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Synthesis of the iridacarborane halide complexes $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})IrX_2]_2$ (X = Cl, Br, or I)

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The reaction of $Na[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]$ with $[(Cod)IrCl]_2$ (Cod is cycloocta-1,5-diene) gave rise to the iridium complex $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Ir(Cod)$. Treatment of the latter with anhydrous acids HX (X = Cl, Br, or I) afforded the corresponding iridacarborane halide complexes $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})IrX_2]_2$ analogous to the cyclopentadienyl complexes $[(C_5Me_5)IrX_2]_2$.

Key words: metallacarboranes, iridium.

Cyclopentadienyl halide rhodium and iridium complexes $[(C_5Me_5)MX_2]_2$ (M = Rh or Ir) are widely used in the synthesis of organic derivatives of these metals.[1] Previously, we have reported the synthesis of the rhodacarborane halide complexes $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ (X = Cl, Br, or I),[2] which represent metallacarborane analogs of compounds $[(C_5Me_5)RhX_2]_2$. These complexes contain the carborane ligand $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (**1**) isolobal with the cyclopentadienide anion. The above-mentioned compounds were prepared by the reactions of (cyclooctadiene)rhodacarborane $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(Cod)$ (Cod is cycloocta-1,5-diene) with aqueous hydrohalic acids HX. In the present study, we prepared iridium analogs of these complexes.

Results and Discussion

The reaction of $[(Cod)IrCl]_2$ with $Na[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]$ [3] afforded (cyclooctadiene)iridacarborane (**2**) (*cf.* Ref. 4) (Scheme 1). The reactions of **2** with hydrohalic acids gave rise to iridacarborane halide complexes **3a—c** (see Scheme 1). However, these reactions proceeded much more slowly than those involving the rhodium complex. The reactions performed with the use of aqueous hydrohalic acids were completed in several days. We succeeded in substantially increasing the reaction rate using solutions of anhydrous acids HX in acetic acid.

Compounds **2** and **3a—c** were characterized by elemental analysis and ^1H and ^{11}B NMR spectroscopy (Table 1). The NMR spectra of these compounds are similar to those of other transition metal π-complexes of anion **1** and, in particular, to the spectra of the corresponding rhodium complexes (see Refs. 2 and 4).

Complexes **3a—c** are air-stable bright-colored crystalline compounds, which are poorly soluble in Me_2CO and MeCN, but are readily soluble in strongly coordinating solvents, such as DMSO and DMF. These facts as well as the similarity of **3a—c** with the complexes $[(C_5Me_5)IrX_2]_2$ suggest that the compounds under study have dimeric structures. Apparently, dissolution in strongly coordinating solvents led to splitting of the dimer to form the solvate complexes $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})IrX_2(Solv)$.

Scheme 1

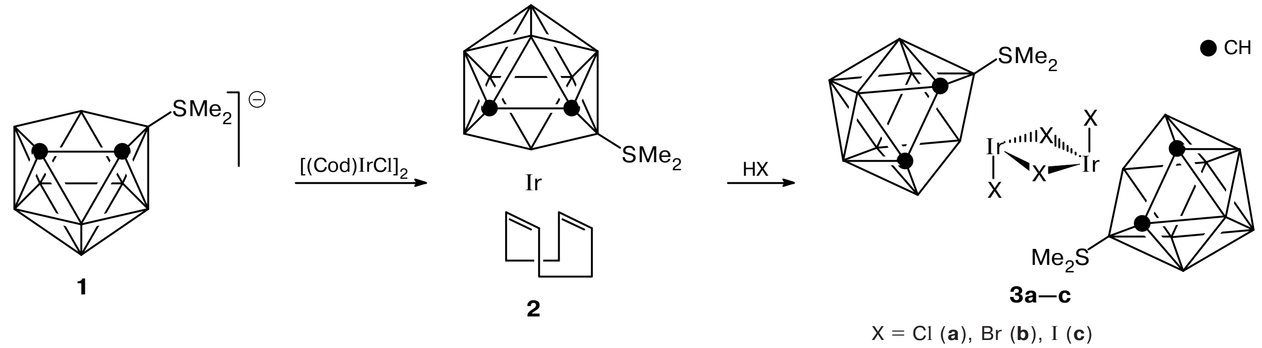

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Table 1. Parameters of the ^{1}H and ^{11}B{ ^{1}H} NMR spectra of compounds **2** and **3a—c**

Compound	Solvent	δ	
		^{1}H	^{1}B{^{1}H}
2	$(CD_3)_2CO$	1.98—1.89 (m, 2 H, CH_2); 2.34—2.25 (m, 2 H, CH_2); 2.51—2.41 (m, 2 H, CH_2); 2.61 (s, 3 H, SMe_2); 2.69—2.63 (m, 2 H, CH_2); 2.86 (br.s, CH of carborane); 2.90 (s, 3 H, SMe_2); 3.45 (br.s, CH of carborane); 3.85—3.80 (m, 2 H, CH); 4.04—3.99 (m, 2 H, CH)	−25.36 (2 B); −22.70 (1 B); −14.35 (1 B); −13.72 (1 B); −11.26 (1 B); −9.17 (1 B); −7.55 (1 B); −6.56 (1 B)
3a	DMF-d_7	2.96 (s, 3 H, SMe_2); 3.01 (s, 3 H, SMe_2); 5.42 (br.s, 1 H, CH); 6.38 (br.s, 1 H, CH)	−26.53 (1 B); −9.69 (1 B); −8.90 (2 B); −5.98 (1 B); −3.05 (2 B); 8.96 (1 B); 10.67 (1 B)
3b	DMF-d_7	2.90 (s, 3 H, SMe_2); 2.97 (s, 3 H, SMe_2); 5.39 (br.s, 1 H, CH); 6.38 (br.s, 1 H, CH)	−27.52 (1 B); −13.92 (1 B); −11.57 (2 B); −10.28 (1 B); −4.87 (2 B); 5.04 (1 B); 9.39 (1 B)
3c	DMF-d_7	2.92 (s, 3 H, SMe_2); 3.04 (s, 3 H, SMe_2); 5.39 (br.s, 1 H, CH); 6.18 (br.s, 1 H, CH)	−28.47 (1 B); −19.65 (1 B); −17.05 (1 B); −14.02 (1 B); −10.97 (1 B); −6.97 (1 B); −5.79 (1 B); −1.03 (1 B); 7.90 (1 B)

Experimental

Complex **2** was synthesized under an atmosphere of argon. Complexes **3a—c** were synthesized in air. A solution of Na[9-SMe_2-7,8-$C_2B_9H_{10}$] in THF was prepared according to a procedure described previously.[3] The NMR spectra were recorded on a Bruker AMX-400 instrument (400 MHz for ^{1}H and 128 MHz for ^{11}B) relative to the residual protons of the solvent (^{1}H) or $BF_3 \cdot Et_2O$ (external standard, ^{11}B).

(Cycloocta-1,5-diene)(9-dimethylsulfonio-7,8-dicarbollyl)iridium (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(C_8H_{12}) (2). The complex [(Cod)IrCl]$_2$ (134 mg, 0.2 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer and then a solution of Na[9-SMe_2-7,8-$C_2B_9H_{10}$] in THF (1.8 mL of a 0.24 *M* solution, 0.43 mmol) was added. The reaction mixture was stirred for 8 h, and the color of the solution slowly changed from bright-red to pale-orange. After completion of the reaction, MeOH (15 mL) was added. The precipitate that formed was filtered off, washed with MeOH (4×3 mL), and reprecipitated with MeOH from THF. After drying, complex **2** was obtained as needle-like white crystals in a yield of 146 mg (74%). Complex **2** is air-stable and is well soluble in acetone, CH_2Cl_2, and THF.

Found (%): C, 29.24; H, 5.69; B, 19.66. $C_{12}H_{28}B_9IrS$. Calculated (%): C, 29.18; H, 5.71; B, 19.70.

Bis[dihalogeno(9-dimethylsulfonio-7,8-dicarbollyl)iridium] [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)IrX_2]$_2$ (X = Cl, Br, or I) (3a—c). A suspension of (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(Cod) (**2**) (79 mg, 0.16 mmol) in acetic anhydride (6 mL) was cooled to 0 °C. Then a concentrated aqueous solution of HX (1 mL) was slowly added through a septa using a syringe. The color of the solution rapidly changed from white to bright-red in the case of **3a,b** and to brown in the case of **3c**. The reaction mixture was stirred for 18 h. Then water (20 mL) was added. The precipitate that formed was filtered off, washed with a small amount of acetone, isopropyl alcohol, and ether, and dried *in vacuo.*

Compound 3a. The yield was 63 mg (86%). Found (%): C, 11.04; H, 3.79; B, 21.15. $C_8H_{32}B_{18}Cl_4Ir_2S_2$. Calculated (%): C, 10.52; H, 3.53; B, 21.31.

Compound 3b. The yield was 86 mg (98%). Found (%): C, 9.02; H, 2.58; B, 17.49. $C_8H_{32}B_{18}Br_4Ir_2S_2$. Calculated (%): C, 8.81; H, 2.96; B, 17.83.

Compound 3c. The yield was 100 mg (97%). Found (%): C, 7.45; H, 2.30; B, 15.41. $C_8H_{32}B_{18}I_4Ir_2S_2$. Calculated (%): C, 7.51; H, 2.52; B, 15.21.

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