻, should interact with the moving positive charges of the PPy wires. Due to benzene substitution in [3]⁻, this is not possible. This, along with the very bulky resulting shape of the anion, clearly limit any compact three-dimensional PPy network formation. When the two phenyl rings of [2]⁻ are bonded to the cluster carbon atoms, similar but more mobile anion shape is obtained and all

cation/BH interactions are possible. Consequently, the PPy/[2] overoxidation potential threshold value is half way between this of PPy/[1] and this of PPy/[3]. Compounds [4]-[7] present the same geometrical characteristics, but differ on the substituents. One of the dicarbollide fragments in the complexes is free of substituents while the second complex moiety is substituted in the B(8) position. In the nude dicarbollide ligand, B-H bonds can interact with the moving positive charge in the PPy wires. Therefore, differences among PPy/[4]-PPy/[7] overoxidation resistances, can only arise from the electron-withdrawing strength of the chain substituents, and from the capacity of hard oxygen donor atoms to compensate the moving polarons, since the volume of these [4]-[7] anions and their shape is similar. The introduction of oxygen atom at position eight of the dicarbollide moiety results in a significant redistribution of electron density in the cluster, part of the charge being accumulated in the B(8)-O oxygen atom, therefore overall producing a cluster with lower charge density than [1]. LSV overoxidation results (Figure 3) are in direct correlation with the previous considerations, PPy/[6] and PPy/[7] being the best overoxidation resistant material. The alkoxy organic groups of complexes [6] and [7] can also participate in the compensation of the PPy positive charges by electrostatic interactions in a similar way as oxygen atoms of $[3,3'-\text{Co}(8-\text{X}-(\text{CH}_2\text{CH}_2\text{O})_2-1,2-\text{C}_2\text{B}_9\text{H}_{10})(1',2'-\text{C}_2\text{B}_9\text{H}_{11})]$ coordinate to Na or hard cations.^{39,59,61,62,67}

3.3. Electron Microscopy Observation. Figure 4 shows micrographs of the best and the worst overoxidation resistant materials, PPy/[7] (Figure 4B) and PPy/[3] (Figure 4C) respectively, and PPy/[1] material that was used as reference (Figure 4A). Although PPy/[1] SEM images have already been reported,³⁶ a different view is reported for clarity. Figure 4A shows a rough and reasonably homogeneous surface in which can be seen the typical empty vesicles already reported.³⁶ The micrograph for PPy/[7] shows a relatively more homogeneous and more compact surface than PPy/[1], whereas in the PPy/[3] image, a less homogeneous, less compact, less cohesive and more irregular layer is observed. Expectedly, this last structure arrangement is less dense and therefore OH⁻, or other degradation species, should find less resistance to attack the polymer chain, leading to an increase of the overoxidation degradation rate and to a less anodic LSV experiment peak.

Conclusions

As a conclusion, the overoxidation resistance properties of polypyrrole were evaluated for six new cobaltabisdicarbollide complex doping anions that could be easily sorted by their geometrical characteristics. In this way, three groups of two doping agents each could be produced (see Chart 2) : [2]-[3], [4]-[5], and [6]-[7]. Although there are noticeable differences in each group, the group components reasonably behave in the same way when acting as doping agents. For instance, concerning the PPy growth rate, three clear different behaviours, in addition to PPy/[1] are observed (see Figure 2). Those different behaviour correspond well with the three groups defined above, to say PPy/[2], PPy/[3] in the first group, PPy/[4], PPy/[5] in a second group and PPy/[6] and PPy/[7] in a third group. In a similar way the same three groups can be generated in the LSV experiments leading to determine the overoxidation threshold. In

doing this grouping, it is found that the expected electronic opposite effects in [4]⁻ and [5]⁻ were found not to be determinant for PPy overoxidation resistance.

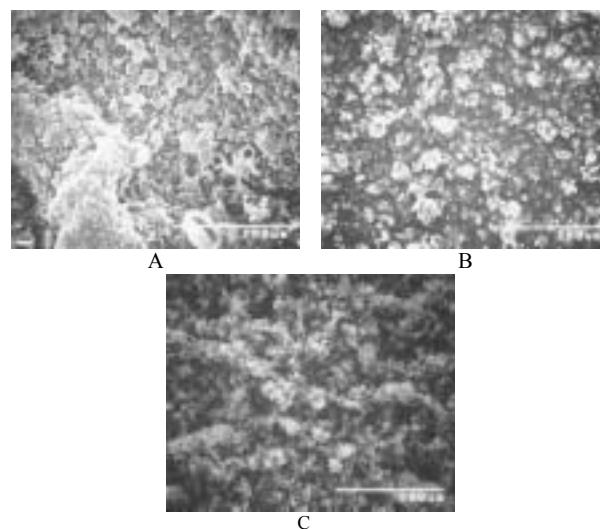


Figure 4. SEM images of electropolymerized PPy/(1) : A, PPy/(7) : B, PPy/(3) : C.

It is also found that for all PPy/[1]-PPy/[7]⁻ materials, low scan voltammetry experiments present a peak corresponding to the overoxidation threshold potential value. This potential is characteristic of the material and highly depends on the nature of the substituents on the carborane cluster cage. The results obtained indicate that polypyrrole overoxidation resistance is enhanced with anions having lower charge density. For the particular case of the excellent $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ anions, this is proven by the influence of substituents able to withdraw negative charge from the cluster. These substituents lower the overall charge of the cluster, hence the charge density, a parameter that is believed to be strongly influential in the polypyrrole overoxidation resistance. Additionally, a steric and anion shape influence is very relevant. The $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ anion has a peanut shape that allows a good interstitial packing and a three-dimensional distribution of the B-H units ready to compensate the polarons. The less availability of B-H units in the doping agents induces a less favourable overoxidation threshold in the material. Contrarily, the existence of extra hard coordinating elements in the external chains induces a more favourable overoxidation threshold. Bulky derivatives of this shape alter the packing type, expectedly producing less dense material, therefore facilitating penetration of hostile and degrading anions.

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A cobaltabisdicarbollide geometrical anionic BINAP analogue. Its synthesis and coordinating habits.

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Introduction

Today synthesizing enantiomerically pure compounds is a very significant endeavour to develop pharmaceuticals, agrochemicals and flavours. Enantioselectivities can be achieved with both C_1 - and C_2 -symmetric ligands, utilizing chirality at carbon, chirality on a donor atom (e.g. phosphorus), axial chirality or planar chirality. In 1968 W.S. Knowles¹ and L. Horner,² independently, reported the first homogeneously catalyzed hydrogenation of olefins with chiral monodentate tertiary phosphine-Rh complexes (C_1 -symmetry ligand). Later Kagan³ devised DIOP, a C_2 -symmetry ligand that represented a major breakthrough in the area. In 1980 Noyori published the synthesis of BINAP (2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl) which is an axially dissymmetric C_2 -ligand able to perform strong steric and electronic influences on transition-metal complexes. It has found extensive applications in asymmetric catalysis.⁴ Since then thousands of chiral ligands and their transition metal complexes have been reported⁵ and many of them are known to be highly effective in the asymmetric formation of C-H, C-C, C-O and C-N bonds, etc. Great many of them resemble very much BINAP and are obtained in racemic form to be later resolved to produce the enantiomeric atropisomers. One example of these is BiPHEP that is represented along with BINAP and $[3,3'\text{-Co}(1\text{-PPH}_2\text{-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**[2]**) in figure 1. While chiral atropisomeric biaryl diphosphines such as BINAP, BiPHEMP, and MeO-BiPHEP are very effective ligands for many asymmetric reactions,^{6,7} sometimes they are not efficient for certain substrates due to the lack of ligand rigidity. Introducing a bridge with variable length to link the diaryl groups has been proposed⁸ to make rigid ligands with tunable bite angles.⁹ Ferrocenyl phosphine ligands, see figure 1, have also been devised.¹⁰ Chiral ligands of the latter are produced introducing a single substituent.

We had a number of reasons for wishing to prepare metallacarboranyl diphosphines: the rapidly developing field of cobaltabisdicarbollide chemistry provides a pool of unprecedented backbones that may be used to stabilize and/or elaborate any chosen metal centre;¹¹ to prove that although metallaboranes may look esoteric their stability and reactivity motivates to consider them; to provide the first intrinsically anionic diphosphines in opposition to sulfonated BINAP,¹² for instance; and finally to show how the metal orientation with regard to the swinging axis can be modulated.

We have not done efforts to separate the racemic mixture. Our aim in presenting this work has been to show the possibilities of these ligands, derivatives of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ (**[1]**), their versatility and their coordinating capacity.

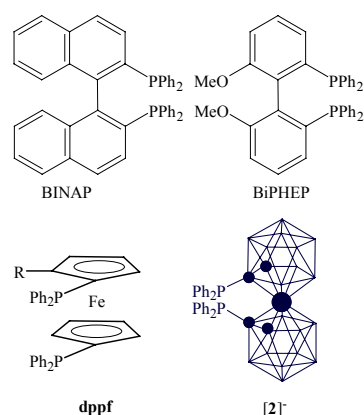


Figure 1. Representation of BINAP, BiPHEP, a diphenyl phosphino ferrocene (**dppf**) and $[3,3'\text{-Co}(1\text{-PPH}_2\text{-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**[2]**).

Results

1. Synthesis of $[3,3'\text{-Co}(1\text{-PPH}_2\text{-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$, **[2]**.

The desired anionic diphosphine may be prepared conveniently by metallation of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ with *n*-BuLi followed by simple reaction with chlorodiphenylphosphine in 1,2-dimethoxyethane (DME) as a solvent. A red solid corresponding to Li**[2]** spontaneously separates from the solution which is filtered in the air. The M**[2]** (M= NMe₄ or Cs) salts are produced by dissolving Li**[2]** in ethanol and adding an aqueous solution of [NMe₄]Cl or CsCl. Solids corresponding to the M**[2]** (M= NMe₄ or Cs) stoichiometry separate well and can be collected by filtration. The formula for **[2]**⁻ was proven by the mass spectrum obtained by Matrix Assisted Laser Desorption Ionization (MALDI-TOF). Full agreement between the experimental and calculated pattern was obtained. The ¹¹B-, ¹H- and ³¹P-NMR spectra of M**[2]** are in accord with the proposed structure shown in figure 1. The ¹¹B-NMR of Li**[2]** displays a 1:1:2:2:1:1:1:1 pattern in the range 9.1 to -20.0 ppm indicative of a *closo* species with all boron atoms in non-equivalent vertices. The resonances of intensity 2 shall be attributed to the coincidental overlap of two absorptions of intensity 1. The former pattern is consistent with a cluster carbon single substitution in each dicarbollide moiety. In agreement with this, the ³¹P-NMR shows only one resonance at 23.48 ppm. Finally, the ¹H-NMR displays a group of resonances between 7.76 and 7.31 ppm corresponding to aromatic protons and one resonance at 4.37 ppm corresponding to the C_{cluster}-H, (C_c-H), in a ratio

20:2. The absence of other peaks in this very informative region, 4-4.8 ppm, indicated that either the racemic or the *meso* form had been generated, but not the two. These two geometrical isomers could be produced in the reaction, and would present a similar ^{11}B -NMR pattern according to the expected C_2 or C_s symmetry, respectively. Therefore a crystal structure determination was necessary to elucidate which one of the two possible isomers had been generated. However, the ^{13}C -NMR of $\text{Li}[\mathbf{2}]$ in the C_c -R region already brought important hints about which isomer had been produced. This ^{13}C -NMR excerpt spectrum is shown in figure 2.

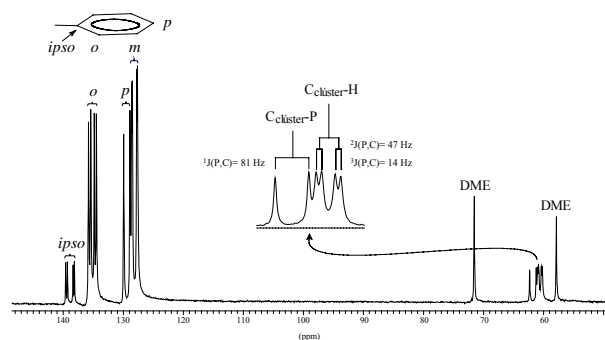


Figure 2. The ^{13}C -NMR spectrum of $[\mathbf{2}]$ with a more detailed view of the $C_{\text{cluster-R}}$ ($R = \text{H}$ or P) region.

The spectrum shows one resonance at 61.41 ppm with a $^1J(\text{C},\text{P}) = 81$ Hz and a doublet of doublets centered at 60.22 ppm with $^2J(\text{C},\text{P}) = 47$ Hz and $^3J(\text{C},\text{P}) = 14$ Hz. Interestingly, the two observed resonances $C_c\text{-P}$ and $C_c\text{-H}$ do not present the same splitting pattern with phosphorus. Diagram in figure 3 provides information on the reasons for the splitting dissimilarity of both C_c atoms.

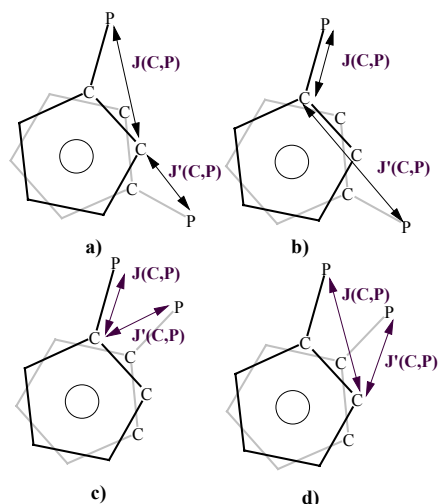


Figure 3. Projection of the pentagonal faces in $[\mathbf{2}]$ (with cobalt in the centre of symmetry). Figures a) and b) correspond to the racemic mixture while figures c) and d) correspond to the *meso* isomer.

$J(\text{C},\text{P})$ stands for the C coupling with the P in the common dicarbollide moiety while $J'(\text{C},\text{P})$ stands for the C coupling with P in the non-common dicarbollide moiety. Figures a) and b) correspond to the racemic mixture while figures c) and d) correspond to the *meso* isomer. Figures b) and c) refer to the ^{13}C resonance for $C_c\text{-P}$ while figures a) and d) stand for the ^{13}C

resonance of $C_c\text{-H}$. The ratio $J(\text{C},\text{P})$ vs $J'(\text{C},\text{P})$, represented by the arrows lengths is similar in c) and d), therefore a similar splitting patterns would be expected for $C_c\text{-P}$ and $C_c\text{-H}$ in the *meso* form. The $J(\text{C},\text{P})$ and $J'(\text{C},\text{P})$ discrepancy is very accentuated in the racemic mixture, figures a) and b) in figure 3, the $C_{\text{cluster-H}}$ having the more similar J and J' values and being subjected then to higher splitting. This would justify the observed pattern in the ^{13}C -NMR of $[\mathbf{2}]$ and prompted us to postulate that the racemic isomer had been generated.

X-ray diffraction. Crystals of $[\text{NMe}_4][\mathbf{2}]$ suitable for an X ray diffraction study were obtained by slow evaporation of a solution of the material in acetone and measured at ambient temperature on a Rigaku AFC5S diffractometer. A total of 7438 unique reflections were collected. The structure was solved by direct methods and refined on F^2 by the SHELXL97 program.¹³ The hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. For $[\text{NMe}_4][\mathbf{2}]$, all non-hydrogen atoms were refined with anisotropic displacement parameters. Tables 1 and 2 shows respectively crystallographic data and structural refinement details and selected interatomic distances and angles for $[\text{NMe}_4][\mathbf{2}]$.

Table 2. Selected Interatomic Distances (\AA) and Angles (deg) for $[\text{NMe}_4][\mathbf{2}]$.

Co3-C1	2.157(5)	C1'-Co3-C1	135.07(17)
Co3-C2	2.072(4)	P1-C1-Co3	108.3(2)
Co3-B8	2.116(6)	C2-C1-P1	114.4(3)
Co3-C1'	2.147(4)	B4-C1-P1	128.2(3)
Co3-C2'	2.094(4)	P2-C1'-Co3	111.3(2)
Co3-B8'	2.122(6)	C2'-C1'-P2	122.9(3)
P1-C1	1.896(5)	B4'-C1'-P2	120.8(3)
P2-C1'	1.893(4)	B10-Co3-B10'	173.84(14)
C1-C2	1.650(6)		
C1'-C2'	1.612(6)		

A straightforward refinement revealed a sandwich structure, in which the $C\text{-PPH}_2$ moieties are in a *cisoid* disposition showing that the anion corresponds to one of the enantiomers of the racemic form, figure 4.

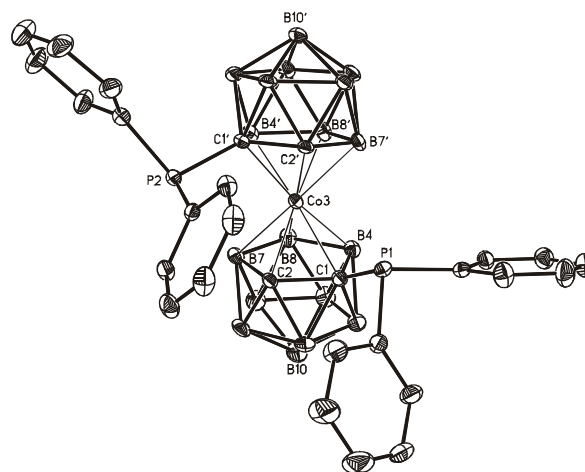


Figure 4. Drawing of anion of $[\text{NMe}_4][\mathbf{2}]$ with 20% thermal displacement ellipsoids.

2. Coordinating capacity.

Two types of metal ions have been studied to assess the coordinating capacity of [2]. Firstly, group 11 elements (Ag, Au) for their tendency to offer lower coordination numbers than other transition metal ions which would provide information on the real chelating predisposition of [2]; secondly transition metal ions of well recognized catalytic importance.

With group 11 elements (Ag, Au)

Treatment of [NMe₄][2] with one equivalent of [MCIPPh₃] (M=Ag, Au) for 0.5 h. in refluxing ethanol afforded complexes [M(PPh₃)₂] (3, M=Ag; 4, M=Au) in 71 and 98% yield, respectively, as shown in figure 5.

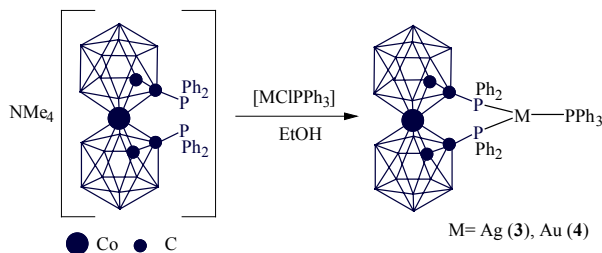


Figure 5. Scheme reaction between ligand [NMe₄][2] and [MCIPPh₃] (M=Ag (3), Au (4)). Non-specified vertices are BH's.

Similarly, treatment of [NMe₄][2] with one equivalent of [AgClO₄] at ambient temperature overnight in ethanol/acetone (10/3) afforded [Ag(acetone)(2)] (5) in 88% yield, see figure 6.

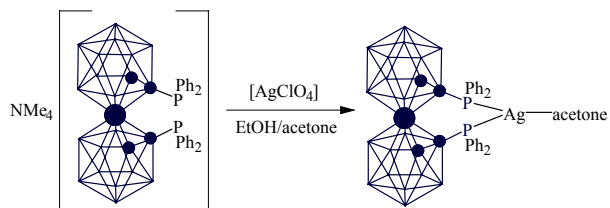


Figure 6. Scheme reaction between ligand [NMe₄][2] and [AgClO₄].

The molecular structure of 4 in solution was derived from the ³¹P- and ¹¹B-NMR spectra in d₆-acetone. Interestingly, the spectra were observed better at -60°C than at room temperature. The ¹¹B-NMR spectra displayed a 1:1:2:2:1:1 pattern, in agreement with a C₂ symmetry, in the range 10.0 to -19.4 ppm. The ³¹P-NMR is simple, showing two sets of resonances: a doublet at 73.61 ppm with ²J(P,P)=146 Hz and a triplet at 45.06 ppm with the same J value. This is in full agreement with Au being trigonally coordinated as shown in figure 5.

More complex is the structural elucidation or behaviour of 3 in solution. In principle a molecular structure such as this for 4 would be expected also in accord with the molecular structure of [Ag{7,8-(PPh₂)₂-7,8-C₂B₉H₁₀}(PPh₃)]¹⁴ where there is a chelating anionic carboranyl diphosphine ligand in which the two phosphorus atoms are in adjacent positions in the same dicarbollide moiety. The ³¹P-NMR for 3 is, however, relatively simple with two absorptions at δ= 43.50 ppm and 42.81 ppm, and a third one at δ= 32.89 ppm. Each absorption is in fact made of two doublets result of the J(³¹P, ¹⁰⁹Ag) and J(³¹P, ¹⁰⁷Ag) couplings. Therefore and quite surprising is the fact that no J(P,P) couplings are observed contrarily to [Ag{7,8-(PPh₂)₂-7,8-C₂B₉H₁₀}(PPh₃)] where all possible cross couplings were found.

Of notice is the fact that the two resonances, although very similar, at δ= 43.50 ppm and 42.81 ppm, indicate that the two phosphorus in [2] are non-equivalent. The spectrum is shown in figure 7. This singular behaviour motivated the synthesis of 5. The ³¹P-NMR of 5 is very simple with only one resonance at δ= 46.01 ppm consisting of two doublets due to the J(³¹P, ¹⁰⁹Ag) and J(³¹P, ¹⁰⁷Ag) couplings.

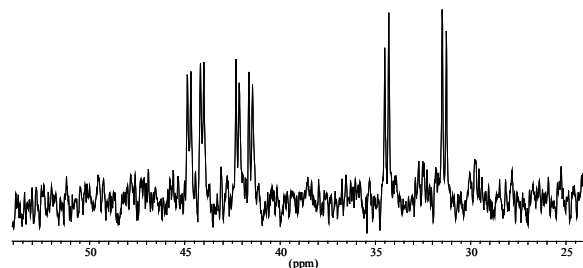


Figure 7. The ³¹P-NMR spectrum of 3.

The chemical shifts of the chelating phosphorus atoms in Ag coordinated to [2] both in 3 and in 5 are very similar which is indicative of a similar surrounding in both complexes although in 3 they are non-equivalent. The only explanation for 3 is that there is not a trigonal coordination around Ag which implies the existence of an extra ancillary ligand that presumably could be the acetone. The existence of this fourth coordinating ligand would render the molecule asymmetric, and no longer the two phosphorus atoms would be equivalent. Also, this tetrahedral environment could be the justification for the lack of phosphorus cross-couplings observed in the ³¹P-NMR. The ambiguity of the situation induced to grow crystals to unambiguously determine the chelating habit of [2].

X-ray Single-Crystal Structures of 3, 4 and 5. Single crystals of 3, 4 and 5 suitable for X-ray structure analysis were obtained from EtOH/acetone (3) or from acetone (4 and 5) at 22 °C after several days. Compound 3 crystallises in the space group C2/c. Compounds 4 and 5 in P2₁/n (no. 14). Single-crystal data collection for 3-OCMe₂, 4 and 5 were performed at -100°C on an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo Kα radiation. A total of 9571, 8850 and 8990 unique reflections were collected for 3-OCMe₂, 4 and 5, respectively.

The structures were solved by direct methods and refined on *F*² by the SHELXL97 program.¹⁵ For all structures, the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. For 3-OCMe₂, one of the phenyl groups connected to P3 and the non-coordinated acetone solvent are disordered both assuming two orientations. The disordered groups were refined as rigid groups and non-hydrogen atoms of the groups were refined with isotropic thermal displacement parameters. Rest of the non-hydrogen atoms were refined with anisotropic displacement parameters. For 4 and 5 all non-hydrogen atoms were refined with anisotropic displacement parameters.

ORTEP plots of the three complexes are shown in figures 8, 9 and 10. Tables 3, 4 and 5 contain selected bond distances and angles for 3-5 and crystallographic data and structural refinement details are shown in Table 1.

Both 3 and 5 can be viewed tetrahedrally coordinated, with three short contacts and one long contact. The long contact in 5 is due to Ag-H12' (2.17 Å) and in 3 is due to Ag-O in acetone (2.91 Å). Two of the short contacts are due to the two phosphorus atoms from [2] and the third by PPh₃ (3) or acetone (5). In 4, Au is tricoordinated to three phosphorus, two being provided by [2] and the third by PPh₃. The trigonal coordination of Au is further

proven by the fact that Au is only 0.0648(5) Å above the plane defined by the three phosphorus atoms. Likewise, the tetrahedral nature of Ag both in **3** and **5** is proven by the distance of Ag to the plane defined by the three closest atoms, in **3** these are the P atoms (Ag distance to the plane = 0.3147 Å), and in **5** they are the two P atoms and the O in acetone (Ag distance to the plane = 0.49690(8) Å).

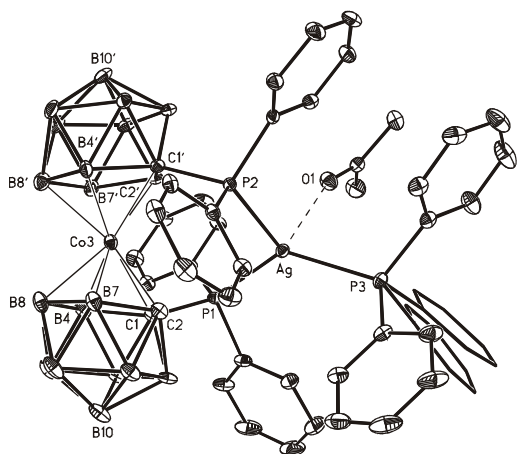


Figure 8. Drawing of **3** with 20% thermal displacement ellipsoids. Only skeletons of the two orientations of the disordered phenyl group are shown.

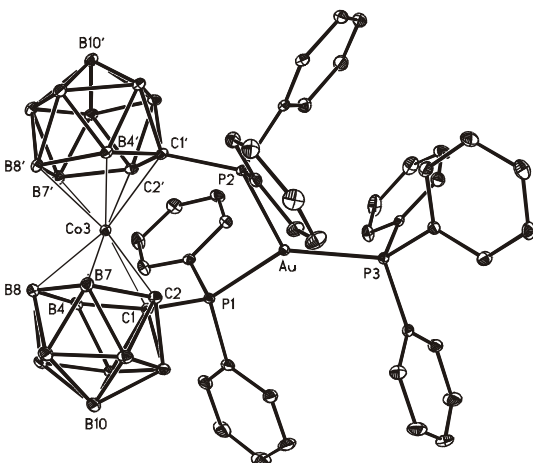


Figure 9. Drawing of **4** with 20% thermal displacement ellipsoids.

The three crystal structures clearly demonstrate the chelating capacity of the two phosphorus atoms in [2]⁻. Although the phosphorus atoms are well separated in [NMe₄][2] as shown by the torsion angle C1-c-c'-C1' (∠ = -102.3°) where c and c' are the centres of the pentagons, ∠ is smaller in the complexes, -77.6°, -54.4° and -76.4° for **3**, **4** and **5**, respectively. Figure 11 shows a top view of [2]⁻ and **3-5** focusing on the influence of the metal in the cobaltabisdicarbollide rotamer produced. Interestingly, **4** and **5**, although having a similar metal coordination, display a large difference in ∠. On the contrary, **3** and **5**, both Ag complexes, display ∠ values almost identical despite having the immediate metal surrounding distinct. This implies that it is the metal covalent radius the factor prevailing in determining the rotational degree of the ligand. The longer the

M-P radius the larger ∠ is. In this regard M-P distances diminish following the sequence **3**>**5**>**4**, which is the same trend observed for ∠, and for the P...P distance in coordinated [2]⁻ which is 4.206 Å in **3**, 4.196 Å in **5**, and 3.837 Å in **4**.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **3**·OCMe₂.

Ag-P1	2.5507(9)	P2-Ag-P1	111.21(3)
Ag-P2	2.5470(10)	P3-Ag-P1	129.99(3)
Ag-P3	2.4713(10)	P3-Ag-P2	114.09(3)
Ag-O1	2.906(3)	C1'-Co3-C1	123.05(14)
Co3-C1	2.156(4)	C1-P1-Ag	103.79(11)
Co3-C2	2.113(4)	C1'-P2-Ag	108.87(11)
Co3-B8	2.153(5)	P1-C1-Co3	112.97(17)
Co3-C1'	2.158(3)	C2-C1-P1	115.1(2)
Co3-C2'	2.096(4)	B4-C1-P1	131.3(3)
Co3-B8'	2.158(5)	P2-C1'-Co3	111.77(17)
P1-C1	1.878(4)	C2'-C1'-P2	114.9(2)
P2-C1'	1.878(4)	B4'-C1'-P2	129.9(3)
C1-C2	1.634(5)	B10-Co3-B10'	173.71(11)
C1'-C2'	1.626(5)		

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **4**.

Au-P1	2.3662(8)	P2-Au-P1	107.00(3)
Au-P2	2.4076(8)	P3-Au-P1	133.08(3)
Au-P3	2.3467(8)	P3-Au-P2	119.69(3)
Co3-C1	2.187(3)	C1'-Co3-C1	115.85(11)
Co3-C2	2.073(3)	P1-C1-Co3	117.10(15)
Co3-B8	2.138(4)	C2-C1-P1	118.6(2)
Co3-C1'	2.163(3)	B4-C1-P1	128.8(2)
Co3-C2'	2.060(3)	P2-C1'-Co3	114.63(15)
Co3-B8'	2.154(4)	C2'-C1'-P2	122.0(2)
P1-C1	1.874(3)	B4'-C1'-P2	124.5(2)
P2-C1'	1.878(3)	B10-Co3-B10'	171.13(8)
C1-C2	1.662(4)		
C1'-C2'	1.653(4)		

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for **5**.

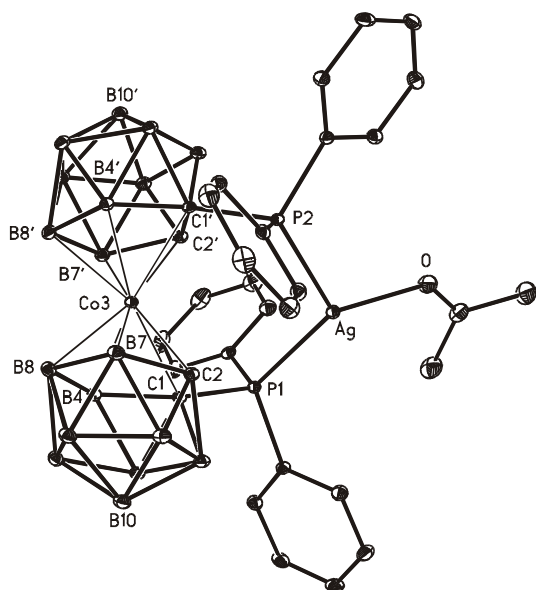
Ag-O	2.3895(17)	O-Ag-P1	114.68(5)
Ag-P1	2.4894(6)	O-Ag-P2	118.65(5)
Ag-P2	2.4933(6)	P1-Ag-P2	114.746(19)
Co3-C1	2.153(2)	C1'-Co3-C1	122.51(8)
Co3-C2	2.095(2)	C1-P1-Ag	104.47(7)
Co3-B8	2.153(3)	C1'-P2-Ag	107.19(7)
Co3-C1'	2.172(2)	P1-C1-Co3	113.96(11)
Co3-C2'	2.103(2)	C2-C1-P1	114.01(14)
Co3-B8'	2.150(3)	B5-C1-P1	118.40(14)
P1-C1	1.882(2)	B4-C1-P1	132.75(17)
P2-C1'	1.880(2)	B6-C1-P1	105.05(14)
C1-C2	1.631(3)	C37-O-Ag	134.76(18)
C1'-C2'	1.622(3)	P2-C1'-Co3	112.52(11)
		B10-Co3-B10'	174.16(5)

Table 1. Crystallographic Data and Structural Refinement Details for Compounds [NMe₄][2], 3-OCMe₂, 4 and 5.

	[NMe ₄][2]	3-OCMe ₂	4	5
empirical formula	C ₃₂ H ₅₂ B ₁₈ CoNP ₂	C ₅₂ H ₆₇ AgB ₁₈ CoO ₂ P ₃	C ₄₆ H ₅₅ AuB ₁₈ CoP ₃	C ₃₁ H ₄₆ AgB ₁₈ CoOP ₂
formula weight	766.20	1178.35	1151.29	858.00
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P2₁/n</i> (no. 14)	<i>C2/c</i>	<i>P2₁/n</i> (no. 14)	<i>P2₁/n</i> (no. 14)
<i>a</i> (Å)	12.705(2)	39.7263(5)	11.15040(10)	12.8241(2)
<i>b</i> (Å)	12.1215(18)	12.5412(2)	18.2288(2)	19.1948(5)
<i>c</i> (Å)	27.988(7)	23.5531(3)	24.9604(2)	16.9761(4)
β (deg)	101.416(16)	95.3792(10)	97.0350(10)	108.1789(14)
<i>V</i> (Å ³)	4225.0(14)	11682.8(3)	5035.22(8)	3970.19(15)
<i>Z</i>	4	8	4	4
<i>T</i> (°C)	21	-100	-100	-100
λ (Å)	0.71069	0.71073	0.71073	0.71073
ρ (g cm ⁻³)	1.205	1.340	1.519	1.435
μ (cm ⁻¹)	5.08	7.41	33.70	10.20
goodness-of-fit	0.996	1.010	1.015	1.034
<i>R</i> ¹ [<i>I</i> > 2σ(<i>I</i>)]	0.0603	0.0434	0.0253	0.0313
<i>wR</i> ² [<i>I</i> > 2σ(<i>I</i>)]	0.1379	0.0867	0.0488	0.0672

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

**Figure 10.** Drawing of 5 with 20% thermal displacement ellipsoids.

With catalytically important elements (Rh and Pd)

We also investigated the reaction of [NMe₄][2] with [Rh(μ-Cl)(cod)]₂. Complex [NMe₄][Rh(2)₂] (**6**) was obtained after stirring 2:0.5 mixtures of the starting materials in methylene chloride at ambient temperature overnight. Complex **6** was isolated in 85% yield as brown powdery solid, which is partially soluble in acetone. The different resonances in the ¹¹B-NMR spectra overlap greatly precluding to provide a definitive pattern. The resonances are observed between δ = 7.5 and -19.5 ppm. The ³¹P-NMR spectra show a doublet at δ = 85.16 ppm with

¹J(P, ¹⁰³Rh) = 205 Hz, in agreement with a structure in which the ligand symmetry in the complex has been preserved suggesting that the Rh surrounding is square-planar. The phosphorus strong chelating capacity towards Rh was checked by mixing [NMe₄][2] with [RhCl(PPh₃)₃] in ethanol at reflux for 1h. The resulting complex was again [NMe₄][Rh(2)₂] (**6**) in 87% yield. The stability of **6** in acetone was proven by ¹¹B-NMR and ³¹P-NMR. After several months no noticeable changes had been observed in the spectra.

The reaction of [NMe₄][2] with [PdCl₂(PPh₃)₂] in refluxing ethanol for 1 hour yielded a brown complex with the stoichiometry [PdCl(2)(PPh₃)] (**7**). Complex **7** is sparingly soluble in acetone. The ³¹P-NMR spectra shows three sets of resonances at δ = 60.39, 54.02 and 30.37 ppm, which indicate the non-equivalency of the two binding phosphorus in (**2**). Resonance at 60.39 ppm corresponds to the PPh₂ trans to PPh₃ and appears as a doublet of doublets with the coupling constants: ²J(P_{PPh₂(trans)}, P_{PPh₃}) = 238 and ²J(P_{PPh₂}, P_{PPh₂}) = 70 Hz. The resonances at 54.02 and 30.37 ppm correspond respectively to the PPh₂ in cis to PPh₃ and PPh₃.

Monitoring the evolution of **7** in acetone with ¹¹B-NMR and ³¹P-NMR spectroscopy showed [PdCl(2)(acetone)] (**8**) to be the major product after four days. Besides, only traces of unconverted **7** together with some minor unidentified phosphorus-containing products were detected. The ³¹P-NMR spectrum of **8** displays two doublets at 64.48 ppm and 54.04 ppm with ²J(P,P) = 72 Hz.

Discussion

Ligand [2] displays similarities with both 1,1'-bis(diphenylphosphino)ferrocene (**dppf**) and BINAP represented in figure 1. All of them have the possibility of various coordination modes reflecting their ability to match the steric demands of the coordinated metal, through axial rotation via a C-C bond (BINAP) or a centroid··metal··centroid axis in **dppf** or [2]. There are, however, important differences among these similar ligands. The most relevant are: i) while [2] is anionic, BINAP and **dppf** are neutral, and ii) while

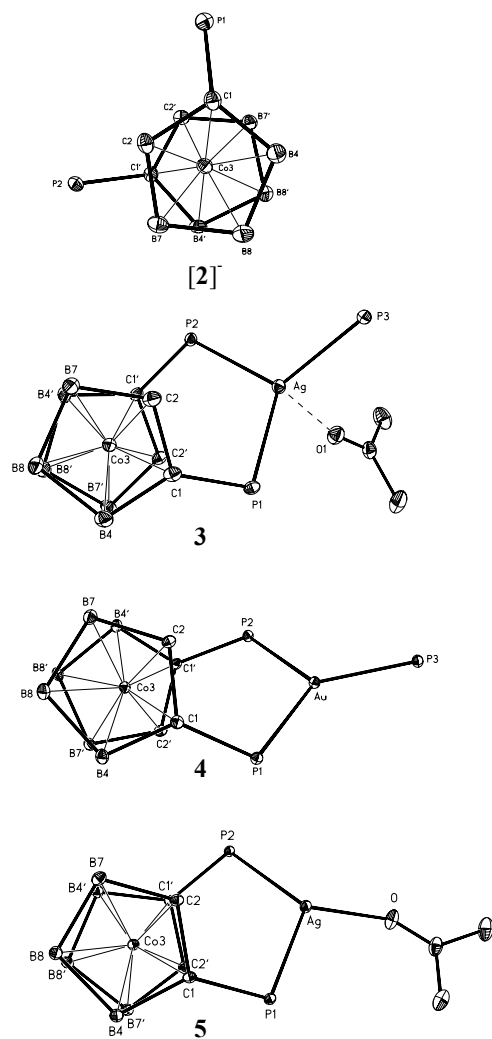


Figure 11. Top view of [2]⁻, 3-OCMe₂, 4 and 5 focusing on the influence of the metal in the cobaltabisdicarbollide rotamer produced.

[2]⁻ and BINAP are produced in racemic form, therefore subjected to be separated into their enantiomers, **dppf** requires the introduction of a stereogenic center to produce a chiral ligand. In this sense [2]⁻ is more similar to BINAP. Additionally, PPh₂ units in BINAP originate radially from the aromatic ring centroids being tilted towards the C-C axis. This is the origin of the atropisomerism. The possible optical isomerism is also originated this way in [2]⁻, although in this case the reason of the racemic mixture has its origin in the C₂B₃ coordinating face with its prochiral carbon atoms. These axial ligands can be regarded as hinges, see figure 13, in which the leaves are each movable fragment, e.g. the anthracenyl in BINAP, or the dicarbollide in [2]⁻. This view helps to explain the great differences among them. If the P...Ag...P coordinating motif is taken as a reference it is found that the P...P distance in most diphosphine Ag complexes is practically constant ranging from 3.8 to 4.0 Å.¹⁶ Therefore Ag demands the two P's to be geometrically separated by this value.

If we look at the hinge shown in figure 13 it is possible to notice that the distance between the holes (-PR₂) is maintained constant in a)-c). This has been possible varying the hole distances in the initial (D₀) position, shown in figure 13a), and swinging one of the leaves to the right ω value. Therefore with the hinge ligands BINAP, **dppf**, and [2]⁻, practically any required P...P distance can be matched. In figure 13 hinge situation a) would be representative of **dppf**, hinge situation b) of [2]⁻, and hinge situation c) could be representative of BINAP. Therefore the plane defined by the “P₂M” moiety will be more aligned with the hinge axis in **dppf** complexes than in BINAP, in which case the “P₂M” plane will be practically orthogonal to the axis. An intermediate situation, although closer to BINAP, would be with [2]⁻. All this can be intuitively visualized just looking at the representations of BINAP, **dppf**, and [2]⁻ in figure 12, and estimating the D₀ values. It would be expected that D₀(**dppf**) > D₀([2]⁻) > D₀(BINAP).

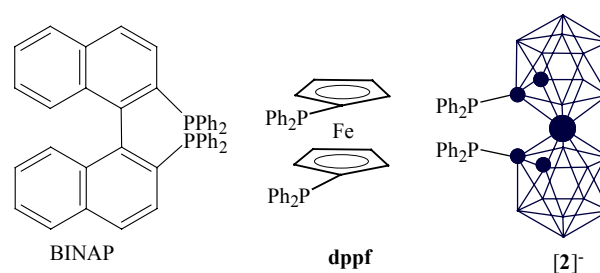


Figure 12. Comparison of BINAP, **dppf** and [2]⁻, all representing initial eclipsed disposition, with ω = 0.

It is possible and of interest to provide a quantitative value that can define a hinge ligand. A good indication comes from the minimum possible P...P distance (D₀). This would be achieved when the two phosphorus are in an eclipsed disposition. As this hypothetical situation is virtually impossible to be obtained, and to account for the metal influence, we have developed equation 1 to get the D₀ value. This value should be taken with caution as it depends on the metal, the coordination, and other factors but it is orientative of the ligand characteristics.

$$D_{\omega}^2 = D_0^2 + 4R^2 \cos^2(90-0.5\omega) \quad (\text{equation 1})$$

D_ω = P...P distance at the ω torsional value.

D₀ = P...P distance at the eclipsed position (ω = 0)

R = Distance of P to the hinge axis.

ω = Torsional angle from the eclipsed position.

Calculations based on equation 1 have been performed on data available from crystal structures¹⁷ and these reported in this paper. The computed values average 3.8 Å, 1.1 Å and 0 Å for **dppf**, [2]⁻ and BINAP, respectively, which are in perfect agreement with these intuitively given above. These three values mean that **dppf** will have to swing very little, small ω value, to fit a 4 Å (P...P) demand, for instance. To fit this value ligand [2]⁻ will have to turn a larger ω angle, while BINAP will be the one with the P...M...P plane orthogonal to the hinge axis. The result is, then, very different geometrical figures with very similar ligands.

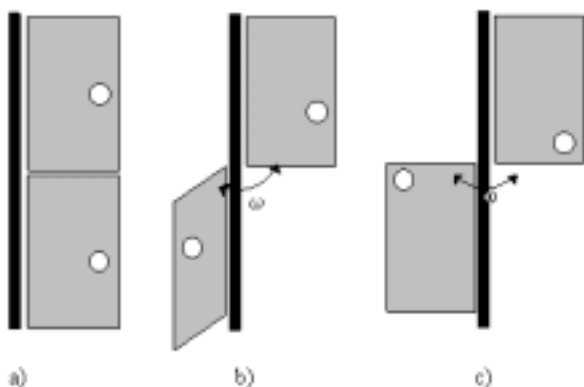


Figure 13. Hole-hole distance preservation by altering D_0 and ω .

Conclusions

In this paper the ligand $[3,3'\text{-Co}(1\text{-PPh}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ (**[2]**) has been synthesized in one pot reaction from $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ in very good yield and with an easy isolation process. Its two dicarbollide halves swing about one axis in the same way as 1,1'-binaphthyl or ferrocene derivatives. We consider these ligands to work as hinges, with the important property of being adjustable to any metal distance demand. Although the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$, 1,1'-binaphthyl and ferrocene backbones have a similar torsional behavior their diphosphino derivatives will meet the metal's requirements very differently. This is due to the spatial origin and disposition of the -PR_2 units. The two -PR_2 units in the eclipsed disposition are more separated in the ferrocene than in the cobaltabisdicarbollide and, in the latter more than in the binaphthyl derivatives. Therefore the " P_2M " plane generated will have a relative orientation with regard to the hinge axis very different. Furthermore the cobaltabisdicarbollide diphosphine derivative brings the novelty of being an intrinsically negative ligand, which apport interesting new possibilities for enhanced coordination and for optional metal site vacancies that otherwise would be fulfilled by a possible anionic monodentate ligand. Ligand **[2]** should be separable into its enantiomers and therefore the possibility to study intrinsically anionic enantiomerically pure diphosphine ligands in catalysis. Finally, the easy synthesis of **[2]** opens the opportunity to use carborene derivatives as real alternatives to conventional organic ligands.

Experimental Section

General Considerations. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. 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)]. ^1H - and $^1\text{H}\{^1\text{B}\}$ -NMR (300.13 MHz), $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.47 MHz), and ^{11}B -NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were recorded from CD_3COCD_3 solutions. Chemical shift values for ^{11}B -NMR spectra were referenced to external BF_3OEt_2 , and those for ^1H -, $^1\text{H}\{^1\text{B}\}$ -, and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were referenced to $\text{Si}(\text{CH}_3)_4$. Chemical shifts are reported

in units of parts per million downfield from reference, and all coupling constants are reported in hertz.

All manipulations were carried out under a dry dinitrogen atmosphere with common Schlenk techniques. 1,2-Dimethoxyethane was distilled from sodium benzophenone prior to use. Ethanol and methylene chloride were dried over molecular sieves and deoxygenated prior to use. Cesium salt of compound **[1]** was supplied by Katchem Ltd. (Prague) and used as received. Reagents were obtained commercially and used as purchased. Bis-(triphenylphosphine)palladium dichloride¹⁸ was synthesized according to the literature.

Synthesis of $[\text{Li}(\text{DME})_2][3,3'\text{-Co}(1\text{-PPh}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ ([Li(DME)₂][2]**).** Under inert atmosphere, *n*-butyllithium (3.4 mL, 5.48 mmol) (1.6 M in hexanes) was added dropwise to a stirred solution of $\text{Cs}[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ (1.25 g, 2.74 mmol) in 120 mL of anhydrous 1,2-dimethoxyethane at -40°C . The resulting purple solution was stirred for 30 min at low temperature. Then chlorodiphenylphosphine (1.0 mL, 5.48 mmol) was added causing a rapid color change to red and precipitation of a red solid. After stirring the mixture for an hour at room temperature, the solid was collected by filtration and washed with water and petroleum ether and, finally, was dried in vacuo. Yield: 2.3 g (96%). Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{B}_{18}\text{CoLiO}_4\text{P}_2$: C: 49.18, H: 6.88 %. Found: C: 48.95, H: 7.00 %. IR: ν (cm^{-1}) = 3049 ($\text{C}_c\text{-H}$), 2927, 2898 ($\text{C}_{\text{aryl}}\text{-H}$), 2548 (B-H), 1433, 1084, 746, 698, 499. ^1H NMR: δ = 7.76, 7.54, 7.46, 7.31 (m, 20H, *Ph*), 4.37 (br s, 2H, $\text{C}_c\text{-H}$), 3.46 (s, 8H, $\text{CH}_2(\text{DME})$), 3.28 (s, 12H, $\text{CH}_3(\text{DME})$), 4.14-1.25 (br m, 18H, B-H). $^1\text{H}\{^1\text{B}\}$ NMR: δ = 7.76, 7.54, 7.46, 7.31 (m, 20H, *Ph*), 4.37 (br s, 2H, $\text{C}_c\text{-H}$), 3.46 (s, 8H, $\text{CH}_2(\text{DME})$), 3.28 (s, 12H, $\text{CH}_3(\text{DME})$), 4.14 (br s, 2H, B-H), 3.21 (br s, 2H, B-H), 2.89 (br s, 4H, B-H), 2.21 (br s, 2H, B-H), 1.92 (br s, 4H, B-H), 1.47 (br s, 2H, B-H), 1.25 (br s, 2H, B-H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 139.05 (d, $^1\text{J}(\text{P,C})$ = 22 Hz, P-C(Ph)), 137.05 (d, $^1\text{J}(\text{P,C})$ = 17 Hz, P-C(Ph)), 135.23 (d, $^2\text{J}(\text{P,C})$ = 29 Hz, *o*-C(Ph)), 134.27 (d, $^2\text{J}(\text{P,C})$ = 26 Hz, *o*-C(Ph)), 129.54 (s, *p*-C(Ph)), 128.51 (s, *p*-C(Ph)), 128.18 (d, $^3\text{J}(\text{P,C})$ = 8 Hz, *m*-C(Ph)), 127.31 (d, $^3\text{J}(\text{P,C})$ = 8 Hz, *m*-C(Ph)), 71.64 (s, $\text{CH}_2(\text{DME})$), 61.41 (d, $^1\text{J}(\text{P,C})$ = 81 Hz, P-C), 60.22 (dd, $^2\text{J}(\text{P,C})$ = 47 Hz, $^3\text{J}(\text{P,C})$ = 14 Hz, $\text{C}_c\text{-H}$), 57.50 (s, $\text{CH}_3(\text{DME})$). ^{11}B NMR: δ = 9.1 (d, $^1\text{J}(\text{B,H})$ = 127 Hz, 2B), 2.3 (d, $^1\text{J}(\text{B,H})$ = 137 Hz, 2B), -3.3 (d, $^1\text{J}(\text{B,H})$ = 106 Hz, 4B), -4.2 (d, $^1\text{J}(\text{B,H})$ = 98 Hz, 4B), -13.7 (d, $^1\text{J}(\text{B,H})$ = 183 Hz, 2B) -15.9 (d, $^1\text{J}(\text{B,H})$ = 163 Hz, 2B), -20.0 (d, $^1\text{J}(\text{B,H})$ = 137 Hz, 2B). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 23.48 (s, C_c-PPh₂). MALDI-TOF-MS: (m/z) = 691.43 (M, 9%), 507.33 (M-PPh₂, 73%) i 323.32 (M-2PPh₂, 100%).

Synthesis of $[\text{Ag}\{3,3'\text{-Co}(1\text{-PPh}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\}(\text{PPh}_3)]\cdot\text{OCMe}_2$ (3**).** To a suspension of $[\text{NMe}_4][3,3'\text{-Co}(1\text{-PPh}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ (0.06 g, 0.08 mmol) in EtOH (10 mL) $[\text{AgClPPh}_3]$ (0.034 g, 0.08 mmol) was added. The suspension was refluxed 30 min. Then the resulting maroon solid was filtered off and washed with ethanol and water. Yield: 59 mg (71 %). Anal. Calcd for $\text{C}_{49}\text{H}_{61}\text{AgB}_{18}\text{CoOP}_3$: C: 52.53, H: 5.49 %. Found: C: 52.79, H: 5.34 %. IR: ν (cm^{-1}) = 3058 ($\text{C}_c\text{-H}$), 2557 (B-H), 1359 (C-O), 1436, 1096, 743, 691, 502. ^1H NMR: δ = 8.30, 7.35, 6.37 (m, 35H, *Ph*), 4.83 (br s, 2H, $\text{C}_c\text{-H}$), 2.09 (s, 6H, CH_3), 4.41-0.88 (br m, 18H, B-H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 205.12 (s, CO), 137.55 (s, *Ph*), 135.82 (s, *Ph*), 133.69 (d, $\text{J}(\text{P,C})$ = 17, *Ph*), 130.01 (s, *Ph*), 128.94 (d, $\text{J}(\text{P,C})$ = 8, *Ph*), 127.95 (s, *Ph*), 126.35 (s, *Ph*), 61.14 (s, C_c), 28.99 (s, CH_3). ^{11}B NMR: δ = 9.9 (d, $^1\text{J}(\text{B,H})$ = 105, 2B), 3.2 (d, $^1\text{J}(\text{B,H})$ = 107, 2B), -3.1 (d, $^1\text{J}(\text{B,H})$ = 110, 8B), -13.1 (d, $^1\text{J}(\text{B,H})$ = 175, 2B) -15.0 (d, $^1\text{J}(\text{B,H})$ = 145, 2B), -19.1 (d, 2B). $^{31}\text{P}\{^1\text{H}\}$ NMR (-60°C): δ = 43.50 (2d, $^1\text{J}(\text{P,C})$ = 330, $^1\text{J}(\text{P,C})$ = 286, 1P, PPh₂), 42.81 (2d, $^1\text{J}(\text{P,C})$ = 330, $^1\text{J}(\text{P,C})$ = 286, 1P, PPh₂), 32.89 (2d, $^1\text{J}(\text{P,C})$ = 392, $^1\text{J}(\text{P,C})$ = 366, 1P, PPh₃).

Synthesis of $[\text{Au}\{3,3'\text{-Co}(1\text{-PPh}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\}(\text{PPh}_3)]$ (4**).** To a solution of $\text{Cs}[3,3'\text{-Co}(1\text{-PPh}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ (0.06 g, 0.07 mmol) in EtOH (10 mL) $[\text{AuClPPh}_3]$ (0.034 g, 0.07 mmol) was

added. The complex, as a red solid, was obtained by filtration after 30 min of reflux. Yield: 89 mg (98 %). Anal. Calcd for $C_{46}H_{55}AuB_{18}CoP_3$: C: 47.99, H: 4.81 %. Found: C: 47.95, H: 4.63 %. IR: ν (cm^{-1}) = 3069 (C_c-H), 2573, 2550 (B-H), 1435, 1094, 746, 692. ¹H NMR: δ = 7.83, 7.61, 7.44, 7.36 (m, 35H, Ph), 4.42 (br s, 2H, C_c-H), 4.17-0.89 (br m, 18H, B-H). ¹H{¹B} NMR: δ = 7.83, 7.61, 7.44, 7.36 (m, 35H, Ph), 4.42 (br s, 2H, C_c-H), 4.17 (br s, 2H, B-H), 3.30 (br s, 2H, B-H), 2.81 (br s, 4H, B-H), 2.19 (br s, 2H, B-H), 1.93 (br s, 4H, B-H), 1.31 (br s, 2H, B-H), 0.89 (br s, 2H, B-H). ¹³C{¹H} NMR: δ = 135.90 (d, J(P,C) = 26, Ph), 134.79 (d, J(P,C) = 25, Ph), 134.02 (d, J(P,C) = 14, Ph), 132.07 (s, Ph), 130.16 (s, Ph), 129.48 (d, J(P,C) = 11, Ph), 128.20 (d, J(P,C) = 34, Ph), 60.77 (s, C_c-H). ¹¹B NMR: δ = 10.0 (d, ¹J(B,H) = 116, 2B), 3.0 (d, ¹J(B,H) = 152, 2B), -3.0 (d, ¹J(B,H) = 135, 4B), -5.1 (d, ¹J(B,H) = 174, 4B), -13.1 (d, ¹J(B,H) = 147, 2B) -15.4 (d, ¹J(B,H) = 144, 2B), -19.4 (d, ¹J(B,H) = 152, 2B). ³¹P{¹H} NMR (-60°C): δ = 73.61 (d, ²J(P_{PPh₂}, P_{PPh₃}) = 146, 2P, PPh₂), 45.06 (t, ²J(P_{PPh₂}, P_{PPh₃}) = 146, 1P, PPh₃).}}}}

Synthesis of [Ag{3,3'-Co(1-PPh₂-1,2-C₂B₉H₁₀)₂}(OCMe₂)] (5). To a solution of [NMe₄][3,3'-Co(1-PPh₂-1,2-C₂B₉H₁₀)₂] (0.06 g, 0.08 mmol) in EtOH/acetone (10 mL/3 mL) a solution of [AgClO₄] (0.016 g, 0.08 mmol) in acetone (1 mL) was added. The mixture was stirred at room temperature overnight. Concentration of the mixture produced the precipitation of a pink solid. This was filtered off, washed with water and petroleum ether, and dried in vacuo. Yield: 59.2 mg (88 %). Anal. Calcd for C₃₁H₄₆AgB₁₈CoOP₂: C: 43.39, H: 5.40 %. Found: C: 43.20, H: 5.31 %. IR: ν (cm^{-1}) = 3058 (C_c-H), 2563, 2509 (B-H), 1310 (C-O), 1436, 1088, 741, 687. ¹H NMR: δ = 8.21 (br s, 5H, Ph), 8.09 (br s, 5H, Ph), 7.53, 7.45 (m, 10H, Ph), 4.73 (br s, 2H, C_c-H), 2.09 (s, 6H, CH₃), 4.47-0.88 (br m, 18H, B-H). ¹³C{¹H} NMR: δ = 205.17 (s, CO), 137.23 (s, Ph), 135.38 (s, Ph), 132.46 (s, Ph), 131.81 (s, Ph), 131.24 (s, Ph), 128.83 (s, Ph), 128.06 (s, Ph), 62.26 (s, C_c-H), 28.90 (s, CH₃). ¹¹B NMR: δ = 12.7 (d, 2B), 3.8 (d, ¹J(B,H) = 132, 2B), -0.2 (d, ¹J(B,H) = 134, 2B), -4.0 (d, ¹J(B,H) = 118, 4B), -7.0 (d, 2B), -12.7 (d, 2B), -15.2 (d, 2B), -20.4 (d, ¹J(B,H) = 141, 2B). ³¹P{¹H} NMR: δ = 46.01 (2d, ¹J(¹⁰⁹Ag, P) = 463, ¹J(¹⁰⁷Ag, P) = 403, 2P, PPh₂).

Synthesis of [NMe₄][Rh{3,3'-Co(1-PPh₂-1,2-C₂B₉H₁₀)₂}] (6). Starting from [Rh(μ-Cl)(cod)]₂: [Rh(μ-Cl)(cod)]₂ (0.032 g, 0.065 mmol) was added to 10 mL of a solution of [NMe₄][2] (0.2 g, 0.26 mmol), in deoxygenated methylene chloride, and the solution was stirred at room temperature overnight. A brown solid was separated by filtering and then washed with ethanol (10 mL) and water, giving 6. Yield: 174 mg (85%). Starting from [RhCl(PPh₃)₃]: [RhCl(PPh₃)₃] (0.120 g, 0.13 mmol) was added to 10 mL of a solution of [NMe₄][2] (0.2 g, 0.26 mmol), in deoxygenated ethanol, and the mixture was refluxed for 1 h. A brown solid was separated by filtering and then washed with ethanol (10 mL) and water, giving 6. Yield: 172 mg (87%). Anal. Calcd for C₆₀H₉₂B₃₆Co₂NP₄Rh: C: 46.16, H: 5.94, N: 0.90 %. Found: C: 45.97, H: 5.72, N: 1.10 %. IR: ν (cm^{-1}) = 3059 (C_c-H), 2558 (B-H), 1481, 1435, 1080, 943, 745, 694. ¹H NMR: δ = 8.53, 8.05-7.01 (m, 40H, Ph), 4.28 (br s, 4H, C_c-H), 3.40 (s, 12H, NMe₄). ¹¹B NMR: δ = 7.5, 3.6, -2.8, -6.5, -13.6, -19.5 (36B). ³¹P{¹H} NMR: δ = 85.16 (d, ¹J(³¹P, ¹⁰³Rh) = 205, PPh₂).

Synthesis of [PdCl{3,3'-Co(1-PPh₂-1,2-C₂B₉H₁₀)₂}(PPh₃)] (7). [PdCl₂(PPh₃)₂] (0.183 g, 0.26 mmol) was added to 10 mL of a solution of [NMe₄][2] (0.2 g, 0.26 mmol), in deoxygenated ethanol, and the mixture was refluxed for 1 h. A brown solid was separated by filtering and then washed with ethanol (10 mL) and water, giving 7. Yield: 270 mg (94%). Anal. Calcd for C₄₆H₅₅B₃₆ClCoP₃Pd: C: 50.40, H: 5.06 %. Found: C: 50.76, H: 4.93 %. IR: ν (cm^{-1}) = 3060 (C_c-H), 2563 (B-H), 1435, 1099, 745, 692. ¹H NMR: δ = 8.25-7.39 (m, 35H, Ph), 4.51 (br s, 1H, C_c-H), 4.31 (br s, 1H, C_c-H). ¹¹B NMR: δ = 9.7, 5.7, -0.05, -2.1, -3.8, -13.1, -20.9 (18B). ³¹P{¹H} NMR: δ = 60.39 (dd, ²J(P_{PPh₂(trans)}, P_{PPh₃}) = 238, ²J(P_{PPh₂}, P_{PPh₂}) = 70, 1P, PPh₂}}}}

in trans to PPh₃), 54.02 (d, ²J(P_{PPh₂}, P_{PPh₂}) = 70, 1P, PPh₂ in cis to PPh₃), 30.37 (d, ²J(P_{PPh₂(trans)}, P_{PPh₃}) = 238, 1P, PPh₃).}}}}

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Supporting information available: Full crystallographic data for the structures of [NMe₄][2], 3-OCMe₂, 4 and 5 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-xxx, CCDC-yyy and CCDC-zzz, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Oxidation and Partial degradation of *closo*-carboranyldiphosphines by using hydrogen peroxide.

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Introduction

The *o*-carborane 1,2-C₂B₁₀H₁₂ is an icosahedral cluster with the two carbon atoms in adjacent positions. One way to comprehend the orbital set of *o*-carborane is to consider that each participating atom contributes with two **sp** and two **p_t** (tangential orbital on cluster carbon) orbitals. This situation is very similar to the atomic orbitals participating in the molecular orbitals of acetylene. In the same way, then, the hydrogen atom connected to the cage carbon (C_c) in *o*-carborane is acidic and may be removed by strong bases. Moreover, the *o*-carborane cluster is electron-withdrawing for the C_c substituents. During our research^{1,2,3,4,5} we have observed many structural features, as well as reactivity behaviour, that make the *o*-carboranyl fragment unique in organic chemistry. Bidentate ligands have played an important role in the development of catalytic applications of metal organic complexes since 1959.⁶ Our group has reported the synthesis of *closo* diphosphines 1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀ that incorporate the *closo* 1,2-C₂B₁₀H₁₂ cluster,^{1e} their partial degradation that produces the anionic diphosphine *nido* [7,8-(PR₂)₂-7,8-C₂B₉H₁₀]⁻ ligands^{1e} and the coordinating capability towards metals of both *closo* 1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀ and *nido* [7,8-(PR₂)₂-7,8-C₂B₉H₁₀]⁻ ligands.⁷

Additionally, diphosphine ligands or their chelating Au(I) complexes are active in several tumoral models in mice.⁸ Oxidation and protonation reactions are of particular importance in understanding the anticancer activity of diphosphines.⁹

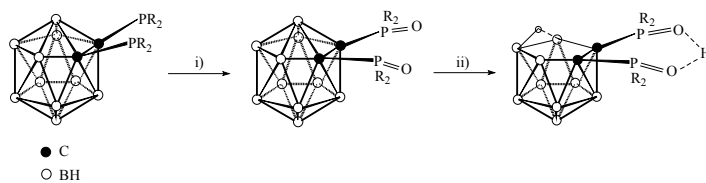
Despite the well-known affinity of trivalent phosphorous for oxygen and the frustrating destruction of metal catalysts via oxidation of phosphorus-containing ligands, there is a lack of kinetic data and mechanistic studies done on this reaction. In this paper, we report the forced oxidation reaction of *closo* 1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀ (R = Ph, **1**; ⁱPr, **2**) compounds to *closo* 1,2-(OPR₂)₂-1,2-C₂B₁₀H₁₀ and the partial degradation process of these ligands to the anionic *nido* [7,8-(OPR₂)₂-7,8-C₂B₉H₁₀]⁻ ones. The reactions have been monitoring by ³¹P-NMR and ¹¹B-NMR spectroscopies. The sequence of the reactions has been proven by the crystal resolution of the *nido* [7,8-(OPⁱPr₂)₂-7,8-C₂B₉H₁₀]⁻ ligand as well as this for an intermediate. The phosphine oxide formation rate constant for compound **1** has also been calculated.

Results and discussion

I. Forced Oxidation of *closo*-carboranyldiphosphines, 1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀. Synthesis and characterization of *closo*-1,2-(OPR₂)₂-1,2-C₂B₁₀H₁₀.

We had observed that, in contrast to other common phosphines, the *closo*-monophosphinocarborane 1-PR₂-2-R'-C₂B₁₀H₁₀ (R' = H, Me, Ph; R = Ph, Et, ⁱPr) derivatives present a

high stability both in solid state and in solution, even under air, in the presence of mild oxidizing agents, alcohols and some acids.^{1a} The behaviour of the *closo*-diphosphinocarboranes towards partial degradation,^{1c} their high chemical stability both in solution and solid state and the difficulty to coordinate to metal^{7b-c} seems to evidence the notable influence of the cluster *closo* on the P atoms. So, *closo*-carboranyldiphosphines have been forced to be oxidized to their corresponding *closo*-carboranyldiphosphine oxides by using hydrogen peroxide in acetone¹⁰ (Scheme 1, i). In the oxidized species, the phosphorus oxidation state has changed from P(III) to P(V).



Scheme 1. Reaction of 1,2-(PPH₂)₂-1,2-C₂B₁₀H₁₀ with H₂O₂ in acetone. i) Phosphines oxidation. ii) *Closo* cluster partial degradation and zwitterion formation. R = Ph, ⁱPr.

The *closo* 1,2-(OPR₂)₂-1,2-C₂B₁₀H₁₀ (R = Ph, **3**; R = ⁱPr, **4**) diphosphine dioxide species have been synthesized and characterized by IR, ¹H-, ¹³C-, ³¹P- and ¹¹B-NMR spectroscopies. Only one singlet resonance at lower field than the corresponding diphosphine one in the starting (see Table 1) was observed in the ³¹P-NMR spectra for **3** and **4**.

Table 1. ³¹P{¹H}-NMR chemical shifts (ppm) for the carboranyldiphosphines.

1,2-(PPH ₂) ₂ -1,2-C ₂ B ₁₀ H ₁₀	8.22 ¹¹
1,2-(OPPh ₂) ₂ -1,2-C ₂ B ₁₀ H ₁₀	23.67
1,2-(P ⁱ Pr ₂) ₂ -1,2-C ₂ B ₁₀ H ₁₀	32.79 ^{1e}
1,2-(OP ⁱ Pr ₂) ₂ -1,2-C ₂ B ₁₀ H ₁₀	59.08
[NMe ₄][7,8-(PPH ₂) ₂ -7,8-C ₂ B ₉ H ₁₀] ⁻	7.13 ^{1e}
[NMe ₄][7,8-(OPPh ₂) ₂ -7,8-C ₂ B ₉ H ₁₀] ⁻	29.33
H[7,8-(OPPh ₂) ₂ -7,8-C ₂ B ₉ H ₁₀] ⁻	47.09
H[7,8-(P ⁱ Pr ₂) ₂ -7,8-C ₂ B ₉ H ₁₀] ⁻	31.04
H[7,8-(OP ⁱ Pr ₂) ₂ -7,8-C ₂ B ₉ H ₁₀] ⁻	77.31

The ν(B-H) in the IR spectrum at 2555 cm⁻¹ for **3** and at 2644, 2622, 2596, 2575, 2550 cm⁻¹ for **4** are in agreement with a *closo* structure for the cluster fragment. The vibration at 1214 cm⁻¹ for **3** and at 1192 cm⁻¹ for **4** confirm the presence of P=O group in

the molecules. The ^{11}B -NMR spectra for compounds **3** and **4**, with a 2:2:6 pattern in the range +2.8 / -9.1 ppm, fully supports a *closo* structure. Just minor differences with regard to the *closo* 1,2-(PR_2)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ precursors (see Figure 1) have been observed in the ^{11}B -NMR spectra of the new diphosphine dioxides 1,2-(OPR_2)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$. It is worth noticing, though, that the resonance corresponding to the antipodal boron atoms (B9 and B12) in **3** and **4** has been shifted to lower field with regard to the non oxidized starting ones. The ^1H -NMR spectrum of **3** shows two different multiplet resonances at 7.52 and 8.03 ppm which indicate two phenyl rings in each - PPh_2 group. The two doublets of doublets in the ^1H -NMR spectrum of **4** evidence two non-equivalent methyl groups in each isopropyl unit. The coupling between ^{31}P and ^{13}C nuclei is clearly observed in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **4**. This shows two different resonances at 17.4 and 18.4 ppm, in agreement with two different methyl groups in each isopropyl unit. The -CH resonance appears as a doublet ($^1\text{J}(\text{P},\text{C})=61$ Hz) at 30.5 ppm and the doublet ($^1\text{J}(\text{P},\text{C})=19$ Hz) at 81.6 ppm corresponds to the carbon cluster atoms (C_c).

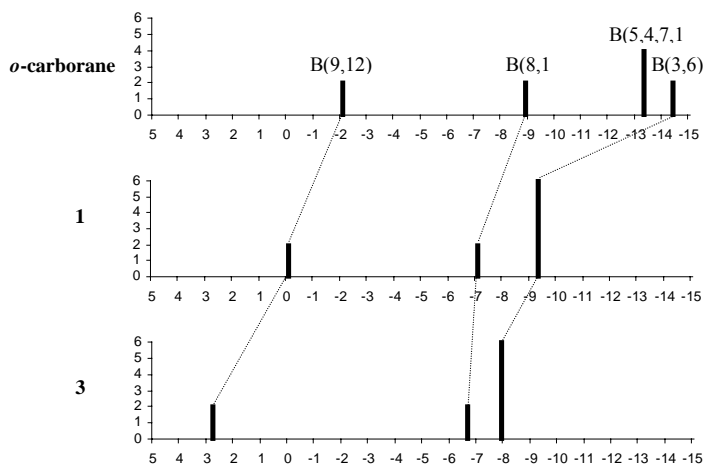


Figure 1. Stick representation of the chemical shifts and relative intensities in the $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of compounds *closo* 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ (*o*-carborane); *closo* 1,2-(PPh_2)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (**1**) and *closo* 1,2-(OPPh_2)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (**3**). Lines join equivalent positions in the three compounds.

II. Partial cluster degradation of the *closo*-carboranyldiphosphine dioxides, 1,2-(OPR_2)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$. Synthesis and characterization of *nido* [7,8-(OPR_2)₂-7,8- $\text{C}_2\text{B}_9\text{H}_{10}$] ligands.

Partial degradation of *closo*-diphosphinocarboranes using the well established procedure¹² with alkoxyde did not produce the expected new *nido* species, instead it yielded 7,8-dicarba-*nido*-undecaborate(1-) by C-P bond cleavage. On the other hand, the reaction carried out in refluxing ethanol in the absence of alkoxyde yielded the *closo*-diphosphinocarboranes unaltered, as it was also the case with piperidine-toluene¹³ in 1:4 ratio of *closo*-diphosphinocarboranes to piperidine at 20 °C. Boron removal to yield the *nido* species while preserving the C_c -P bond was successfully obtained in a 99% yield by reaction of 1,2-(PR_2)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ with piperidine in ethanol in a ratio 1:10.¹⁶

We later demonstrated that proton can induce partial degradation, thence conversion of the *closo*- C_2B_{10} to the *nido*- C_2B_9 species given the necessary chemical and geometrical arrangements to produce proton chelation.¹⁴ For this purpose, an *o*-carborane adequately C-disubstituted with H^+ scavenger elements, such as oxygen was used. The *closo* 1,2-(OPR_2)₂-1,2-

$\text{C}_2\text{B}_{10}\text{H}_{10}$ species (**3**, **4**) did fulfill these requirements as are chelating agents and contain oxygen atoms. Hydrogen peroxide which has recently¹⁵ been used to produce *closo*- $[\text{B}_{12}(\text{OH})_{12}]^{2-}$ was a suitable oxidizing agent, and a source of H^+ . Thus it was expected that upon oxidation of the phosphorus atoms, and the availability of protons, the *closo* cluster would progress to the anionic *nido* cluster $[\text{7,8-(OPR}_2)_2\text{-7,8-}\text{C}_2\text{B}_9\text{H}_{10}]^-$ (R= Ph, [**5**], R= ^iPr , [**6**]) liberating one boron atom and overall producing a neutral species. Indeed this is what happened. The reaction is schematically represented in Scheme 1 ii).

The *nido* nature of the cluster was clearly demonstrated in the ^1H -NMR by the apical proton resonance at δ -2.05 and -2.56 ppm for compounds H[**5**] and H[**6**] respectively, and by the ^{11}B -NMR, 2:2:1:2:1:1 pattern (low field to high field) observed in the range δ -5.6/-33.9 typical for *nido*- C_2B_9 derivatives.¹⁶ The resonances were separated enough to permit their unambiguous assignment by means of $^{11}\text{B}\{^1\text{H}\}$ - $^{11}\text{B}\{^1\text{H}\}$ COSY (see Figure 2). The peak at -29.1 ppm is easily assigned to B(10) since it appears as a doublet of doublets in the ^{11}B -NMR spectrum due to coupling with the H bridge as well as the *exo*-H. The peak at -31.8 ppm, which is at highest field, corresponds to B(1), the antipodal position to the open face. The spectrum also exhibits a singlet at -14.0 ppm that do not show any cross peak and correspond to B(3) which is adjacent to both cluster carbon atoms.¹⁷ With the resonances due to B(1), B(3) and B(10) thus established, analysis of the cross peaks easily allowed the assignment of the 2:2:1:2:1:1 pattern to B(9,11): B(5,6): B(3): B(2,4): B(10): B(1), respectively.

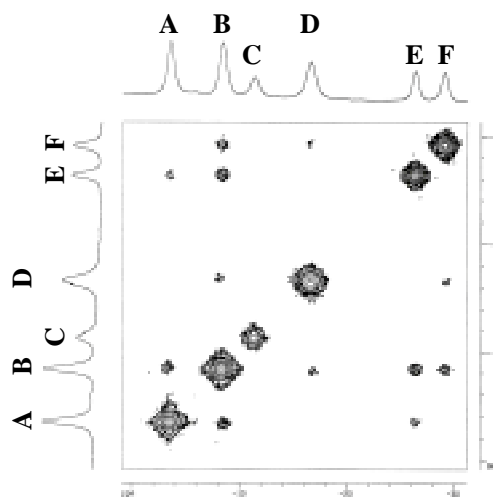


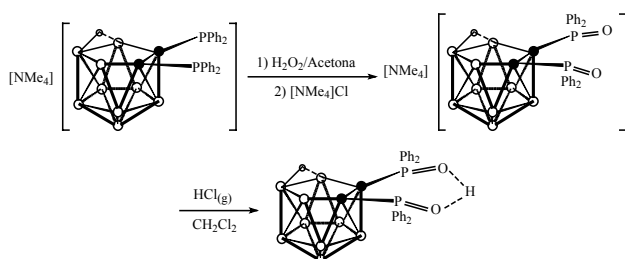
Figure 2. The $^{11}\text{B}\{^1\text{H}\}$ - $^{11}\text{B}\{^1\text{H}\}$ 2D-COSY NMR spectrum of H[**6**]. The resonance marked **A** corresponds to B(9, 11), **B** to B(5, 6), **C** to B(3), **D** to B(2, 4), **E** to B(10), **F** to B(1).

Although the negative charge of the *nido* cluster is maintained in the oxidized species, the phosphorus oxidation state has changed from P(III) to P(V). This is clearly reflected on the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra (Table 1) in which the chemical shifts for the oxidized species have shifted to lower field as much as 46 ppm.

The $\nu(\text{B-H})$ in the IR spectra at 2605, 2584, 2526 cm^{-1} for H[**5**] and at 2629-2608 cm^{-1} for H[**6**] are in agreement with a *nido* structure of the *o*-carboranyl fragment and the vibration at 1184 and 1081 cm^{-1} respectively confirm the presence of P=O groups.

To ensure that H_2O_2 was the sole agent causing the *closo* to *nido* conversion, an alternative sequential process was developed, which is indicated in Scheme 2. Oxidation of $[\text{NMe}_4][\text{7,8-}$

(PPh₂)₂-7,8-C₂B₉H₁₀], ([NMe₄][7]),¹⁴ with H₂O₂ was performed in acetone at 0°C to yield after stirring for 4 h a white solid that corresponds to [NMe₄][7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀], [NMe₄][8].



Scheme 2. Synthesis of H[7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀] starting from [NMe₄][7,8-(PPh₂)₂-7,8-C₂B₉H₁₀].

III. Identification of the removed Boron vertex.

The partial degradation of **1** with hydrogen peroxide in THF and at room temperature for 24 hours was carried out to identify the nature of the removed B⁺ containing species. The H[5] species was isolated by filtration. The ¹¹B{¹H} spectrum of the remaining aqueous solution shows a resonance at +19.3 ppm corresponding to a boron atom with no B-H bond. According to the literature, the chemical shift for B(OH)₃ appears at +19.3 ppm,¹⁸ confirming that the removed B⁺ stays in solution as B(OH)₃.

IV. Forced protonation of the *nido*-carboranyldiphosphine dioxides.

As it is well known, phosphines react with perchloric acid in ethanol to give the corresponding phosphonium salts.¹⁹ Acidification of [NMe₄][8] in CH₂Cl₂ with HCl gas produces a white solid corresponding to [NMe₄]Cl. Subsequent evaporation of the CH₂Cl₂ yields a H[5].

The ν(O-H) in the IR spectra at 3082 and 3059 cm⁻¹ confirmed the formation of the protonated zwitterionic species. This IR data could not be further supported by the observation of a resonance attributed to the chelated proton neither in the ¹H-NMR spectra of H[5] nor H[6]. To get a precise structure determination, crystals were grown from an acetone solution of H[6] after slow evaporation.

V. Molecular and crystal structure of H[6]

Good quality crystals for X-Ray diffraction studies were grown by slow evaporation of compound H[5] in EtOH solutions and by slow evaporation of H[6] in acetone (Figure 3).

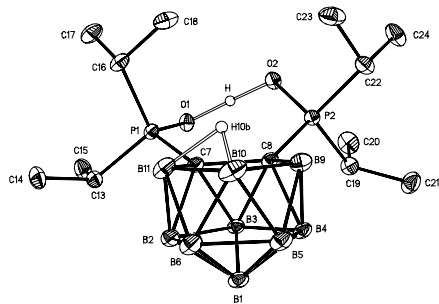


Figure 3. Perspective drawings of H[7,8-(OPⁱPr)₂-7,8-C₂B₉H₁₀] grown from compound **6** in acetone.

VI. Mechanistic considerations

The reaction of *closo*-carboranyldiphosphines 1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀ (R= Ph and ⁱPr) with H₂O₂ implies two processes: the partial degradation of the *closo* cluster and the oxidation of the phosphorus atoms. The progress of the reaction has been studied as a function of time to determine which process takes place first. In this sense, the progress of the reaction of both *closo* species **1** and **2** with H₂O₂ was monitored by ³¹P{¹H} (see Figure 4 for **1** and Figure 5 for **2**) and ¹¹B{¹H}-NMR (see Figure 6 for **1**) spectroscopies. The study provides useful information about the structure of the compounds in solution. The resonance at 8.22 ppm in the ³¹P{¹H}-NMR spectrum that corresponds to non-altered **1** decreases with time while a new peak at 23.67 ppm increases (See Figure 4). In four hours there is no starting compound left while only the peak at 23.67 ppm is observed. The latter resonance also decreases with time while a new one at 47.09 ppm emerges. This final resonance persists indefinitely. The ¹¹B{¹H}-NMR spectra also shows the process of conversion of the starting *closo* material into a *nido* species (See Figure 6) but is not as informative as the ³¹P{¹H}-NMR. The peak at 47.09 ppm in the ³¹P{¹H}-NMR spectrum corresponds to the end species H[7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀]. Definitive proof of the proton containing P-O-H-O-P moiety has been confirmed by X-ray diffraction.

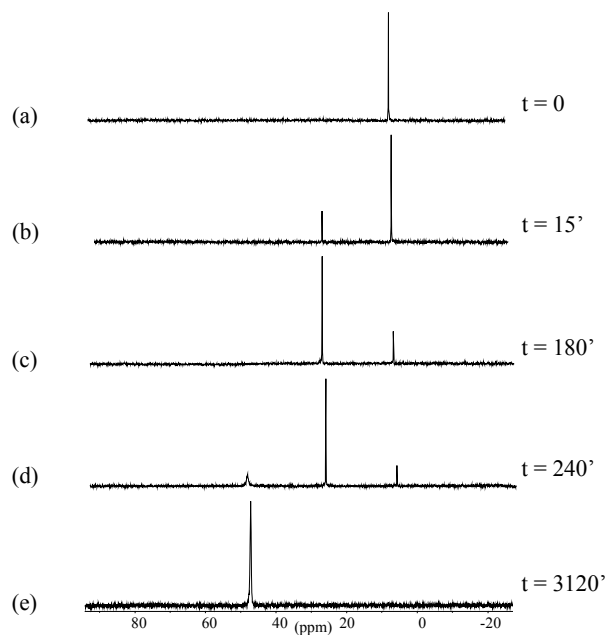


Figure 4. ³¹P{¹H} spectra of the *closo* 1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀ showing its conversion to *nido* H[7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀] after *closo* 1,2-(OPPh₂)₂-1,2-C₂B₁₀H₁₀ formation.

If the reaction is quenched when the peak at 23.67 ppm in the ³¹P{¹H}-NMR is the dominant one important information about the nature of the intermediate species is obtained. The ¹¹B{¹H}-NMR spectrum indicates that the cluster is *closo*, which is also supported by the lack of hydrogen bridge in the ¹¹H{¹B}-NMR spectrum. The elemental analysis is in agreement with a *closo* species with two P(O) units. All these data demonstrate that the first step of the reaction is the phosphorus oxidation with cluster preservation and the second one is cluster decapitation at it is shown in Scheme 1.

This mechanistic study allows accurate determination of the time to complete the two steps of the reaction: phosphorus

oxidation and cluster partial degradation. In the case of 1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀ 4 hours are necessary to accomplish the formation of both P-O bonds while the cluster partial degradation of 1,2-(OPPh₂)₂-1,2-C₂B₁₀H₁₀ into H[7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀] is essentially done after 52 hours. It is then clear that the slow step of the total process is the cluster partial degradation.

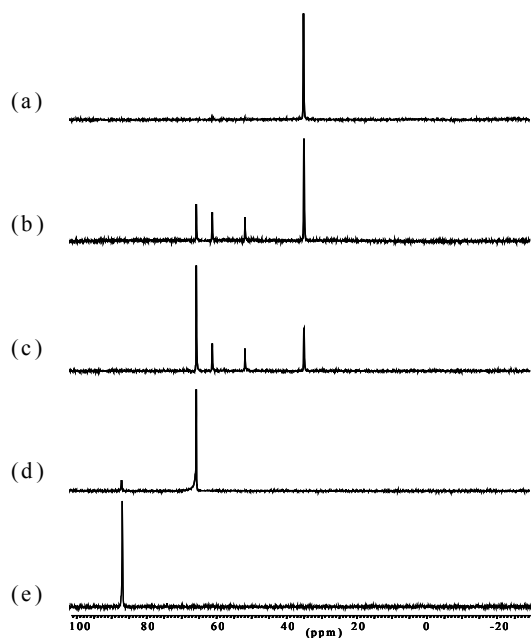


Figure 5. ³¹P{¹H} spectra of the *closo* 1,2-(PⁱPr₂)₂-1,2-C₂B₁₀H₁₀ showing its conversion to *nido* H[7,8-(OPⁱPr₂)₂-7,8-C₂B₉H₁₀] after *closo* 1,2-(OPⁱPr₂)₂-1,2-C₂B₁₀H₁₀ formation.

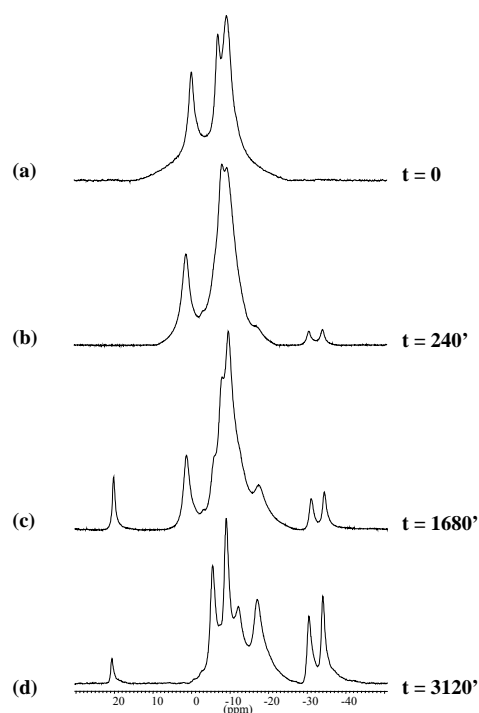


Figure 6. ¹¹B{¹H} spectra of the *closo* 1,2-(OPPh₂)₂-1,2-C₂B₁₀H₁₀ showing its partial degradation to *nido* H[7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀].

When the H₂O₂ reaction study was done on 1,2-(PⁱPr₂)₂-1,2-C₂B₁₀H₁₀, resonances at 33.27, 47.20, 55.08, 59.08, 65.48 and 77.31 ppm were observed in the ³¹P{¹H}-NMR spectra. There were three additional resonances on top of the awaited ones. The resonance at 33.27 corresponds to the starting *closo* compound **2**, the one at 59.08 corresponds to the *closo* compound **4** and the one at 77.31 to the *nido* compound **6**. Therefore it seems that the extra resonances at 47.20, 55.08 and 65.48 ppm, might be attributed to other intermediate species. One interpretation is that the two phosphorus atoms are not oxidized at the same time and a *closo* species containing a P(III) atom and P(V) is obtained which would possibly account for the resonances at 55.08 and 47.20 ppm. The additional resonance could correspond to the equivalent phosphorus in the H⁺ bonded P-O-H-O-P *closo* species, just the previous step to B⁺ removal and zwitterions. The crystal structure shown in Figure 7 fully supports this theory.

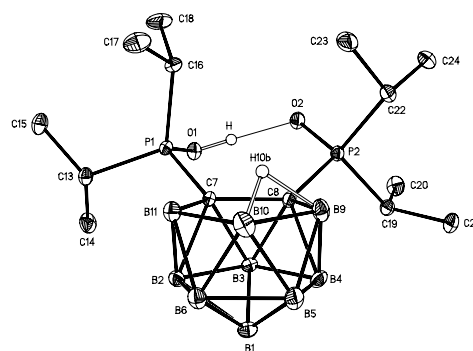


Figure 7. Perspective drawings of H[7,8-(OPⁱPr₂)₂-7,8-C₂B₉H₁₀] grown in OCMe₂.

The mechanistic study shows that **2** is fully oxidized to compound **4** after 15 minutes. So, *closo* 1,2-(PⁱPr₂)₂-1,2-C₂B₁₀H₁₀ is more susceptible to oxidation than *closo* 1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀ which is foreseeable considering the greater donating character of the isopropyl group.

VII. Kinetics of formation of 1,2-(OPPh₂)₂-1,2-C₂B₁₀H₁₀

The P(III) to P(V) oxidation reaction study on both *closo* specie **1** and **2** by using H₂O₂ in acetone or tetrahydrofuran at 23°C was monitored by ³¹P{¹H} (see Figure 4 for **1** and Figure 5 for **2**) and ¹¹B{¹H}-NMR (see Figure 6 for **1**) spectroscopies. The reaction was found to be first-order rate constant with respect to concentration of 1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀. The calculated rate constant is (1.23 ± 0.09) × 10⁻⁴ s⁻¹ (Figure 8, 9).

Conclusions

The carborane influence into the directly connected phosphorus atom is not only perceived in the chemical shift but also in the chemical properties. The electron-acceptor character of the cluster induces a lower charge density in the phosphorus atom which causes the P resonance to be shifted at lower field in the ³¹P-NMR spectra. In addition, it makes the ligand to have a lower coordinating capacity towards transition metals and a higher stability in solid state and in solution, even under air. An influence of the R group in *closo* 1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀ compounds has also been recognized. In this sense, an electron donating group (ⁱPr) facilitates the oxidation reaction more than an electron withdrawing group (Ph).

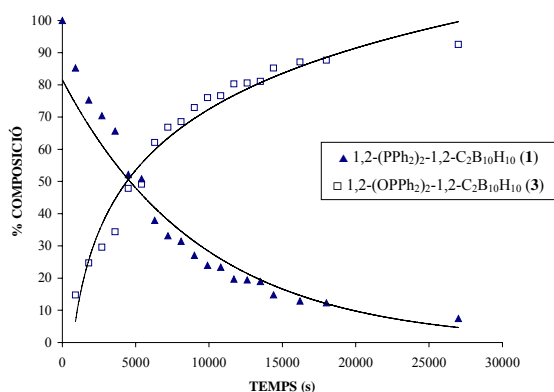


Figure 8. Plot of material balance vs. time for the reaction between *closo* 1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀ and *closo* 1,2-(OPPh₂)₂-1,2-C₂B₁₀H₁₀.

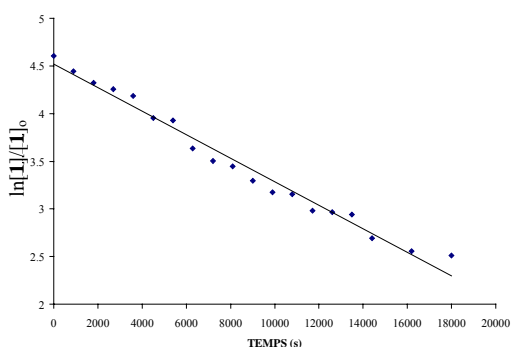


Figure 9. First-order kinetic plot for the reaction between *closo* 1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀ and *closo* 1,2-(OPPh₂)₂-1,2-C₂B₁₀H₁₀.

Experimental Section

Instrumentation. Elemental analyses were performed in our laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra (ν , cm⁻¹; KBr pellets) were obtained on a Shimadzu FTIR-8300 spectrophotometer. The ¹H- and ¹H{¹¹B}-NMR (300.13 MHz), ¹³C{¹H}-NMR (75.47 MHz), ¹¹B-NMR (96.29 MHz) and ³¹P{¹H}-NMR (121.48 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in deuterated solvents at 22 °C. The ¹¹B-NMR shifts were referenced to external BF₃·OEt₂, while the ¹H, ¹H{¹¹B}, and ¹³C{¹H}-NMR shifts were referenced to SiMe₄ and the ³¹P{¹H}-NMR to external 85% H₃PO₄. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz.

Materials. All manipulations were carried out under atmosphere. THF was distilled from sodium benzophenone prior to use. EtOH was dried over molecular sieves and deoxygenated prior to use. Reagents were obtained commercially and used as purchased. 1,2-Bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane²⁰ and 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane^{1e} were prepared from *o*-carborane according to the literature.

Synthesis of 1,2-(OPPh₂)₂-1,2-C₂B₁₀H₁₀ (3). To a round bottom flask (25 mL) containing 1,2-bis(difenilfosfino)-1,2-dicarba-*closo*-dodecaborà (50 mg, 0.10 mmol) was added

tetrahydrofuran (5 mL). The mixture was cooled (ice-water) during the dropwise addition of a 0.2 M solution of H₂O₂ (1.5 mL, 0.40 mmol). After stirring for 3h and 25 min at room temperature the solvent was removed. The evaporation of the solvent yield a white solid. Yield: 48 mg (98 %). Anal. Calcd for C₂₆H₃₀B₁₀O₂P₂: C: 57.34, H: 5.55 %. Found: C: 57.12, H: 5.80 %. FTIR: 3048, 2962 (C_{aryl}-H), 2555 (B-H), 1214, 1191 (P=O). ¹H NMR (CDCl₃) δ : 8.03 (m, 10H, Ph), 7.52 (m, 10H, Ph), 2.68-2.09 (br m, 10H, B-H). ¹H{¹¹B} NMR (CDCl₃) δ : 8.03 (m, 10H, Ph), 7.52 (m, 10H, Ph), 2.68 (br s, 2H, B-H), 2.49 (br s, 1H, B-H), 2.35 (br s, 2H, B-H), 2.30 (br s, 3H, B-H), 2.09 (br s, 2H, B-H). ¹³C{¹H} NMR (CDCl₃) δ : 132.58 (d, ²J(C,P)= 8, Ph), 132.27, 130.80, 129.33 (s, Ph), 128.25 (d, ²J(C,P)= 14, Ph). ¹¹B-NMR (CDCl₃) δ : 2.8 (d, ¹J(B,H)= 88, 2B), -6.7 (4B), -7.9 (4B). ³¹P{¹H}-NMR (CDCl₃) δ : 23.67 (s, OPPh₂).

Synthesis of 1,2-(OPⁱPr₂)₂-1,2-C₂B₁₀H₁₀ (4). To a round bottom flask (25 mL) containing 1,2-bis(diisopropilfosfino)-1,2-dicarba-*closo*-dodecaborà (50 mg, 0.13 mmol) was added tetrahydrofuran (5 mL). The mixture was cooled (ice-water) during the dropwise addition of a 0.2 M solution of H₂O₂ (2.0 mL, 0.40 mmol). After stirring for 40 min at room temperature the solvent was removed. The evaporation of the solvent yield a white solid. Yield: 54 mg (99 %). Anal. Calcd for C₁₄H₃₈B₁₀O₂P₂: C: 41.16, H: 9.38 %. Found: C: 41.04, H: 9.25 %. FTIR: 2996, 2970, 2933, 2878 (C-H_{alkyl}), 2644, 2622, 2596, 2575, 2550 (B-H), 1192 (P=O). ¹H NMR (CDCl₃) δ : 3.10 (br s), 2.02 (m, 4H, CH), 1.41 (dd, ³J(P,H)= 11, ³J(H,H)= 7, 12H, Me), 1.35 (dd, ³J(P,H)= 13, ³J(H,H)= 7, 12H, Me). ¹³C{¹H} NMR (CDCl₃) δ : 81.61 (d, ¹J(C,P)= 19, C_c), 30.53 (d, ¹J(C,P)= 61, CH), 17.4 (s, Me), 18.4 (s, Me). ¹¹B NMR (CDCl₃) δ : 2.8 (d, ¹J(B,H)= 140, 2B, B(9,12)), -6.5 (d, ¹J(B,H)= 211, 2B, B(8,10)), -9.1 (d, ¹J(B,H)= 138, 6B, B(3,4,5,6,7,11)). ³¹P NMR (CDCl₃) δ : 59.08 (d, ³J(P,H)= 16, OPⁱPr₂).

Synthesis of H[7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀] (5). Procedure a: A solution of [NMe₄][7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀] (1.0 g, 1.64 mmol) in CH₂Cl₂ (50 mL) was bubbled with a HCl stream for 15 min. A precipitate of [NMe₄]Cl was separated, and the solution was evaporated in vacuo. A white solid was obtained. Yield: 0.86 g (98 %). **Procedure b:** To a solution of [1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀] (0.1 g, 0.20 mmol) in THF at 0°C was added 5.56 mL (0.56 mmol) of a solution of 0.1 M H₂O₂. The mixture was stirred for 24 hours, and a precipitate was formed. The solid was filtered off, washed with water, and dried in vacuo. Yield: 0.10 g (94 %). Anal. Calcd for C₂₆H₃₁B₉O₂P₂: C: 58.40, H: 5.84 %. Found: C: 58.22, H: 5.78 %. FTIR: 3082, 3059 (O-H), 3016, 2961, 2918 (C-H_{aryl}), 2605, 2584, 2526 (B-H), 1184 (P=O). ¹H NMR (CDCl₃) δ : 7.91 (m, 5H, Ph), 7.51 (m, 5H, Ph), 7.38 (m, 5H, Ph), 7.20 (m, 5H, Ph), 3.10-0.74 (br s, 9H, B-H), -2.05 (br s, 1H, BHB). ¹H{¹¹B} NMR (CDCl₃) δ : 7.91 (m, 5H, Ph), 7.51 (m, 5H, Ph), 7.38 (m, 5H, Ph), 7.20 (m, 5H, Ph), 3.10 (br s, 1H, B-H), 2.65 (br s, 1H, B-H), 1.84 (br s, 3H, B-H), 1.07 (br s, 3H, B-H), 0.74 (br s, 1H, B-H), -2.10 (br s, 1H, BHB). ¹³C{¹H} NMR (CDCl₃) δ : 133.95, 133.82 (s, Ph), 133.05 (d, ¹J(P,C)= 21, Ph), 129.18 (d, ²J(P,C)= 41, Ph). ¹¹B NMR (CDCl₃) δ : -5.6 (d, ¹J(B,H)= 128, 2B), -8.9 (d, ¹J(B,H)= 133, 2B), -12.1 (1B), -17.0 (2B), -30.4 (d, ¹J(B,H)= 123, 1B), -33.9 (d, ¹J(B,H)= 147, 1B). ³¹P{¹H} NMR (CDCl₃) δ : 47.09 (s, OPPh₂).

Synthesis of H[7,8-(OPⁱPr₂)₂-7,8-C₂B₉H₁₀] (6). To a solution of 1,2-bis(diisopropilfosfino)-1,2-dicarba-*closo*-dodecaborà (50 mg, 0.13 mmol) in THF at 0°C was added 2.0 mL (0.40 mmol) of a solution of 0.2 M H₂O₂. The mixture was stirred during a weekend. Acetone (8mL) was added to the white solid and 2.4 mL (0.96 mmol) of a solution of 0.4 M H₂O₂ were added at room temperature. The solution was stirred for another weekend. Then this was concentrated until a white solid precipitated. The solid was filtered off and dried in vacuo. Yield: 38 mg (71 %). Anal. Calcd for C₁₄H₃₉B₉O₂P₂: C: 42.17, H: 9.86 %. Found: C: 41.82, H: 10.04 %. FTIR: 2995, 2973, 2936, 2877 (O-H, C-

H_{alkyl}), 2629, 2596, 2587, 2581, 2543, 2552, 2536, 2526, 2608 (B-H), 1081 (P=O). ¹H NMR (CD₃COCD₃) δ: 2.82 (m, 2H, CH), 2.59 (m, 2H, CH), 1.47 (dd, ³J(P,H)= 11, ³J(H,H)= 7, 6H, Me), 1.42 (dd, ³J(P,H)= 11, ³J(H,H)= 7, 6H, Me), 1.37 (dd, ³J(P,H)= 17, ³J(H,H)= 7, 6H, Me), 1.31 (dd, ³J(P,H)= 15, ³J(H,H)= 7, 6H, Me), 2.49-0.68 (br s, 9H, B-H), -2.56 (br s, 1H, BHB). ¹H{¹¹B} NMR (CD₃COCD₃) δ: 2.82 (m, 2H, CH), 2.59 (m, 2H, CH), 2.49 (br s, 1H, B-H), 2.42 (br s, 1H, B-H), 1.77 (br s, 2H, B-H), 1.61 (br s, 3H, B-H), 1.47 (dd, ³J(P,H)= 11, ³J(H,H)= 7, 6H, Me), 1.42 (dd, ³J(P,H)= 11, ³J(H,H)= 7, 6H, Me), 1.37 (dd, ³J(P,H)= 17, ³J(H,H)= 7, 6H, Me), 1.31 (dd, ³J(P,H)= 15, ³J(H,H)= 7, 6H, Me), 0.68 (br s, 2H, B-H), -2.56 (br s, 1H, BHB). ¹³C{¹H} NMR (CD₃COCD₃) δ: 16.78, 16.71, 16.67, 16.31, 16.21 (s, CH, Me). ¹¹B NMR (CD₃COCD₃) δ: -6.2 (d, ¹J(B,H)= 138, 2B, B(9,11)), -11.1 (d, ¹J(B,H)= 142, 2B, B(5,6)), -14.0 (d, ¹J(B,H)= 169, 1B, B(3)), -19.4 (d, ¹J(B,H)= 155, 2B, B(2,4)), -29.1 (dd, ¹J(B,H)= 138, ¹J(B,H)= 30, 1B, B(10)), -31.8 (d, ¹J(B,H)= 143, 1B, B(1)). ³¹P{¹H} NMR (CD₃COCD₃) δ: 77.31 (s, OP¹Pr₂).

Synthesis of [NMe₄][7,8-(OPPh₂)₂-7,8-C₂B₉H₁₀] (8). To a solution of [NMe₄][7,8-(PPh₂)₂-7,8-C₂B₉H₁₀] (0.5 g, 0.87 mmol) in acetone (15 mL) at 0°C was added dropwise 17.4 mL (1.74 mmol) of a solution of 0.1 M in H₂O₂. The mixture was stirred for 4 hours at room temperature and then an aqueous solution with an excess of [NMe₄]Cl was added to precipitate the white product. This was filtered off, washed with water (3x10 mL) and dried in vacuo. Yield: 0.39 g (74 %). Anal. Calcd for C₃₀H₄₂B₉NO₂P₂: C: 59.27, H: 6.96, N: 2.30 %. Found: C: 58.95, H: 7.00, N: 2.45 %. FTIR: 3019 (C-H_{aryl}), 2959 (C-H_{alkyl}), 2535 (B-H), 1183 (P=O). ¹H NMR (CD₃COCD₃) δ: 7.91-7.23 (m, 20H, Ph), 3.43 (s, 12H, NMe₄), 2.84-0.42 (br m, 9H, B-H), -1.95 (br s, 1H, BHB). ¹H{¹¹B}-NMR (CD₃COCD₃) δ: 7.91-7.23 (m, 20H, Ph), 3.43 (s, 12H, NMe₄), 2.84 (br s, 2H, B-H), 2.33 (br s, 1H, B-H), 1.59 (br s, 2H, B-H), 1.20 (br s, 2H, B-H), 0.88 (br s, 1H, B-H), 0.42 (br s, 1H, B-H), -1.95 (br s, 1H, BHB). ¹³C{¹H} NMR (CD₃COCD₃) δ: 137.72 (d, ¹J(C,P)= 87, Ph), 136.34 (d, ¹J(C,P)= 88, Ph), 132.53 (s, *p*-Ph), 132.01 (s, *p*-Ph), 129.63 (d, ²J(C,P)= 25, *o*-Ph), 126.82 (s, *m*-Ph), 126.21 (s, *m*-Ph), 54.89 (s, NMe₄). ¹¹B NMR (CD₃COCD₃) δ: -5.6 (d, ¹J(B,H)= 119, 2B), -11.1 (d, ¹J(B,H)= 133, 3B), -19.0 (d, ¹J(B,H)= 111, 2B), -32.2 (d, ¹J(B,H)= 142, 1B), -34.0 (d, ¹J(B,H)= 150, 1B). ³¹P{¹H} NMR (CD₃COCD₃): 29.33 (s, OPPh₂).

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