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Direct synthesis of an anionic 13-vertex closo-cobaltacarborane cluster†

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Reaction of 1,2-bis(diphenylphosphino)-*ortho*-carborane (L) with $[K(thf){(^{Mes}BIAN)Co(\eta^4-cod)}]$ (1, $^{Mes}BIAN = bis(mesityliminoace-naphthene)diimine, cod = 1,5-cyclooctadiene) affords an anionic 13-vertex$ *closo*-cobaltacarborane cluster (2) in one step. The mechanism of this transformation has been studied by experimental and quantum chemical techniques, which suggest that a series of outer-sphere electron transfer and isomerisation processes occurs. This work shows that low-valent metalate anions are promising reagents for the synthesis of anionic metallacarborane clusters.

Supraicosahedral metallacarboranes are of interest due to various applications in catalysis, materials science, and biomedicine.¹ 13-Vertex metallacarboranes (MC₂B₁₀) dominate this area. The first member of this class of compounds, [CpCo- $(C_2B_{10}H_{12})$] (Cp = cyclopentadienyl), was reported by Hawthorne and co-workers in 1971.² In this seminal work, the synthesis of the 13-vertex cobaltacarborane was achieved by reduction of the parent 1,2-dicarba-closo-dodecaborane $(C_2B_{10}H_{12})$ with elemental sodium and subsequent treatment with NaCp, CoCl₂ and air. This synthetic scheme was called "polyhedral expansion", a term coined by Hawthorne. Subsequently, a large variety of 13-vertex cobaltacarborane derivatives was synthesised following this approach in the next decades.3-13 Notably, Stone, Welch and co-workers established another synthetic route towards such species in 1984 by treating the parent 12-vertex carborane with the low-valent cobalt complex $[Co(PEt_3)_4]$. Here a $Co(PEt_3)_2$ fragment was directly inserted into

^bLeipzig University, Institute of Inorganic Chemistry, Johannisallee 29, 04103 Leipzig, Germany. E-mail: hey@uni-leipzig.de; https://research.uni-leipzig.de/hh/ ^cVan't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam (UvA) Science Park 904, 1098 XH Amsterdam, The Netherlands the cluster with the cobalt phosphane complex simultaneously acting as the reducing agent and metal source.¹⁴

As shown by several groups in electrochemical investigations, neutral 13-vertex cobaltacarboranes can be reduced reversibly.^{3,8,9,15} Such reduced species were used *in situ* as nucleophilic intermediates for the synthesis of 14-vertex bimetallacarboranes.^{12,16-18} Despite their synthetic value, only a few anionic 13-vertex cobaltacarboranes have been well characterised. One important example is the homoleptic complex anion $[4,4'-\text{Co-}(1,6-closo-\text{C}_2\text{B}_{10}\text{H}_{12})_2]^-$ (**A**) reported as its tetraethylammonium salt by Hawthorne in 1973.³ Shortly afterwards, Hawthorne published the fascinating complex **B**, where the B–H moieties in the 5-position of both cluster units in **A** were formally substituted by cyclopentadienyl cobalt fragments.¹⁹ Homoleptic complex **C** shown in Fig. 1, an isomer of **A**, was synthesised and characterised by X-ray crystallography by Welch and co-workers.⁸

Fig. 1 Examples of anionic 13-vertex cobaltacarboranes. For clarity, only the 4,1,6-isomer of D is shown, the respective 4,1,8-, 4,1,10- and 4,1,12-isomers were described in the same work.⁹



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Further detailed electrochemical and spectroscopic studies have shown that a series of anionic 13-vertex indenyl cobaltacarboranes with 4,1,6-, 4,1,8-, 4,1,10- and 4,1,12- CoC_2B_{10} architectures, *e.g.* **D**, are accessible by the reduction of neutral precursors.⁹ These anions were characterised *in situ* by UV-vis and EPR spectroscopy.

Here we report the synthesis and characterisation of a new anionic 13-vertex cobaltacarborane, 2, which contains a redoxactive bis(iminoacenapthene) (BIAN) ligand at cobalt and two phosphanyl moieties attached to the cluster carbon atoms. Similar to Stone's approach, this complex is obtained in a facile one-pot procedure from 1,2-bis(diphenylphosphino)*closo*-carborane L and a highly reduced cobaltate anion 1 (Scheme 1).^{20,21} We describe the structural and spectroscopic characteristics of 2, and we propose a mechanism for its formation based on model reactions, NMR spectroscopic monitoring and quantum chemical calculations.

As part of a research program studying the chemistry of phosphanyl-substituted carborane compounds,²² it was presumed that bis-phosphane L might be a suitable chelate ligand for the [Co(BIAN)]⁻ fragment due the strongly electronwithdrawing properties of L.^{20,21} In order to test this hypothesis, the 1:1 reaction of 1 with L was performed in THF as shown in Scheme 1. Upon mixing 1 and L in THF, a deep purple reaction mixture is formed immediately. In contrast to initial expectations, the desired adduct 2' is not observed at any stage of the reaction; instead, polyhedral expansion occurs, resulting in a 13-vertex cluster anion. The deep purple crystalline potassium salt 2 can be isolated in 59% yield after work-up and crystallisation of the crude product from DME/ *n*-hexane. ${}^{31}P{}^{1}H$ NMR spectroscopic monitoring shows that the reaction takes approximately 40 h at 50 °C to go to completion. Several reaction intermediates can be observed (vide infra), yet the formation of the final product is very selective when the reaction is finished.

Crystals of **2** suitable for single-crystal X-ray diffraction (XRD) were obtained by slow diffusion of *n*-hexane into a DME solution. The molecular structure is shown in Fig. 2. A contact ion pair between $[K(dme)_3]^+$ and a 13-vertex cobaltacarborane cluster anion is observed, in which the cobalt atom caps a sixmembered CB₅ ring with typical Co–B distances of 2.149(2)–2.197(2) Å and Co1–C3 of 2.090(1) Å.^{4,5,7,23} During the course of the reaction an isomerisation takes place, and in the final

Ph₂P

•BH •C

L

DME

50 °C, 40 h

- cod

59%

Scheme 1 Synthesis of 2 and initially attempted synthesis of 2'.

[K(thf)]

1



Fig. 2 Solid-state structure of **2** with thermal ellipsoids at 40% probability. Selected bond lengths [Å] and angles [°]: N1–C1 1.332(2), N2–C2 1.325(2), C1–C2 1.420(2), N1–Co1 1.960(1), N2–Co1 1.935(1), Co1–C3 2.090(1), C3–B1 1.549(2), K1…B5 3.409(1), K1…B6 3.409(1), C3–P1 1.837(1), C4–P2 1.867(1), N1–Co1–N2 82.20(5). Hydrogen atoms are omitted for clarity.

13-vertex cluster, the carbon atoms occupy the positions 1 and 8.²³ Thus, 2 can be classified as a 4,1,8-cobaltacarborane according to common numbering schemes of such clusters.⁵ Such an isomerisation is frequently observed for related 13-vertex metallacarboranes.^{1,24} The potassium cation K1 interacts with two B-H moieties (K1-B5/B6 3.409(1) Å) of the carborane cluster. Cobalt is additionally coordinated by the ^{Mes}BIAN ligand with unexceptional Co-N distances of 1.960(1) Å and 1.935(1) Å. Key bond lengths within the MesBIAN framework of this α -diimine ligand suggest that it is present in its monoanionic form. In particular, the C1-C2 bond (1.420(2) Å) is slightly longer than in the structures of closely related dianionic BIAN ligands (1.402(4) Å for Na₂[^{Dipp}BIAN], ^{Dipp}BIAN = bis(2,6diisopropylphenyliminoacenaphthene)diimine), and the N1-C1 (1.332(2) Å), and N2-C2 bonds (1.325(2) Å) are also shorter than expected for a dianionic ligand (1.387(4) Å for Na₂[^{Dipp}BIAN]).²⁵

Multinuclear NMR spectra of 2 in THF-d₈ are consistent with the crystallographically determined molecular structure. The ³¹P{¹H} NMR spectrum shows two singlets at 28.9 ppm and 24.1 ppm (*cf.* a shift of 7.8 ppm for the starting material L), while the ¹H and ¹³C{¹H} NMR data show that the *ortho*-methyl substituents of the mesityl groups are diastereotopic presumably due to hindered rotation around the C_(mesityl)-N bond. These methyl groups show four resonances in the ¹³C{¹H} NMR spectrum. Two of them split into a doublet due to through-space coupling to the phosphorus atom P1, proven by a ¹³C{¹H, ³¹P} NMR experiment. The hydrogen atoms of the carborane unit give rise to a very broad signal from 4.0 to 0.0 ppm. The ¹¹B and ¹¹B{¹H} NMR spectra are typical for a metallacarborane framework and show four broad signals in the range of 13.3 to -20.9 ppm.

DME

[K(thf)]

2

not observed

Mes

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Due to the presence of three potentially redox-active sites (cobalt atom, MesBIAN and carborane ligand), the redox properties of 2 were of interest. A cyclic voltammogram recorded in THF/^{*n*}Bu₄NPF₆ shows a reversible wave at $E_{1/2} = -0.6$ V vs. Fc/Fc^+ , which may be assigned to the oxidation of anion 2 by one electron to a neutral compound (see the ESI[†]). In addition, two irreversible waves are observed at +0.5 V and -2.5 V vs. Fc/Fc^+ , which can be assigned to a second oxidation and a reduction process, respectively. The UV-vis spectrum of deep purple 2 shows intense absorptions at 320 nm and 504 nm (ϵ = 51000 L mol⁻¹ cm⁻¹) with a shoulder at 605 nm. A calculated spectrum obtained with TD-DFT methods qualitatively agrees with the experimental spectrum (see Fig. S24, ESI[†]) and shows that the intense absorptions observed in the visible region arise from MLCT transitions involving cobalt and the MesBIAN ligand (see the ESI[†]) as in other main group and transition metal BIAN complexes.²⁶ The electronic structure of 2 was additionally probed by CASSCF calculations (see the ESI[†] for details). These calculations reveal the strongly covalent nature of the bonding between cobalt and the BIAN ligand, making the assignment of an oxidation state to the cobalt centre somewhat ambiguous. An MO analysis clearly shows that a BIAN-centred π^* orbital is partially occupied and thus indicates a redox-non-innocent behaviour of the ligand (see the ESI[†] for details). This is in line with the solid state molecular structure of 2, which suggests that a monoanionic BIAN ligand is present (vide supra).

To gain insight into the reaction mechanism, a 1:1 reaction between cobaltate 1 and L was monitored by ³¹P{¹H} NMR spectroscopy at room temperature, where the rate of the reaction was slow enough to detect reaction intermediates (Fig. 3). After 30 min, a signal at 17.9 ppm was observed (see Fig. 3a), which can presumably be assigned to 1,2-bis(diphenvlphosphanyl)-1,2-dicarba-*nido*-dodecaborate(12) (*nido*- L^{2-}) as independently confirmed by the detection of the protonated derivative (nido-HL⁻) in electrospray ionisation mass spectra (vide infra).[‡] After work-up and crystallisation of the crude product from *n*-hexane, a mixture of dark orange crystals of $[(^{Mes}BIAN)Co(\eta^4-cod)]$ (Int-A) and a few crystals of a second complex [(^{Mes}BIAN)Co(L)] (3) were isolated.§ 3 is likely formed by reaction of Int-A and remaining L. An isolated yield of 17% can be estimated for Int-A assuming that it is by far the major species in this mixture. Complex 3 was not detected by ³¹P{¹H} NMR spectroscopy due to its paramagnetic nature. The molecular structure of Int-A was determined by single-crystal XRD and is shown in Fig. 4a. A square-planar cobalt(1) complex is observed, which contains an η^4 -coordinated 1,5-cyclooctadiene molecule. In addition, a ^{Mes}BIAN ligand binds via the two nitrogen atoms. Using the midpoints of the C=C bonds of cod, the dihedral angle between the planar MesBIAN moiety and the cod ligand was determined to be 5.3°, which shows that the coordination geometry for cobalt is essentially square planar. The C-C and C-N bond lengths of the diimine fragment (C1-C2 1.428(5) Å, C1-N1 1.316(5) Å, and C2-N2 1.332(5) Å) are similar to those



Fig. 3 ${}^{31}P{}^{1}H{}$ NMR spectra (161 MHz, 300 K, C₆D₆) of a 1 : 1 reaction of 1 and L in THF at 25 °C (a–c); reaction NMR at 50 °C in THF (d); signal at -15.1 ppm = P_2Ph_4 .

in the closely related Ni complex $[(^{\rm Dipp}BIAN)Ni(\eta^4\text{-cod})].^{27}$ These values suggest the presence of a monoanionic diimine ligand and, consequently, a $_{+1}$ oxidation state for cobalt.²⁵

 $[(^{Mes}BIAN)Co(\eta^4-cod)]$ (Int-A) is paramagnetic with a magnetic moment of $\mu_{\rm eff}$ = 1.8(1) $\mu_{\rm B}$ determined by the Evans method in C₆D₆ solution. An EPR spectrum of Int-A in toluene glass at 20 K is slightly axial (nearly isotropic) with simulated gvalues of 2.01 (g_{\parallel}) and 2.00 (g_{\perp}) (see the ESI, Fig. S10[†]) indicating a ligand-centred radical. This is also supported by DFT calculations, which show that the spin density mainly resides on the MesBIAN ligand (see the ESI, Fig. S11[†]). Fig. 4b shows the single-crystal XRD structure of 3. Both the MesBIAN ligand and the ortho-carboranyl bis-phosphane L act as bidentate chelate ligands, while the cobalt atom shows a distorted tetrahedral coordination environment (83.7° between the planes P1-Co1-P2 and N1-Co1-N2) (Fig. 4b). The bite angle of the bis-phosphane P1-Co1-P2 (90.1°) is similar to our previously reported cobalt(III)-phosphanido (90.7°) complex.²⁸ The C-N and C-C distances in the diimine unit of the MesBIAN framework (C1-N1 1.340(3) Å, C2-N2 1.322(3) Å, and C1-C2 1.432(3) Å) indicate the presence of a $^{\rm Mes}{\rm BIAN}^-$ monoanion similar to Int-A.25 Assuming that the bis-phosphane ligand L remains neutral, this would result in the +1 oxidation state for cobalt, for which a square-planar coordination is normally preferred. A tetrahedral structure is probably observed due to steric repulsion between the bulky mesityl groups and the phenyl substituents on L. Further spectroscopic characterisation of 3 was



Fig. 4 Solid-state structures of (a) $[(^{Mes}BIAN)Co(\eta^4-cod)]$ (Int-A) and (b) $[(^{Mes}BIAN)Co(L)]$ (3) with thermal ellipsoids at 40% probability. Selected bond lengths [Å] and angles [°]: For Int-A: N1–C1 1.316(5), N2–C2 1.332(5), C1–C2 1.428(5), N1–C01 1.963(3), N2–C01 1.976(3), C31–C32 1.391(6), N1–C01–N2 83.0(1); For 3: N1–C1 1.340(3), N2–C2 1.322(3), C1–C2 1.432(3), N1–C01 2.042(2), C01–P1 2.169(6), C01–P2 2.198(1), P1–C31 1.902(2), P2–C32 1.908(2), C31–C32 1.697(3). P1–C01–P2 90.08(2), N1–C01–N2 83.16(8). Hydrogen atoms are omitted for clarity.

unfortunately not possible due to the small amount of isolated crystalline material, which could not be successfully separated from the major species **Int-A**.

When the 1:1 reaction between cobaltate 1 and L is carried out for a longer reaction time, the formation of additional intermediates can be observed. As shown in Fig. 3b and c, a new, broad singlet (20.9 ppm, $\Delta v_{1/2}$ = 74 Hz) was detected by ³¹P{¹H} NMR spectroscopy after several hours. The chemical shift is very similar to the final product 2, thus, this signal can likely be assigned to the symmetric 13-vertex cobaltacarborane Int-C shown in Scheme 2. After four days at room temperature, the signals of *nido*-L²⁻ and Int-C are still present, while significant quantities of 2 are formed at this point. As shown by Fig. 2d, 2 is by far the dominant species observed by ${}^{31}P{}^{1}H{}$ NMR spectroscopy after heating at 50 °C for 40 h, showing that the reaction is eventually very selective towards the formation of the final product 2. The mechanism shown in Scheme 2 can be proposed based on the experimental observations discussed above in conjunction with quantum chemical calculations. According to DFT calculations at the M06-D3(0)/def2-TZVP CPCM(THF) level of theory (see the ESI[†]),²⁹ it is conceivable that the *ortho*-carboranyl bis-phosphane ligand L is reduced by 1 in the first step of the reaction, forming *ortho*- L^{2-} and Int-A. The calculations suggest that this step is exothermic by -8.4 kcal mol⁻¹. In addition, such a redox reaction is in agreement with the reduction and oxidation potentials determined by cyclic voltammetry for 1 ($E_{1/2} = -1.72$ V vs. Fc/Fc⁺ in THF) and for L ($E_{1/2} = -1.9$ V vs. Fc/Fc⁺ in MeCN).³⁰ ortho-L²⁻ was not directly observed, because it rapidly isomerises to *nido*-L²⁻ (step 2) in an exothermic process $(-7.7 \text{ kcal mol}^{-1})$. The latter species was detected by ³¹P{¹H} NMR spectroscopy



Scheme 2 Proposed mechanism based on experimental and quantum mechanical methods. Cations are omitted for clarity. Reaction energies were calculated on the M06-D3(0)def2-TZVP CPCM(THF) level of theory.

(vide supra). Moreover, the protonated species *nido*-HL⁻ was also detected in electrospray ionisation mass spectra of the reaction mixture (see the ESI[†]). A substitution of 1,5-cyclooctadiene in Int-A by *nido*- L^{2-} (step 3) followed by concomitant oxidation of the resulting intermediate Int-B yields the symmetric 13-vertex metallacarborane Int-C, also detected by ³¹P{¹H} NMR spectroscopy. Taken together, steps 3 and 4 are exothermic by -7.4 kcal mol⁻¹. An isomerisation to the unsymmetrical complex 2 is the final step of this sequence (step 5, again exothermic by -13.3 kcal mol⁻¹). Such an isomerisation is commonly observed for related 13-vertex metallacarboranes.^{1,24} The mechanism proposed in Scheme 2 is thus in line with all NMR spectroscopic and crystallographic observations. The proposed intermediates Int-A-Int-C are viable species based on the DFT calculations, and the (mostly exothermic) reaction steps add up to a total reaction energy of -36.8 kcal mol⁻¹.¶

Conclusions

The anionic 13-vertex closo-cobaltacarborane cluster was synthesised by a direct route using α -diimine cobaltate [K(thf)- $\{(^{\text{Mes}}\text{BIAN})\text{Co}(\eta^4\text{-cod})\}\}$ (1) and isolated in a high yield of 59%. The mechanism of this transformation was studied by experimental techniques (single-crystal XRD, multinuclear NMR spectroscopy and ESI-MS) and through DFT calculations. An intermediate $[(^{Mes}BIAN)Co(\eta^4 - cod)]$ (Int-A) was isolated, while ESI-MS data and DFT investigations hint at the formation of a dianionic *nido*-carborane *nido*- L^{2-} as a key intermediate en route to the final cluster 2. These results suggest a redox mechanism that is initiated by an electron transfer from 1 to the 1,2-bis(diphenylphosphino)-orthocarborane ligand L. Based on the work presented here, the synthesis of new anionic metallacarborane derivatives by reaction of further carborane derivatives with low-valent metalate anions³¹ should be an appealing subject for future investigations.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

 $^{+}$ The possible formation of **nido-L**²⁻ as a reaction intermediate is additionally corroborated by an independent experiment, where diphosphane L was reduced with two equivalents of potassium graphite (KC₈, see the ESI†).

Note that the CHN analysis for Int-A is not in agreement with the calculated values for $C_{38}H_{40}N_2Co$ [found (calc.): C: 76.26 (78.20), H: 6.95 (6.91), N: 4.09 (4.80)]. The observed discrepancies are likely due to the contamination of Int-A with a minor amount of 3.

¶The chelate complex 2' was not observed in any of our NMR spectroscopic investigations. In fact, this complex lies higher in energy than 2 by 5.7 kcal mol^{-1} at the M06-D3(0)/def2-TZVP CPCM(THF) level of theory.

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