Acenaphthylene-1,2-diamine radical cation. 
Molecular structure of the [(dpp-BIAN)H₂]⁺+[X]⁻ complex 
((dpp-BIAN)H₂ is N,N'-bis(2,6-diisopropylphenyl)-acenaphthylene-1,2-diamine; X = Cl or I)

I. L. Fedushkin,* N. M. Khvoinova, A. Yu. Baurin, and G. K. Fukin

Fax: +7 (831 2) 62 7497. E-mail: igorfed@imoc.sinn.ru

Oxidation of N,N'-bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diamine (dpp-BIAN)H₂ with silicon tetrachloride or mercury(II) chloride affords the [(dpp-BIAN)H₂]⁺+[Cl]⁻ compound. The corresponding iodine derivative, [(dpp-BIAN)H₂]⁺+[I]⁻, was prepared by hydrolysis of the reaction products of the magnesium complex (dpp-BIAN)Mg(THF)₃ with tetraiodosilane. X-ray diffraction study demonstrated that the [(dpp-BIAN)H₂]⁺ radical cation in these compounds chelates the corresponding halide anion.

Key words: acenaphthylene-1,2-diamines, diamines, oxidation, radical cations, chelation of halide ions, X-ray diffraction study, ESR spectroscopy.

In the last decade, acenaphthene-1,2-diimines (BIAN) have been widely used as ligands in coordination chemistry. Transition metal complexes with diimine ligands are efficient catalysts for alkylene hydrogenation, carbon—carbon bond formation, cyclosimerization, hydroisylation, polymerization of alkenes and acrylic monomers, and copolymerization of CO₂ and methylenecyclopropene, of ethylene and norbornene, and of CO and styrene. The so-called Brookhart catalysts, vic., acenaphthene-1,2-dimine complexes of transition metals, are the most well-known olefin polymerization catalysts. The π-acceptor properties of acenaphthene-1,2-diimines in metal complexes induce an electron deficiency at the metal atom, which is responsible for high reactivity of these complexes toward organic compounds.

In our recent studies, we have demonstrated that main-group metals, unlike transition metals, can form complexes with different anionic forms of BIAN ligands. We used primarily 1,2-bis(2,6-diisopropylphenyl)iminoacenaphthene (dpp-BIAN). A remarkable property of the dpp-BIAN ligand is that it shows variable "oxidation states" in complexes with main-group metals. Diamine dpp-BIAN can be reduced with alkali metals in ethereal media to the mono-, di-, tri-, and tetraanions to form the (dpp-BIAN)Mₙ(Et₂O)ₙ salts (M = Li or Na; n = 1—4). In tetrahydrofuran, alkaline-earth metals reduce dpp-BIAN only to the dianion to give the monomeric (dpp-BIAN)M(THF)ₙ complexes (M = Mg, Ca, Sr, or Ba; n = 2—4). Reduction of dpp-BIAN with metallic aluminum in the presence of its halides in toluene or Et₂O affords the radical-anionic compound (dpp-BIAN)AlCl₂ and the dianionic products (dpp-BIAN)AlI(Et₂O) and (dpp-BIAN)AlCl(Et₂O), respectively. We synthesized aluminum alkyl complexes with both the radical-anionic and dianionic dpp-BIAN ligands by the exchange reactions of the corresponding sodium derivatives of dpp-BIAN with alkylaluminum halides. The reactions of sodium salts of dpp-BIAN with the dioxane complex of GeCl₃ gave the divalent germanium compounds (dpp-BIAN)GeCl and (dpp-BIAN)GeCl₂. Using the (dpp-BIAN)Mg(THF)₃ complex (1) with the dianionic dpp-BIAN ligand as an example, we demonstrated that acenaphthene-1,2-diimine complexes of main-group metals have specific reactivity toward various organic compounds. Complex 1 acts as a one-electron reducing agent for organic halides and aromatic ketones. The reactions of 1 with compounds containing a labile hydrogen atom, for example, with aliphatic ketones, nitriles, and phenylacetylene, involve the addition of these substrates to the complex through protonation of one nitrogen atom of the dpp-BIAN ligand to give, respectively, enolate, ketimide, and phenylethynyl derivatives. Hydrolysis of complex 1 in vacuo yields acenaphthylene-1,2-diamine (dpp-BIAN)H₂(2), which is immediately transformed into acenaphthene-1,2-diimine dpp-BIAN when exposed to atmospheric oxygen (Scheme 1). Recently, we have observed the transformation of the dpp-BIAN radical anion into the (dpp-BIAN)H₂ radi...
In the present study, we performed oxidation ofacenaphthylene-1,2-diamine (dpp-BIAN)H₂ with mercuric(II) and silicon(IV) chlorides giving rise to the radical-cationic derivative [(dpp-BIAN)H₂]⁺[Cl]⁻ (3). The iodine analog [(dpp-BIAN)H₂]⁺I⁻ (4) was synthesized by the reaction of compound 1 with SiI₄ followed by hydrolysis.

**Scheme 2**

![Scheme 2](image)

In the present study, we performed oxidation ofacenaphthylene-1,2-diamine (dpp-BIAN)H₂ with mercuric(II) and silicon(IV) chlorides giving rise to the radical-cationic derivative [(dpp-BIAN)H₂]⁺[Cl]⁻ (3). The iodine analog [(dpp-BIAN)H₂]⁺I⁻ (4) was synthesized by the reaction of compound 1 with SiI₄ followed by hydrolysis.

**Results and Discussion**

**Synthesis of** [(dpp-BIAN)H₂]⁺[Cl]⁻ (3) and [(dpp-BIAN)H₂]⁺I⁻ (4).** After the addition of an excess of SiCl₄ to a solution of diamine 2 in tetrahydrofuran at room temperature, the color of the reaction mixture changed from violet to red and then to green. After removal of the solvent and volatile products *in vacuo*, compound 3 was obtained in 57% yield as dark-green prismatic crystals by crystallization of the solid residue from benzene (Scheme 3). An analogous transformation occurs in the reaction of diamine 2 with mercury(II) chloride.

**Scheme 3**

![Scheme 3](image)

Compound 2 reacts with neither iodine nor mercuric iodide. However, iodine analog of 3, *viz.*, the [(dpp-BIAN)H₂]⁺I⁻ compound (4), was generated by hydrolysis of the reaction mixture, which was obtained in the reaction of complex 1 with SiI₄ (Scheme 4).

**Scheme 4**

![Scheme 4](image)

This result was surprising. We expected that the reaction of compound 1 with SiI₄ would afford the (dpp-BIAN)SiI₂ compound. The latter, in turn, could serve as the starting reagent for the synthesis of silylene (dpp-BIAN)Si, which is a silicon analog of germylene (dpp-BIAN)Ge synthesized earlier. Unfortunately, we failed to isolate the primary product of this reaction in individual form. Apparently, the [(dpp-BIAN)H₂]⁺I⁻ compound (4) is formed as a result of the transformations presented in Scheme 4. The silicon derivative (tms-BIAN)SiCl₂ (tms is trimethylsilyl) analogous to the intermediate presented in Scheme 4 was prepared in the