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Facile synthesis of mixed-ligand bis(dicarbollyl) complexes of nickel

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ABSTRACT

Four mixed-ligand bis(dicarbollyl)nickel(IV) complexes **4b-e** were prepared in good yields via a two-step procedure including (1) ligand exchange reactions between the nickelacarborane complex 3,3-$(PPh_3)_2$-*closo*-3,1,2-$NiC_2B_9H_{11}$ (**1**) and the appropriate substituted dicarbollide-dianions generated from the TBA-salts of *nido*-carborane anions $[7,8\text{-}C_2B_9H_{11}(R)]^-$ {R = 3-$[(CH_2)_5C_{16}H_9]$ (**2b**); 5-[*m*-$CF_3C_6H_4$] (**2c**); 5-[*p*-$CH_3OC_6H_4$] (**2d**); and 1-[C≡CTIPS] (**2e**)} in THF and (2) subsequent oxidation of the prepared paramagnetic intermediate Ni(III) complexes **3b-e** by $FeCl_3$ in acetonitrile. Target compounds were characterized using a combination of spectroscopic techniques. The structure of **4e** was determined using X-ray diffraction.

1. Introduction

A synthetic route to bis(dicarbollyl)metal complexes was established over 40 years ago [1]. Among the numerous bis(dicarbollyl) complexes prepared and characterized to date, nickel complexes [2] are unique because of the documented ligand conformational changes caused by changes in the formal oxidation state of the nickel atom. The importance of these properties for nano material science was realized only very recently after DFT calculations combined with photo- and electrochemical studies showed that the bis(dicarbollyl)nickel core could be used to build electro- or photo-driven molecular motors/switches for nano material applications [3]. The design of such molecular switches based on a mixed-ligand bis(dicarbollyl)nickel complex was proposed later [4] (Fig. 1). Depending on the oxidation state of the metal atom and the pH of the medium, the conformational stabilization of the molecule would be achieved either through the formation of an intramolecular ligand-metal charge-transfer complex [Ni(IV)] or an intramolecular ligand-ligand hydrogen bond [Ni(III)].

Mixed ligand bis(dicarbollyl) complexes of transition metals are uncommon. These complexes are typically [5] prepared by substitution reactions of the bis(dicarbollyl)metal core [6]. The direction of such substitution is limited by cage carbon atoms or the B(8) position in the complex (central boron atom in the coordinated pentagonal face of the ligand). Because the synthesis of nickelacarborane-based molecular motors/switches is of significant interest in our laboratory, a ligand exchange reaction between substituted dicarbollide-dianions and semi-sandwich nickelacarboranes bearing triphenylphosphine ligands was studied in search for a new synthetic approach to mixed-ligand bis(dicarbollyl) complexes of nickel [7].

2. Results and discussion

For the test reaction, a phosphine nickelacarborane, 3,3-$(PPh_3)_2$-*closo*-3,1,2-$NiC_2B_9H_{11}$ (**1**) [8], and an unsubstituted *nido*-carborane, TBA[*nido*-7,8-$C_2B_9H_{12}$] (**2a**), were chosen as the starting materials. Compound **2a** was deprotonated by *n*-BuLi in THF at room temperature, and the resulting dicarbollide-dianion solution was then added to the THF solution of complex **1** (Scheme 1). The pale orange reaction mixture instantly changed color to deep orange, and the mass spectrum of the reaction mixture sample after 1 h of stirring at room temperature showed the presence of the product **3a** as the only carborane-containing species.

Compound **3a**—paramagnetic complex of formal Ni(III) formed after air-oxidation of the reaction mixture—was further oxidized into the diamagnetic Ni(IV) complex **4a**. This oxidation was

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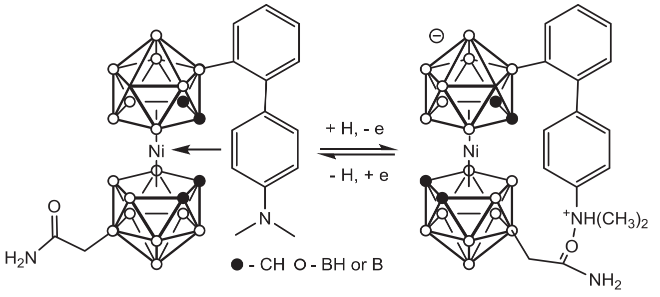


Fig. 1. Suggested design of nickelacarborane complexes with dual conformational stabilization [4].

achieved through the addition of aqueous ferric chloride to the acetonitrile solution of **3a**, followed by isolation of complex **4a** by column chromatography. The ^{1}H, ^{11}B, ^{11}B{^{1}H}, and ^{13}C{^{1}H} NMR spectra of compound **4a,** as well as its high-resolution mass spectrum, corresponded to the data reported for $[3,3'\text{-Ni}^{IV}(C_2B_9H_{11})_2]$ (see Experimental).

Recently, the necessity for a mixed-ligand nickelacarborane synthesis arose during the probing of nickelacarborane conformations in solution [9]. A complex containing a single pyrenylpentyl substituent in position B(6) of the bis(dicarbollyl)nickel core was prepared in a moderate yield (24%) via a three-component reaction between two *nido*-carborane salts and Ni(acac)$_2$. After the proof-of-concept synthesis of compound **4a**, the reaction was repeated under the same conditions using **1** and a substituted *nido*-carborane, **2b** (Scheme 1). Similarly, the MS data of the reaction mixture after 1 h at room temperature revealed the presence of a single product, complex **3b**, which was oxidized to the Ni(IV) complex **4b**. The analytical data for compound **4b** also corresponded to the reported data [9] (see Experimental).

In several recent publications, the potential for substituted nickelacarborane complexes to be used as redox shuttles in dye-sensitized solar cells and their 'tuning' by varying the substituents in the carborane cage were reported [10]. It was decided to further test the ligand exchange reaction using phenyl-substituted *nido*-carboranes, **2c** and **2d**, to synthesize mixed-ligand analogs of the published redox shuttle compounds. Both starting *nido*-carborane salts **2c** and **2d** contain substituted phenyl rings in position B(5) of the carborane cage. In both cases, the reaction of the generated dicarbollide-dianions with complex **1** afforded the expected mixed-ligand complexes **3c** and **3d** according to MS data. Ferric chloride oxidation (Scheme 1) of the Ni(III) compounds yielded the corresponding Ni(IV) complexes **4c** and **4d**, which were characterized using multinuclear NMR and HRMS (see Experimental).

Finally, another recent publication described various precursors and synthetic pathways to metallacarborane-based molecular rods [11]. It was decided to use the described *nido*-carborane **2e,** which has an ethynyl group at the B(1) position, to prepare a mixed-ligand nickelacarborane complex that could be used, for example, as the terminal group during the preparation of metallacarborane-based rigid rods. The reaction of the dicarbollide-dianion generated from **2e** with complex **1** afforded complex **3e** (Scheme 1), which was oxidized and deprotected to form the Ni(IV) compound **4e** in 65% yield (see Experimental).

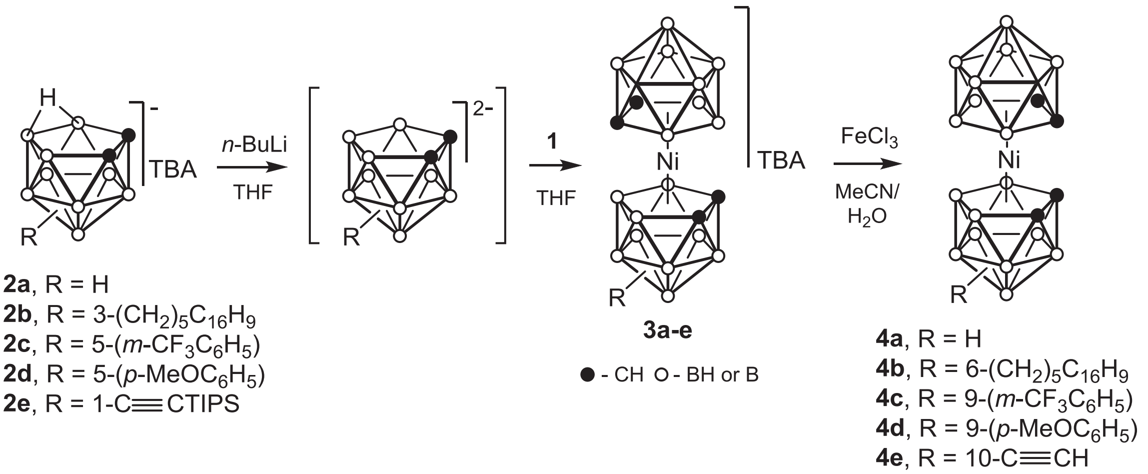
Single crystals of compound **4e** were obtained and studied using X-ray diffraction. The structure of the compound (Fig. 2) was found to contain a nickel atom ligated by two *nido*-carborane fragments in an η^5-fashion. One of the *nido*-carborane cages contains no substituents, whereas the second cage contains an ethynyl group at the B(10) position; therefore, the triple bond of the substituent, boron atoms B(10) and B(10′), and the nickel atom are on the main axis of the molecule. The averaged Ni—C and Ni—B distances are 2.069(2) and 2.102(3) Å, respectively, and the η^5-coordinated C$_2$B$_3$ faces are nearly parallel (dihedral angle of 6.24°). The determined distances in the ethynyl substituents are C(3)-B(10′) – 1.540(4) and C(3)-C(4) – 1.171(4) Å, which are within the normal range. The cage carbon atoms in the carborane fragments are in the *cis* conformation with respect to each other, which is characteristic for bis(dicarbollyl) nickel(IV) compounds [12].

3. Conclusions

It was demonstrated that mixed-ligand bis(dicarbollyl) complexes of nickel(IV) can be prepared in good yields via a ligand exchange reaction between bis(phosphine)nickelacarborane and substituted dicarbollide-dianions. The reaction was proven to work for a variety of substituents in different positions of the carborane cage.

4. Experimental

The ^{1}H, ^{11}B, ^{11}B{^{1}H}, ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance-400 spectrometer. Boron NMR spectra were referenced to 15% BF$_3$•Et$_2$O in CDCl$_3$. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra



Scheme 1. Synthesis of mixed-ligand bis(dicarbollyl)nickel(III) complexes.