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Widely Applicable Metallacarborane Reagents for π-Conjugated Systems

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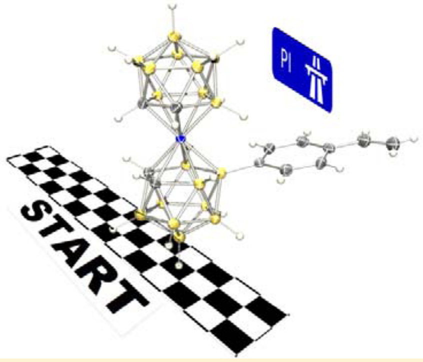
Supporting Information

ABSTRACT: The compounds $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(p\text{-}C_6H_4C_2H_3)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(p\text{-}C_6H_4CHO)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, and $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(m\text{-}C_6H_4CHO)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ were synthesized using an easy methodology, in very good yields and large quantities, which are important requisites to be employed as starting reagents. They have been fully characterized by elemental analysis, IR, NMR, and MALDI-TOF-MS, and the crystal structures of $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(p\text{-}C_6H_4C_2H_3)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ and $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(p\text{-}C_6H_4CHO)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ were elucidated by single-crystal X-ray diffraction. These compounds, having terminal formyl and vinyl functional groups, are suitable platforms to involve the aromatic cobaltabisdicarbollide unit into extended π-conjugated systems. It is expected that these synthons will facilitate the applicability of metallacarboranes in a wide variety of different fields, where π-conjugated systems are needed to keep electronic communication.



■ INTRODUCTION

The cobaltabisdicarbollide sandwich is an anionic compound made of two $[C_2B_9H_{11}]^{2-}$ units that coordinate Co^{3+} in a η^5 way to generate $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$, $[\mathbf{1}]^-$.[1] This anion is remarkable in that it is chemically and thermally stable in a large diversity of scenarios,[2] can be substituted at carbon or at boron atoms,[3] and has a peculiar globular shape and many options to produce hydrogen and dihydrogen bonds that grant the anion a unique self-assembling capacity.[4,5] The central core of this anion, $Co(C_2B_3)_2$, is very similar to the core of ferrocene, $Fe(C_5)_2$, and thus they bear resemblances in some respects, for example, the reversible electrochemistry and the high chemical and thermal stability,[6] but are different in others, such as an enhanced protection of the cobalt atom in $[\mathbf{1}]^-$ by a canopy of hydrogen atoms[7] and properties derived from the six additional boron atoms placed in two further planes from the core (B_5 plane and B_1) that are responsible for singular physicochemical properties. One of the most obvious differences between $[\mathbf{1}]^-$ and ferrocene (Fc) is the charge of $[\mathbf{1}]^-$, which makes the latter and its congeners among the few examples of metallocene-type complexes with a negative charge. In a like manner as Fc, which is widely used as a signaling unit in molecular materials to produce physically recordable signals, $[\mathbf{1}]^-$ could also be very attractive in this field and, very importantly, could be complementary to Fc. As an example, our group has shown that $[\mathbf{1}]^-$ has unique properties to tune its redox potential by the substitution of B−H to B−X vertices (where X can be Cl, Br, or I), a property not found elsewhere.[8] These properties should have opened up many new applications and possibilities for this and similar metallacarboranes. However, so far, this has not been the case. In our view, the reason must be found without adequate starting materials from which to produce well-studied organic reactions as is the case for Fc. Most probably, the most at hand metallacarborane is the cobaltabisdicarbollide dioxanate, with formula $[3,3'\text{-}Co(8\text{-}(C_2H_4O_2)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, **3**, commonly known as COSAN dioxanate, see Chart 1. This reacts easily with any nucleophile, opening the dioxane ring, producing diethoxy linkers joining the cluster and the nucleophile.[9,10] Thus, **3** is good at decorating organic molecules of potential practical interest, for example, porphyrins, dendrimer cores, smaller organic moieties, etc., with metallacarborane clusters;[10,11] however, with few exceptions the involvement of the metallacarborane is one “add on” to the central core, only sought for the inherent properties of the metallacarborane. The more spread methods to generate $B_{cluster}{-}C$ bonds in small metallacarboranes[12] and cobaltabisdicarbollide are based on a Kumada-modified palladium-catalyzed alkylation/arylation of $B_{cluster}{-}I$ vertices in iodocobaltabisdicarbollide with Grignard reagents[13] or in a Heck-adapted $B_{cluster}{-}C_{alkene}$ bond formation[14] or iodonium derivative of cobaltbisdicarbollide $[\mu\text{-}8,8'\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ with activated aromatics[15] and more recently in the absence of transition metal catalysts but in the presence of Li^+.[16]

In this Paper, we sought to produce suitable starting reagents incorporating the fragment $[\mathbf{1}]^-$ so that by using well-developed organic chemistry reactions new molecules are

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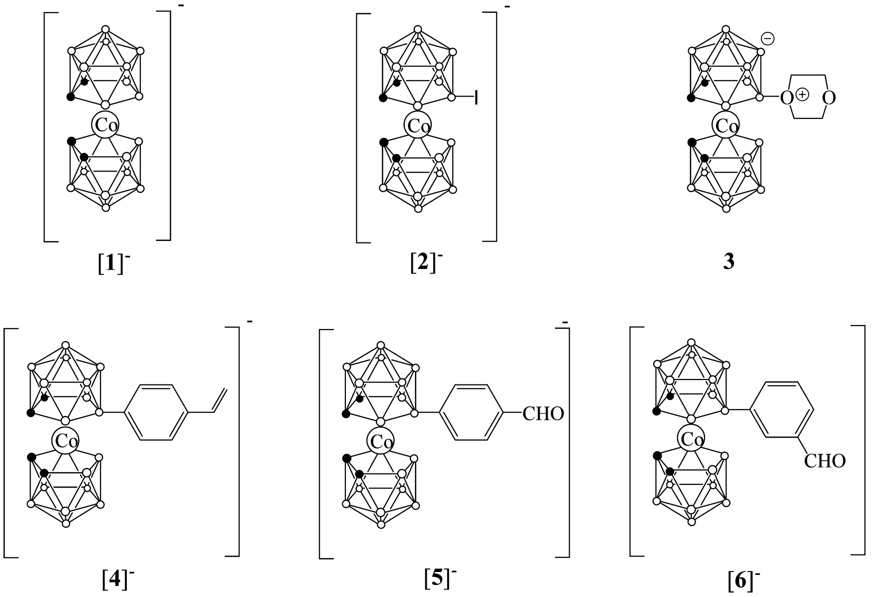
Chart 1. Cobaltabisdicarbollide and Its B-substituted Derivatives $[2]^-$ to $[6]^-$



generated in which donor−acceptor dyad molecules are produced with the particularity that the interaction between the donor and acceptor is done through a delocalized bond system, to influence the first on the second. The molecules have been designed to have an aryl system linked to one boron atom of the cluster, and on this aryl unit one formyl or one vinyl fragment was incorporated (Chart 1). The Wittig, Wittig-Hormer, or some other procedures to synthesize imine, imidazole, or benzimidazole derivatives for the formyl reagent, or cross metathesis or Heck reactions for the vinyl derivative, are just some examples that should lead to compounds in which the communication between the metallacarborane/second active center would be ensured.

■ EXPERIMENTAL SECTION

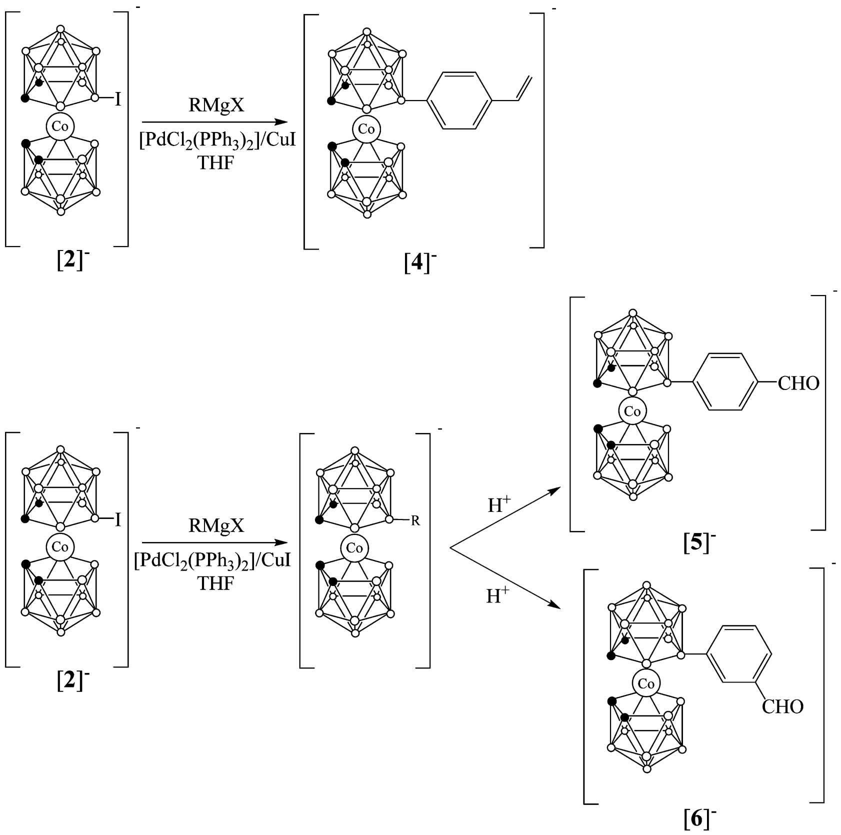
Instrumentation. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra (ν, cm^{-1}; ATR or KBr pellets) were recorded on a Shimadzu FTIR-8300 spectrophotometer. The ^1H NMR, $^1H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B NMR, $^{11}B\{^1H\}$ NMR (96.29 MHz), and $^{13}C\{^1H\}$ NMR (75.47 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, and those for ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$ NMR spectra were referenced to $Si(CH_3)_4$. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz. 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) with a voltage ion source of 20.00 kV (Uis1) and 17.50 kV (Uis2)).

Materials. Experiments were carried out, except when noted, under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Tetrahydrofuran (THF) was distilled from sodium benzophenone before use. Other solvents were reagent-grade. All organic and inorganic salts were Fluka or Aldrich analytical reagent-grade and were used as received. Cs[**2**], see Chart 1, was prepared according to the literature.[13]

Synthesis of $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(p\text{-}C_6H_4C_2H_3)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, $[N(CH_3)_4]$[4]. A round-bottom flask (250 mL) with Mg (1.27 g, 52.39 mmol) was dried under vacuum with a heat gun for 10 min. Then, it was cooled to room temperature, and 60 mL of anhydrous THF and 4-bromostyrene (2.95 mL, 22.58 mmol) were added. A solution of dibromoethane (1.95 mL, 22.59 mmol, 40 mL of anhydrous THF) was added dropwise using an addition funnel, and the reaction mixture was kept at 30 °C overnight. A white precipitate was formed, and it was filtered under nitrogen. Cs[**2**] (2.0 g, 3.44 mmol), $[PdCl_2(PPh_3)_2]$ (200 mg, 0.29 mmol), and CuI (60 mg, 0.30 mmol) were dried under vacuum for 30 min. Then, a solution of the styrenemagnesium bromide (50 mL) generated before was added, and the mixture refluxed for 4 h. Water (10 drops) was added to quench the excess Grignard reagent, a gray precipitate formed, which was filtered, and the solvent was removed under vacuum. The residue was extracted with diethyl ether (50 mL) and HCl (0.5 M) (3 × 30 mL) at 0 °C, and the organic layer was dried over anhydrous magnesium sulfate. After evaporating the organic phase, the residue was dissolved in the minimum volume of EtOH, and an aqueous solution containing an excess of $[N(CH_3)_4]Cl$ was added, resulting in the formation of a precipitate. This was filtered off, washed with water and petroleum ether, and dried under vacuum. Yield: 2.16 g (92%). Elemental analysis calcd (%) for $C_{16}H_{40}B_{18}CoN$: $C = 38.43$, $H = 8.06$, $N = 2.80$; found: $C = 38.26$, $H = 8.04$, $N = 2.85$. IR: ν (cm^{-1}) 3038 ($C_c{-}H$), 2950, 2922, 2854 ($C_{alkyl}{-}H$), 2542 (B−H), 1624 (C═C), 1479 ($C_{alkyl}{-}H$), 945 (C−N), 748, 721 (B−C). ^1H NMR: δ 7.29 (d, $^3J(H,H) = 8$, 2H, C_6H_4), 7.20 (d, $^3J(H,H) = 8$, 2H, C_6H_4), 6.64 (dd, $^3J(H,H_a) = 18$, $^3J(H,H_b) = 11$, 1H, CH), 5.69 (dd, $^3J(H,H_a) = 18$, $^2J(H_b,H_a) = 1$, 1H, CH_aH_b), 5.07 (dd, $^3J(H,H_b) = 11$, $^2J(H_a,H_b) = 1$, 1H, CH_aH_b), 4.56 (br s, 2H, $C_c{-}H$), 3.79 (br s, 2H, $C_c{-}H$), 3.41 (s, 12H, $N(CH_3)_4$), 3.11−1.48 (m, 17H, B−H). $^1H\{^{11}B\}$ NMR: δ 7.29 (d, $^3J(H,H) = 8$, 2H, C_6H_4), 7.20 (d, $^3J(H,H) = 8$, 2H, C_6H_4), 6.64 (d, $^3J(H,H_a) = 11$, d, $^3J(H,H_b) = 18$, 1H, CH), 5.69 (dd, $^3J(H,H_b) = 18$, $^2J(H_b,H_a) = 1$, 1H, CH_aH_b), 5.07 (dd, $^3J(H,H_a) = 11$, $^2J(H_a,H_b) = 1$, 1H, CH_aH_b), 4.56 (br s, 2H, $C_c{-}H$), 3.79 (br s, 2H, $C_c{-}H$), 3.41 (s, 12H, $N(CH_3)_4$), 3.11 (s, 2H, B−H), 2.77 (s, 2H, B−H), 2.55 (s, 2H, B−H), 1.93 (s, 2H, B−H), 1.75 (s, 4H, B−H), 1.71 (s, 2H, B−H), 1.48 (s, 3H, B−H). $^{13}C\{^1H\}$ NMR: δ 137.11 (s, C_6H_4), 135.93 (s, C_6H_4), 131.85 (s, C_6H_4), 126.21 (s, C_6H_4), 123.99 (s, C_6H_4), 112.90 (s, $CHCH_2$), 110.57 (s, $CHCH_2$), 54.62 (s, $N(CH_3)_4$), 53.55 (s, $C_c{-}H$), 49.62 (s, $C_c{-}H$). ^{11}B NMR: δ 13.19 (s, 1B, B8), 6.07 (d, $^1J(B,H) = 137$, 1B), 2.44 (d, $^1J(B,H) = 136$, 2B), −2.86 (d, $^1J(B,H) = 154$, 2B), −4.50 (d, $^1J(B,H) = 146$, 4B), −5.90 (d, $^1J(B,H) = 142$, 2B), −16.46 (d, $^1J(B,H) = 138$, 2B), −17.70 (d, $^1J(B,H) = 141$, 2B), −21.10 (d, $^1J(B,H) = 145$, 1B), −22.23 (d, $^1J(B,H) = 122$, 1B). MALDI-TOF-MS: (m/z) 426.38 (M, 100%), calcd (m/z).

Synthesis of $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(p\text{-}C_6H_4CHO)\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, $[N(CH_3)_4]$[5]. Cs[**2**] (200 mg, 0.34 mmol) in THF (5 mL), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.03 mmol), CuI (6 mg, 0.03 mmol), a solution of 4-benzaldehyde dimethyl acetal magnesium bromide (5

Scheme 1. Cross-Coupling Reaction between $[2]^-$ and the Corresponding Organohalide Compounds[a]



[a] For $[5]^-$ and $[6]^-$, the deprotection of the acetal group is done under acidic conditions.

mL, 1.38 mmol), prepared from magnesium turnings (0.080 g, 3.3 mmol), and 4-bromobenzaldehyde dimethyl acetal (0.46 mL, 2.75 mmol), were reacted at 0 °C. After 30 min at room temperature, the brown solution was heated under reflux for 10 h. Water (10 drops) was added to quench the excess Grignard reagent, a gray precipitate formed, which was filtered, and the solvent was removed under vacuum. The residue was extracted with diethyl ether (20 mL) and HCl (0.1 M) (3 × 10 mL), and the organic layer was dried over anhydrous magnesium sulfate. After evaporating the organic phase the residue was dissolved in the minimum volume of EtOH, and an aqueous solution containing an excess of $[N(CH_3)_4]Cl$ was added, resulting in the formation of an orange precipitate. This was filtered off, washed with water and petroleum ether, and dried. The product was dissolved in the minimum quantity of acetone and passed through a silica-gel column. The existing impurity was removed using a mixture of ethyl acetate/acetone (20:1) as mobile phase, and the pure compound was collected using acetone as eluent to give the desired tetramethylammonium salt $[N(CH_3)_4][5]$. Yield: 0.14 g (83%). Elemental analysis calcd (%) for $C_{15}H_{38}B_{18}CoNO{\cdot}2(CH_3COCH_3)$: $C = 40.94$, $H = 7.85$, $N = 2.27$; found: $C = 40.97$, $H = 7.54$, $N = 1.90$. IR (ATR): ν (cm^{-1}) 3043 (C_c–H), 2847 (C_{alkyl}–H), 2526 (B–H), 1667 (C=O), 1589 (C_{alkyl}–H). ^1H NMR: δ 9.90 (s, 1H, CHO), 7.63 (d, $^3J(H,H) = 9$, 2H, C_6H_4), 7.55 (d, $^3J(H,H) = 6$, 2H, C_6H_4), 4.43 (br s, 2H, C_c–H), 3.86 (br s, 2H, C_c–H), 3.43 (s, 12H, $N(CH_3)_4$), 3.13–1.48 (m, 17H, B–H). $^{13}C\{^1H\}$ NMR: $\delta = 191.65$ (s, CHO), 136.40 (s, C_6H_4), 133.03 (s, C_6H_4), 130.05 (s, C_6H_4), 127.97 (s, C_6H_4), 55.25(s, $N(CH_3)_4$), 53.31 (s, C_c–H), 50.39 (s, C_c–H). ^{11}B NMR: δ 13.48 (s, 1B, B8), 8.04 (d, $^1J(B,H) = 133$, 1B), 2.86 (d, $^1J(B,H) = 134$, 2B), −2.74 (d, $^1J(B,H) = 115$, 2B), −3.73 (d, $^1J(B,H) = 128$, 2B), −5.21 (d, $^1J(B,H) = 143$, 4B), −15.86 (d, $^1J(B,H) = 140$, 2B), −17.14 (d, $^1J(B,H) = 128$, 2B), −21.16 (d, $^1J(B,H) = 133$, 1B), −22.21 (d, $^1J(B,H) = 132$, 1B). MALDI-TOF-MS: found (m/z) 427.85 (M, 100%), calcd (m/z) 428.31 (M).

Synthesis of $[N(CH_3)_4][3,3'\text{-}Co(8\text{-}(m\text{-}C_6H_4CHO)\text{-}1,2\text{-}C_2B_9H_{10})\text{-}(1',2'\text{-}C_2B_9H_{11})]$, $[N(CH_3)_4][6]$. Similarly, $Cs[2]$ (200 mg, 0.34 mmol) in THF (5 mL), $[PdCl_2(PPh_3)_2]$ (20 mg, 0.03 mmol), CuI (6 mg, 0.03 mmol), 5 mL of the Grignard reagent prepared from magnesium turnings (0.090 g, 4.1 mmol), and 2-(3-bromophenyl)-1,3-dioxolane (0.52 mL, 3.43 mmol) were reacted at 0 °C. After 30 min at room temperature, the brown solution was heated under reflux for 10 h. Workup and purification as described for compound $[N(CH_3)_4][5]$ gave the desired tetramethylammonium salt $[N(CH_3)_4][6]$. Yield: 0.13 g (78%). Elemental analysis calcd (%) for $C_{15}H_{38}B_{18}CoNO{\cdot}2(CH_3COCH_3)$: $C = 40.94$, $H = 7.85$, $N = 2.27$; found: $C = 40.73$, $H = 7.70$, $N = 1.95$. IR (ATR): ν (cm^{-1}) 3039 (C_c–H), 2855 (C_{alkyl}–H), 2527 (B–H), 1679 (C=O), 1479 (C_{alkyl}–H). ^1H NMR: δ 9.99 (s, 1H, CHO), 7.92 (s, 1H, C_6H_4), 7.69 (d, $^3J(H,H) = 6$, 1H, C_6H_4), 7.59 (d, $^3J(H,H) = 9$, 1H, C_6H_4), 7.31 (t, $^3J(H,H) = 6$, 1H, C_6H_4), 4.45 (br s, 2H, C_c–H), 3.87 (br s, 2H, C_c–H), 3.43 (s, 12H, $N(CH_3)_4$), 3.17–1.48 (m, 17H, B–H). $^1H\{^{11}B\}$ NMR: δ 9.99 (s, 1H, CHO), 7.92 (s, 1H, C_6H_4), 7.69 (d, $^3J(H,H) = 6$, 1H, C_6H_4), 7.59 (d, $^3J(H,H) = 9$, 1H, C_6H_4), 7.31 (t, $^3J(H,H) = 6$, 1H, C_6H_4), 4.45 (br s, 2H, C_c–H), 3.87 (br s, 2H, C_c–H), 3.43 (s, 12H, $N(CH_3)_4$), 3.17–1.48 (m, 17H, B–H). $^{13}C\{^1H\}$ NMR: δ 193.29 (s, CHO), 138.77 (s, C_6H_4), 134.90 (s, C_6H_4), 134.03 (s, C_6H_4), 126.69 (s, C_6H_4), 125.72 (s, C_6H_4), 55.17 (s, $N(CH_3)_4$), 53.19 (s, C_c–H), 50.40 (s, C_c–H). ^{11}B NMR: δ 14.01 (s, 1B, B8), 8.26 (d, $^1J(B,H) = 139$, 1B), 2.94 (d, $^1J(B,H) = 139$, 2B), −2.71 (d, $^1J(B,H) = 88$, 2B), −3.37 (d, $^1J(B,H) = 149$, 4B), −5.10 (d, $^1J(B,H) = 151$, 2B), −15.73 (d, $^1J(B,H) = 138$, 2B), −17.04 (d, $^1J(B,H) = 139$, 2B), −20.87 (d, $^1J(B,H) = 143$, 1B), −22.09 (d, $^1J(B,H) = 123$, 1B). MALDI-TOF-MS: found (m/z) 427.85 (M, 100%), calcd (m/z) 428.31 (M).

X-ray Structure Determination of $[N(CH_3)_4][4]$. Orange crystals were grown from dichloromethane and used for X-ray structure determination. Single-crystal X-ray data for $[N(CH_3)_4][4]$ were collected at 120 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. The measurements were

Table 1. $^{11}B\{^1H\}$ NMR Spectra [ppm] of B8-monosubstituted Derivatives of $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$

compound	$\delta(^{11}B\{^1H\})$ integration[a]									
$[\mathbf{1}]^-$	6.50 (2)		1.40 (2)		−6.00 (8)		−17.20 (4)		−22.70 (2)	
$[\mathbf{2}]^-$	6.54 (1)	3.51 (1)	1.28 (1)	−1.73 (2)	***−4.78 (5)***	−5.38 (2)	−16.02 (2)	−17.45 (2)	−20.92 (1)	−23.06 (1)
$[\mathbf{4}]^-$	***13.19 (1)***	6.07 (1)	2.44 (2)	−2.86 (2)	−4.50 (4)	−5.90 (2)	−16.46 (2)	−17.70 (2)	−21.10 (1)	−22.23 (1)
$[\mathbf{5}]^-$	***13.48 (1)***	8.04 (1)	2.86 (2)	−2.74 (2)	−3.73 (2)	−5.21 (4)	−15.86 (2)	−17.14 (2)	−21.16 (1)	−22.21 (1)
$[\mathbf{6}]^-$	***14.01 (1)***	8.26 (1)	2.94 (2)	−2.71 (2)	−3.37 (4)	−5.10 (2)	−15.73 (2)	−17.04 (2)	−20.87 (1)	−22.09 (1)

[a] Numbers in bold and italics relate to the resonances due to B−R (R ≠ H).

made in the range from 3.17 to 27.48° for θ. A total of 70 217 reflections were collected, of which 12 263 [R(int) = 0.115] were unique. The structures were solved by direct methods and refined against F^2 using the SHELXL-97 program; final $R1 = 0.0611$.[17] For all structures, the hydrogen atoms were treated as riding atoms using the SHELXL-97 default parameters.

X-ray Structure Determination of $[N(CH_3)_4][\mathbf{5}]$. Orange crystals were grown from acetone and used for room temperature and 300 K X-ray structure determination. The measurement was carried out on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.710 73 Å) from an X-ray Tube. The measurements were made in the range from 2.40 to 28.38° for θ. Full-sphere data collection was carried out with ω and φ scans. A total of 42 824 reflections were collected, of which 6783 [R(int) = 0.0412] were unique. Programs used: data collection, Smart;[18] data reduction, Saint+;[19] absorption correction, SADABS.[20] Structure solution and refinement was done using SHELXTL Version 6.14 (Bruker AXS 2000−2003). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Final $R1 = 0.042$. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in geometrically optimized positions and forced to ride on the atom to which they are attached.

■ RESULTS AND DISCUSSION

The target of this research was to produce readily available reagents enabling placement of sandwich metallacarboranes, in particular $[\mathbf{1}]^-$, in organic frameworks so that the cores of both main bodies can be joined by a conjugate linker. Our aim was to produce derivatives of $[\mathbf{1}]^-$ that had a yield above 60%, with a high degree of purity, stable in normal performance laboratories, and produced in one-pot reaction from a readily available reagent, using a wide range of possible solvents. In the search for a stable reagent able to facilitate conjugation and ease of synthesis we opted for a B−aryl substitution because these can be produced from readily available Grignard reagents and the monoiodo derivative of $[\mathbf{1}]^-$, which is also easily produced. Further, a modification of the Kumada reaction was successfully applied in boron clusters to produce B−C(aryl) bonds. Thus, this reaction was the one chosen to produce the sought-after reagents for wide application.

Palladium-Catalyzed B−C Cross-Coupling Reactions on $Cs[3,3'\text{-Co-}(8\text{-I-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ with Grignard Reagents. Previous work in our group demonstrated the feasibility of the cross-coupling methodology applied to iodinated derivatives of *o*-carborane and cobaltabisdicarbollide.[13] Reactions proceed smoothly producing the corresponding B−C derivatives in very good yields. However, none of the compounds synthesized had a terminal functional group enabling the possibility of further exploring the reactivity of such molecules. Successful B−C coupling reactions were achieved by using $Cs[3,3'\text{-Co-}(8\text{-I-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, Cs[**2**], as the starting compound. The B−I unit was transformed into B−R by using a Grignard reagent in the presence of a palladium catalyst and copper(I) iodide as a cocatalyst.[21] In a typical experiment, the Cs[**2**] salt, the palladium catalyst, and CuI were dissolved in THF and treated with the appropriate Grignard reagent at low temperatures (Scheme 1). The mixture was allowed to warm to room temperature and heated under reflux. After cooling the reaction mixture, some drops of water were added to quench the excess of Grignard reagent, which was filtered off, and the filtrate evaporated to dryness. Workup and functional-group deprotection, for $[\mathbf{4}]^-$ and $[\mathbf{5}]^-$, yielded the desired compounds in very good yields (between 78 and 92%), making them readily accessible as starting reagents for π-conjugated systems. The versatility of the reaction was explored by producing B8-aryl (4-styrene $[\mathbf{4}]^-$, 4-benzaldehyde $[\mathbf{5}]^-$, and 3-benzaldehyde $[\mathbf{6}]^-$) derivatives. Thus, it can be considered a general reaction for the regioselective generation of 8-aryl derivatives of compound $[\mathbf{1}]^-$ with terminal functional groups such as formyl or vinyl.

The formation of the Grignard reagent was done in two different ways, depending on the nature of the organic molecule. For $[\mathbf{5}]^-$ and $[\mathbf{6}]^-$, the Grignard reagent was prepared following the usual method described by Gilman and Kirby,[22] which relies on the activation of the magnesium surface by iodine. However, this method did not work well in the preparation of the Grignard reagent having a vinyl group, leading to $[\mathbf{4}]^-$. In the latter, where a vinyl group is present on the organohalide compound, the formation of the Grignard reagent was done following the procedure described by Pearson et al.[23] A solution of dibromoethane in THF was added dropwise for several hours to a solution containing the organohalide with magnesium, which had been carefully dried in vacuo with a heat gun. The reaction mixture was kept overnight at 35 °C to maintain the reflux. It was then necessary to filter under nitrogen the white precipitate (magnesium salts) that was formed during the reaction. Once the Grignard reagent was generated, a titration was done to check the concentration lay between 0.2 and 0.25 M, as at lower concentration the reaction did not take place, while at higher concentration the starting metallacarborane decomposed leading to *nido*-carborane derivatives. The nature of $[\mathbf{4}]^-$, $[\mathbf{5}]^-$, and $[\mathbf{6}]^-$ was corroborated by elemental analysis, MS, IR, ^1H, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$, ^{11}B, and $^{11}B\{^1H\}$ NMR spectroscopies, and the nature of $[N(CH_3)_4][\mathbf{4}]$ and $[N(CH_3)_4][\mathbf{5}]$ was corroborated by X-ray crystal-structure determination.

NMR Spectral Considerations. The $^{11}B\{^1H\}$ NMR data of the monosubstituted compounds prepared in this work are shown in Table 1 along with the resonances of anions $[\mathbf{1}]^-$ and $[\mathbf{2}]^-$. The spectra can be interpreted considering the $^{11}B\{^1H\}$ NMR spectra of $[\mathbf{1}]^-$ and $[\mathbf{2}]^-$, the latter also being a derivative of $[\mathbf{1}]^-$. The $^{11}B\{^1H\}$ NMR spectrum of $[\mathbf{1}]^-$ displays five resonances in the range from −6.5 to −22.7 ppm with a 2:2:8:4:2 pattern, in agreement with an averaged C_{2v} symmetry. The ^{11}B NMR chemical shifts of $[\mathbf{1}]^-$ were assigned with the aid of a two-dimensional $^{11}B\{^1H\}\text{-}^{11}B\{^1H\}$ NMR correlation spectroscopy (COSY) experiment and correspond to B(8,8′), B(10,10′), B(4,4′,7,7′,9,9′,12,12′), B(5,5′,11,11′), and B(6,6′)

from low to high field. Incorporation of one iodine atom at position B8 lowers the symmetry to C_s, maintaining only one plane of symmetry and rendering the two dicarbollide moieties nonequivalent. Therefore, the $^{11}B\{^1H\}$ NMR spectrum of [**2**]$^-$ displays 10 resonances in the range from −6.5 to −23.1 ppm, with a 1:1:1:2:*5*:2:2:2:1:1 pattern. The resonance in italics integrating as five corresponds to the B−I signal, which overlaps with four B−H signals. Substitution of iodine by aryl groups keeps the same C_s symmetry, and therefore the observed pattern is almost the same. In Table 1, the B−C resonance is shown in italics. The rather complex $^{11}B\{^1H\}$ spectra of $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ derivatives with a B8−C bond consist of one set of signals for each carborane ligand moiety, one set of which is perturbed by the B−C substitution and the second set, almost unchanged, corresponding to that of the parent unsubstituted anion [**1**]$^-$. Only when no peak coincidence overlap was found could the positions be assigned by cross-peaks in the $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ NMR COSY experiments. The resonance at 13−14 ppm is not split into a doublet in the ^{11}B NMR spectra of [**4**]$^-$−[**6**]$^-$, indicating that this resonance corresponds to the B−C vertex (Figure 1).

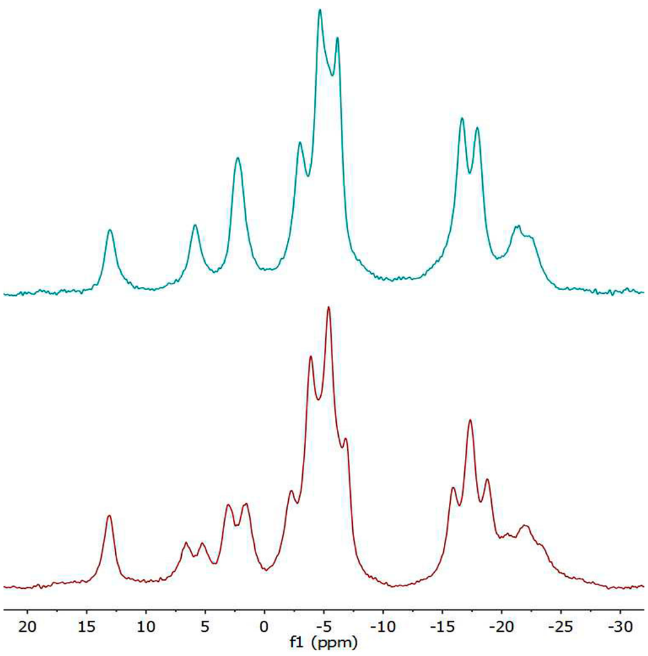


Figure 1. ^{11}B and $^{11}B\{^1H\}$ NMR spectra of $[N(CH_3)_4]$[**5**].

In agreement with the C_s symmetry, the ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit two slightly different C−H carborane signals due to the substituted and the unsubstituted cage for [**2**]$^-$−[**6**]$^-$ (Table 2), and one C−H carborane signal for [**1**]$^-$. The difference in chemical shift can also be observed in Figure 2 where it can be seen that, for the substituted cage, the C−H groups are being affected by the R group. Meanwhile, the unsubstituted cage remains unchanged because the influence of the R group is localized to the cluster that it is bound to. Both ^1H and $^{13}C\{^1H\}$ NMR spectra also display resonances attributable to the R groups at the expected positions. Moreover, a quantitative description on the effect of the metallacarborane can be drawn from the positions of the hydrogen atoms on the aromatic unit. It is noteworthy that ^1H NMR resonances in [**4**]$^-$ corresponding to the aryl group appear very close at 7.29 and 7.20 ppm. The same behavior is seen in [**5**]$^-$, at 7.63 and 7.55 ppm. This is indicative of a π-system between the boron cluster and the aryl group as the σ-bonding is compensated by π back-donation. Finally, the resonances corresponding to the formyl or vinyl functional groups are standard, ensuring that the reactivity is unchanged.

Table 2. Chemical Shift Values [ppm] of the Hydrogen and Carbon Cluster Atoms in the ^1H and $^{13}C\{^1H\}$ NMR Spectra of B(8)-monosubstituted Derivatives of $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$

compound	$\delta(^1H)$ NMR	$\delta(^{13}C\{^1H\})$ NMR
[**1**]$^-$	3.94	51.03
[**2**]$^-$	4.54, 4.29	59.34, 49.16
[**4**]$^-$	4.56, 3.79	53.55, 49.62
[**5**]$^-$	4.43, 3.86	53.31, 50.39
[**6**]$^-$	4.45, 3.87	53.19, 50.40

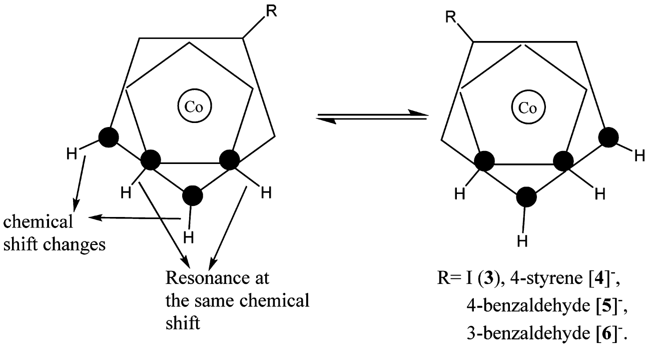


Figure 2. Schematic representation of the influence of the R group on the ^1H and ^{13}C NMR chemical shift.

Stuctures of the Salts in the Solid State. Suitable single crystals of $[N(CH_3)_4]$[**4**] and $[N(CH_3)_4]$[**5**] were obtained by slow evaporation of the solvent from solutions of dichloromethane and acetone, respectively. The X-ray structures are presented in Figures 3 and 4, and the crystallographic data is given in Table 3. Crystallographic analyses confirmed the expected B(8)-substituted cobaltabisdicarbollide structure for the compounds. In each compound, the B10−Co3−B10′ jackknife angle is close to 180° [175.38(8) ± 176.45(6)°], and the Co3−B8 distance is slightly longer than the Co3−C_c distances. Also, the Co3−B8 distance is longer than the unsubstituted Co3−B8′.

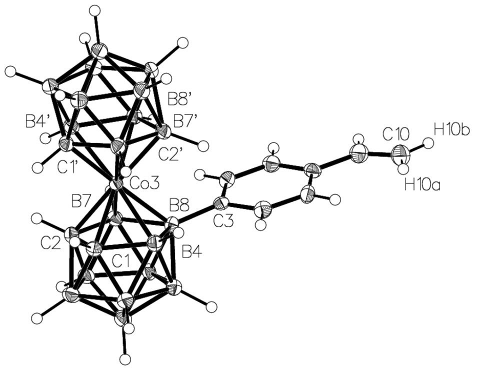


Figure 3. Drawing of $[N(CH_3)_4]$[**4**] with 50% thermal displacement ellipsoids; the $[N(CH_3)_4]^+$ cation is omitted.

In $[N(CH_3)_4]$[**4**], the two five-membered coordinating sites are in a staggered conformation. The rotamers of $[N(CH_3)_4]$-

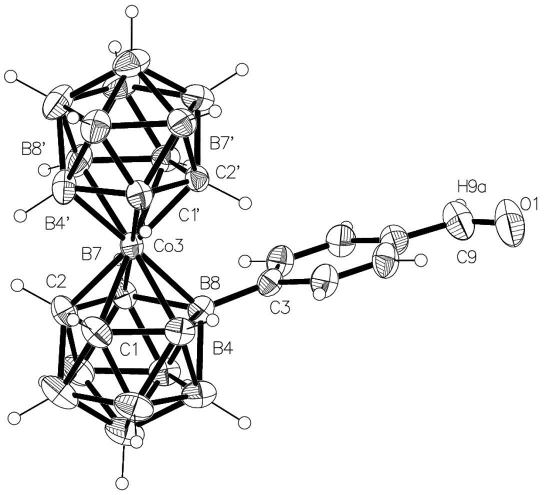


Figure 4. Drawing of $[N(CH_3)_4][5]$ with 50% thermal displacement ellipsoids; the $[N(CH_3)_4]^+$ cation is omitted.

Table 3. Crystallographic Data and Structural Refinement Details for Compounds $[N(CH_3)_4][4]$ and $[N(CH_3)_4][5]$

	$[N(CH_3)_4][4]$	$[N(CH_3)_4][5]$
empirical formula	$C_{16}H_{40}B_{18}CoN$	$C_{15}H_{38}B_{18}CoNO$
formula weight	500.00	501.97
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a [Å]	19.554(3)	13.3965(15)
b [Å]	13.533(2)	22.411(2)
c [Å]	20.323(4)	9.3249(10)
β [deg]	90.811(15)	102.980(2)
V [Å^3]	5377.5(17)	2728.1(5)
Z	8	4
T [K]	120(2)	300(2)
ρ [g cm^{-3}]	1.235	1.222
μ [cm^{-1}]	0.648	0.642
goodness-of-fit	1.041	1.038
$R1^a$ $[I > 2\sigma(I)]$	0.0611	0.0420
$wR2^b$ $[I > 2\sigma(I)]$	0.1289	0.1092

$^a R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $^b wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$.

[4] (defined by two cobaltabisdicarbollide moieties) are similar. The configuration having C2′ oriented between C1 and C2, being away from the B8 of the substituted cage, has been observed in most cases.[13] On the other hand, $[N(CH_3)_4][5]$ presents a different configuration, being B8-oriented between C2′ and B7′. The reason for the unusual rotamer may be found in the interactions between B4 and B7 with the phenyl hydrogen atoms, being 2.975 Å.

The packing of both compounds is also different. While compound $[N(CH_3)_4][4]$ presents many intramolecular interactions between phenyl hydrogen atoms and B−H and C_c−H of neighboring molecules, the interactions found in $[N(CH_3)_4][5]$ for the phenyl hydrogen atoms are intramolecular with B−H and C_c−H atoms. Finally, the position of the $[N(CH_3)_4]^+$ cation differs in the unit cell because in $[N(CH_3)_4][5]$ it is fixed by the presence of an interaction between a methyl hydrogen atom of the cation and the oxygen of the formyl group, at a distance of 2.359 Å.

CONCLUSIONS

Cross-coupling reactions between metallacarborane cobaltabisdicarbollide and organic molecules were already achieved by Kumada coupling, Heck reactions, and Li^+-mediated B−C generation. However, we have successfully accomplished the synthesis and full characterization of a new set of compounds bearing terminal functional groups that can be used as starting reagents in π-conjugated systems. The compounds can be synthesized using an easy methodology and in very good yields and large quantities, which are important requisites to be employed as starting materials. Moreover, NMR spectroscopy showed that the formyl and vinyl functional groups possess similar properties than compounds without the metallacarborane moiety, indicating that well-developed organic chemistry reactions can be employed. Therefore, it is expected that these reagents will facilitate the applicability of metallacarboranes in a new variety of different fields, where π-conjugated systems are needed to keep electronic communication.

ASSOCIATED CONTENT

Supporting Information

Spectral data for compounds $[N(CH_3)_4][4]$, $[N(CH_3)_4][5]$, and $[N(CH_3)_4][6]$. Crystallographic data (CIF) for $[N(CH_3)_4][4]$ and $[N(CH_3)_4][5]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[¶] A.D.M. is enrolled in the Ph.D. program of the UAB. Portions of the experimental section appear in P.F. dissertation available through http://tdx.cat/handle/10803/3305.

Notes

The authors declare no competing financial interest.

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