



First example of the formation of a Si–C bond from an intramolecular Si–H···H–C dihydrogen interaction in a metallacarborane: A theoretical study

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ABSTRACT

The recently reported crystal structure of $[\text{NMe}_4][1\text{-SiMe}_2\text{H-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ shows short contacts between the Si–H proton acceptor group and the C_c–H proton donor moiety in the dicarbollide ligand. These short contacts were studied within the framework of the Quantum Theory of Atoms in Molecules (QTAIM) at different levels of DFT theory (B3LYP/6-311(d,p) and BP86/TZ2P(+)) that shows the existence of a bifurcated Si–H···H–C_c dihydrogen bond. This paper presents the study of an experimental uncommon Si–H group playing as proton acceptor bond in a dihydrogen bond where hydrides like M–H (M, as metal transition), B–H or Al–H usually perform this role. Furthermore, this paper accounts with a new simple method to estimate bonding energies for closed-shell intramolecular interactions in the scheme of Voronoi charge population analysis and Coulomb's Law.

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1. Introduction

In the course of our investigations to incorporate silane groups on the cluster carbon of the sandwich complex $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ we observed an unexpected reaction [1]. By mixing 1 equiv. of Me_2SiHCl with 1 equiv. of $[1\text{-Li-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^-$, at -40°C that expectedly should have produced $[1\text{-Me}_2\text{SiH-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^-$, it was obtained instead $[1,1'\text{-}\mu\text{-Me}_2\text{Si-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$. The reaction conditions implied that an intramolecular hydride-protonic reaction had taken place. This was unanticipated because the charges on both hydrogen atoms had to be very weak. The reaction is shown in Scheme 1. Our hypothesis was that a dihydrogen bond develops as a result of the favorable geometric characteristics of the cobaltabisdicarbollide anion, that weakens both the C_c–H and Si–H bonds producing a Si–C_c. The C_c–H stands for the hydrogen bonded to the cluster carbon. It is well established that agostic C–H interactions can significantly weaken the C–H bond, thereby rendering it susceptible to a wide range of inter- and intramolecular reactions. Likewise dihydrogen interactions may play an important role in lowering the activation energy for dihydrogen evolution and in influencing the generation of new covalent bonds. We could not find, however, any example in the literature of a Si–H and C–H interacting groups that at low temperatures evolved to a Si–C

bond. Thus we wanted to confirm first, the existence of a C_c–H···H–Si dihydrogen bond in $[1\text{-Me}_2\text{SiH-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^-$ and, second, its particular characteristics that made it to react so uniquely.

The dihydrogen bond (DHB) is a type of unconventional hydrogen bond in which a proton donating moiety D–H interacts with a proton acceptor A–H, see Scheme 2. They display characteristics similar to conventional hydrogen bonding [2].

The usual functional groups performing proton donating characteristics are F–H, O–H, N–H or C–H with a remarkable excess of positive charge on the hydrogen atom, and the usual proton acceptor groups contain hydridic atoms connected to Al, B, Ga, Ir, Mo, Mn, Os, Re, Ru or W atoms. Other systems have been described where two interacting hydrogen atoms do not show a clear protic and hydridic character [3]; it is the case of the H–H bonding interaction. The latter results from the close approach of two bonded hydrogen atoms bearing the same or similar net charges that stabilize the whole system. While it is also a closed shell interaction, the H–H bonding is distinct from DHB in its atomic and geometric characteristics [4]. Since the first DHB was found [5] until present, the DHB has been extensively studied in theoretical and experimental aspects [6]. The Quantum Theory of Atoms in Molecules of Bader [7] (QTAIM) is an important tool often applied to study DHB; Popelier established a sort of criteria based on the QTAIM to characterize DHB [8], and recently, Alkorta and co-workers [6b] have applied natural bond orbital methods (NBO) to determine whether intramolecular H···H interactions can be classified as DHB.

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