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First metallacarborane ethene complex [1,8-Me_2-2,2-$(C_2H_4)_2$-7-SMe_2-2,1,8-$IrC_2B_9H_8$] and its reaction with iodine

Mikhail M. Vinogradov, Yulia V. Nelyubina, Nikolay S. Ikonnikov, Tatyana V. Strelkova, Alexander R. Kudinov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow GSP-1, Russian Federation

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ABSTRACT

Metallacarborane [1,8-Me2-2,2-(C_2H_4)2-7-SMe2-2,1,8-$IrC_2B_9H_8$] (1) was obtained by an interaction of $[(C_2H_4)2IrCl]_2$ with Tl[9-SMe_2-7,8-Me2-7,8-$C_2B_9H_8$]. Reaction proceeds with a low temperature "1,2 → 1,7" polyhedral rearrangement. Ethene complex 1 reacts with iodine in toluene with the formation of ionic compound 3, consisting of cationic [(1,8-Me2-7-SMe2-2,1,8-$IrC_2B_9H_8$)2I_3]+ (3a+) and anionic [(1,8-Me_2-7-SMe-2,1,8-$IrC_2B_9H_8$)2I_3]− (3b−) iodide species. The structures of 1 and 3 were determined by X-ray diffraction.

1. Introduction

Reactions of transition metal olefin complexes with halogens [1] or hydrohalogens [2] are widely applicable for the preparation of complex halides, which are useful in organometallic synthesis [3]. In the case of the late transition metal compounds with a strong metal olefin bonding this reaction requires applying of ethene complexes [4], so far as ethene ligand tends to easier decomplexation. For example, 1,5-cyclooctadiene complex CpIr(cod) reacts with iodine providing cationic iodide $[CpIr(cod)I]^+$ [5], while reaction of ethene complex $CpIr(C_2H_4)_2$ affords iodide $[CpIrI_2]_2$ with elimination of ethene molecules [6]. However, the related metallacrborane chemistry is much less studied. Although a plenty of metallacarboranes with metal-coordinated olefin ligands are known to date [7], none of the metallacarboranes with ethene ligands were synthesized yet.

Herein we describe the synthesis of the first metallacarborane ethene complex [1,8-Me_2-2,2-$(C_2H_4)_2$-7-SMe_2-2,1,8-$IrC_2B_9H_8$] and its reaction with iodine.

2. Results and discussion

The reaction of $[(C_2H_4)_2IrCl]_2$ with Tl[9-SMe_2-7,8-Me_2-7,8-$C_2B_9H_8$] affords bis-(ethene)iridacarborane **1** (Scheme 1). According to the $^{11}B\{^1H\}$ NMR data, the sample taken 2 h after the reaction start (at −10 ÷ −7 °C) contained only a small amount of complex **1** together with major uncharacterized compound which we assume was iridacarborane with unaltered carborane cage as in initial thallium salt Tl[9-SMe_2-7,8-Me_2-7,8-$C_2B_9H_8$]. The same reaction mixture after being kept for 2 h at RT contained only complex **1** with a small amount of carborane 9-SMe_2-7,8-Me_2-7,8-$C_2B_9H_9$. Thereby, reaction proceeds with low temperature "1,2 → 1,7" rearrangement at the metallacarborane cage. That was an unexpected result in view of our previous work, where reaction of 1,5-cyclooctadiene complex $[(cod)IrCl]_2$ with Tl[9-SMe_2-7,8-Me_2-7,8-$C_2B_9H_8$] at RT affords iridacarborane with no rearrangement in the carborane ligand [8]. We suspect the ability of such a low temperature process proceeding could be associated with a higher conformational mobility of ethene in comparison with 1,5-cyclooctadiene ligand which should decrease transition-state barrier energy in the case of iridacarborane **1**.

Reaction between complex **1** and 1 equiv of I_2 results in a loss of the two ethene molecules and formation of product **3**, consisting of cationic $\mathbf{3a}^+$ and anionic $\mathbf{3b}^-$ iodide species (Scheme 2). The ability of direct SMe_2 demethylation in cationic metallacarboranes by

* Corresponding author.
E-mail address: arkudinov@ineos.ac.ru (A.R. Kudinov).

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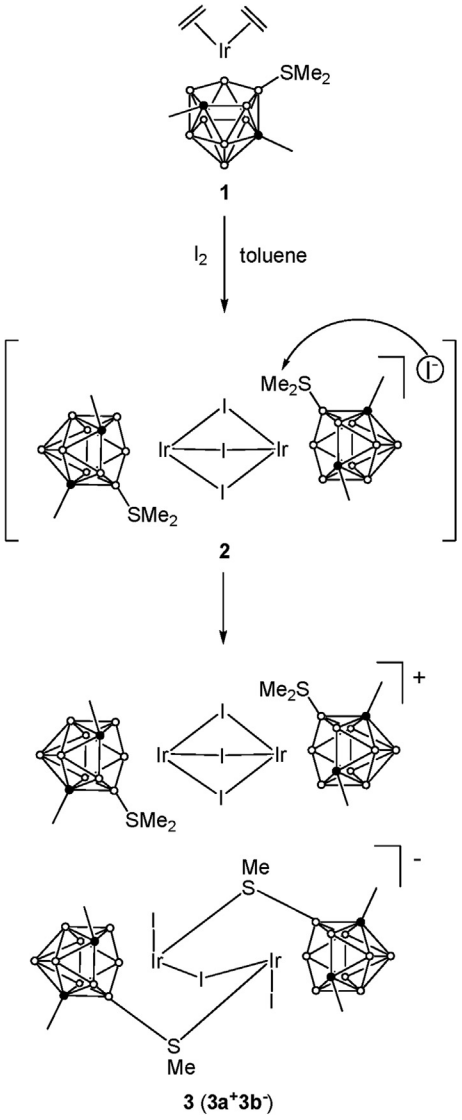
external halide ions was shown recently [9]. We assume that complex **3** is formed as a result of nucleophilic attack by I^- on the one of methyl groups of SMe_2 substituents in the intermediate **2** with subsequent reorganization of organometallic frameworks. In order to verify this hypothesis, the reaction of compound **3** with NBu_4I was monitored by ESI-MS. The ESI-MS spectrum of compound **3** represents the anion **3b**$^-$ (main peak $m/z = 1178.0$, Fig. 2) and two main cations formed by dissociation of cation **3a**$^+$ (Fig. 1). After 10 min reaction of **3** with NBu_4I in dichloroethane solution at RT, ESI-MS spectrum of reaction mixture still exhibits the presence of anion **3b**$^-$ in the solution but in positive-ion mode the only peak corresponds to NBu_4^+ ($m/z = 242.1$) with no organometallic cations. This result clearly confirms the possibility of an interaction between **3a**$^+$ and I^-. It is worth to note, that relative tricarbollide iridium complex [(η-1-Bu^{t}NH-1,7,9-$C_3B_8H_{10}$)Ir(cod)] reacts with iodine affording dimeric iodide [(η-1-Bu^{t}NH-1,7,9-$C_3B_8H_{10}$)IrI_2]$_2$ [10] similar to the known [Cp*IrI_2]$_2$ [11].

Positions of the cage carbon atoms in iridacarborane **1** were determined by X-ray diffraction (Fig. 3). The structure of cation **3a**$^+$ (Fig. 4) is similar to the known iodide complex [(Cp*Ir)$_2I_3$]$^+$ [12], whereas anion **3b**$^-$ (Fig. 5) is a new type compound with bridged mercapto groups formed by demethylation of the SMe_2 substituent. The Ir–I bond in anion **3b**$^-$in case of bridged iodine atom is shorter (av. 2.692(1) Å) than with a terminal one (av. 2.760(1) Å). In cation **3a**$^+$ the average Ir–I distance (av. 2.755(1) Å) is slightly elongated in comparison with [(Cp*Ir)$_2I_3$]$^+$ (2.726(2) Å) [12]. The Ir···Ir distance in **3a**$^+$ (3.717(1) Å) is less than in **3b**$^-$ (3.930(1) Å). Both **3a**$^+$ and **3b**$^-$ comprise two chiral iridacarborane frameworks, but **3a**$^+$ consists of different stereoisomers whereas **3b**$^-$ contains identical ones.

3. Conclusion

We demonstrated that the reaction of [$(C_2H_4)_2IrCl]_2$ with Tl[9-SMe_2-7,8-Me_2-7,8-$C_2B_9H_8$] proceeds with a low temperature "1,2 → 1,7" polyhedral rearrangement giving iridacarborane [1,8-Me_2-2,2-$(C_2H_4)_2$-7-SMe_2-2,1,8-$IrC_2B_9H_8$] (**1**). The latter reacts with iodine with elimination of the ethene molecules affording ionic compound **3**, consisting of cationic [(1,8-Me_2-7-SMe_2-2,1,8-$IrC_2B_9H_8)_2I_3$]$^+$ (**3a**$^+$) and anionic [(1,8-Me_2-7-SMe-2,1,8-$IrC_2B_9H_8)_2I_3$]$^-$ (**3b**$^-$) iodide species. The possibility of anion **3b**$^-$ formation by demethylation in cation **3a**$^+$ with iodide anion was proven by ESI-MS.

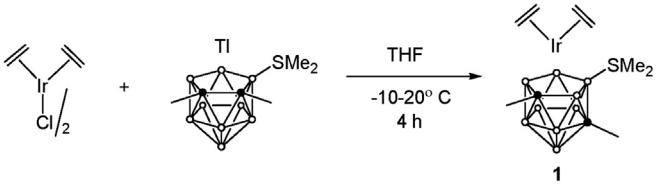


Scheme 2.

3.1. Experimental

3.1.1. General

The reactions were carried out under an inert atmosphere in dry solvents. The isolation of products was conducted in air. Starting materials [$(C_8H_{14})_2IrCl]_2$ [13] and Tl[9-SMe_2-7,8-Me_2-7,8-$C_2B_9H_8$] [8] were prepared as described in the literature. ^1H and $^{11}B\{^1H\}$ NMR spectra (δ in ppm) were recorded on a Bruker Avance-400 spectrometer operating at 400.13 and 128.38 MHz, respectively. The ESI mass-spectra were registered on the Finnigan LCQ Advantage tandem dynamic mass-spectrometer (USA), equipped by octapole ion trap mass analyzer operated in positive and negative ion modes with the Surveyor MS pump and the nitrogen generator Schmidlin-Lab (Germany). Nitrogen 10/0 served as a sheath and auxiliary gas. Flow rate acetonitrile 50 μl/min. The temperature of the heated capillary was 150°C, the electric potential between the needle and the counter electrode was 4.5 kV. The samples with the concentration of 10^{-4} mol/l in acetonitrile solution were introduced into the ion source through the Reodyne injector with the 5 μl loop. Acetonitrile of the Merck company was used for the gradient analysis. The data collection and treatment was fulfilled using the program *X Calibur* version 1.3.



Scheme 1.

3.1.2. Synthesis of [2-Ir(C_2H_4)$_2$-1,8-Me_2-7-SMe_2-1,8-$C_2B_9H_8$] (1)

Ethene was bubbled through a stirred suspension of [$(C_8H_{14})_2IrCl]_2$ (150 mg, 167 μmol) in THF (15 ml) for 15 min. Resulting yellow solution was added to Tl[9-SMe_2-7,8-Me_2-7,8-$C_2B_9H_8$] (150 mg, 350 μmol) and cooled to −10 °C. Then the mixture was stirred with a slow temperature rise from −10 to −7 °C during 2 h, warmed to the RT and stirred for 2 h more. The solvent was