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σ-Borane complexes of nickel, palladium and platinum: A theoretical study

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Abstract

Quantum chemical calculations at the gradient corrected DFT level using the exchange correlation functionals BP86 of the complexes $[(dmpe)M(HBR_2)]$ (M = Ni, Pd, Pt; R = Et, Me) are reported. The calculated electronic and molecular structures of the complexes $[(dmpe)M(HBR_2)]$ (M = Ni, Pd; R = Et, Me) are consistent with $[(dmpe)M(\eta^2\text{-}HBR_2)]$ being Ni(0) and Pd(0) complexes in which both hydrogen and boron of the $[HBR_2]$ ligands have a bonding interaction with the metal preserving B–H bond character. The results of the theoretical investigation suggest that the complex $[(dmpe)Pt(HBEt_2)]$ is a platinum(II) hydride boryl complex rather than σ-borane complex, while complex $[(dmpe)Pt(HBMe_2)]$ with some residual B–H interaction, is an example of elongated σ-borane complex. The nature of the metal–ligand interactions is quantitatively analyzed with an energy decomposition analysis. The bond dissociation energy is slightly larger in $[(dmpe)M(\eta^2\text{-}HBMe_2)]$ than in $[(dmpe)M(\eta^2\text{-}HBEt_2)]$ (M = Ni, Pd). The values of interaction energy, ΔE_{int} as well as orbital interactions ΔE_{orb} decrease on going from nickel to palladium. For M-η^2-H-BR_2 (M = Ni, Pd) bonds, the contribution of electrostatic attractions ΔE_{elstat} are greater than the orbital interactions, ΔE_{orb}. The repulsive terms ΔE_{Pauli} were larger in each case. All four $[(dmpe)M(HBR_2)]$ (M = Ni, Pd; R = Et, Me) complexes exhibit about 40–44% covalent bonding of the borane ligand to the metal fragment. For the platinum complexes $[(dmpe)Pt(HBR_2)]$ (R = Et, Me), the preparation energy, ΔE_{prep} as well as interaction energy, ΔE_{int} and its components, ΔE_{Pauli}, ΔE_{elstat}, and ΔE_{orb} are large, since the HBR_2 unit near the dissociation limit. The complex $[(dmpe)Pt(HBMe_2)]$ is intermediate between σ-borane complexes and hydride boryl complex.

Keywords: Borane complexes; Structure; Bonding analysis; DFT calculations

1. Introduction

Transition metal σ-complexes have attracted much attention due to their role in the oxidative addition and reductive elimination steps occurring in a wide variety of catalytic processes [1]. Since the report of the first dihydrogen σ-complex [2] in 1984, numerous examples of σ-dihydrogen [3–11] and σ-silane [12–21] complexes have been reported. In contrast to the large number of dihydrogen complexes and σ-silane complexes, reports on stable σ-borane complexes are scarce (Chart 1) [22–29]. σ-Borane complexes of titanium, manganese and rhenium reported by Hartwig et al. are the most representative examples with coordination of the B–H bond of a neutral borane to a transition metal center [22–25]. Sabo-Etienne et al. have reported σ-borane complexes of ruthenium [28,29]. Garcia and coworker have recently reported the σ-borane complexes of nickel(0) [30]. Synthesis and bonding of the transition metal complexes containing residual B···H interaction have been reported [31–38]. Mechanistic studies have revealed that σ-borane complexes can be intermediates in catalytic hydroboration processes [33,39–41].

Theoretical calculations have been performed for σ-borane complexes of titanium [22,40], manganese [42], rhenium [43] and ruthenium [29] as well as σ-borate complexes $[(\eta^5\text{-}C_5H_5)_2Nb\{H_2B(OH)_2\}]$ [44], $[(\eta^5\text{-}C_5H_5)_2Nb\{H_2B(C_8H_{14})]$ and $[\eta^5\text{-}C_5H_5)_2Nb\{H_2B(H)_2\}]$ [45].

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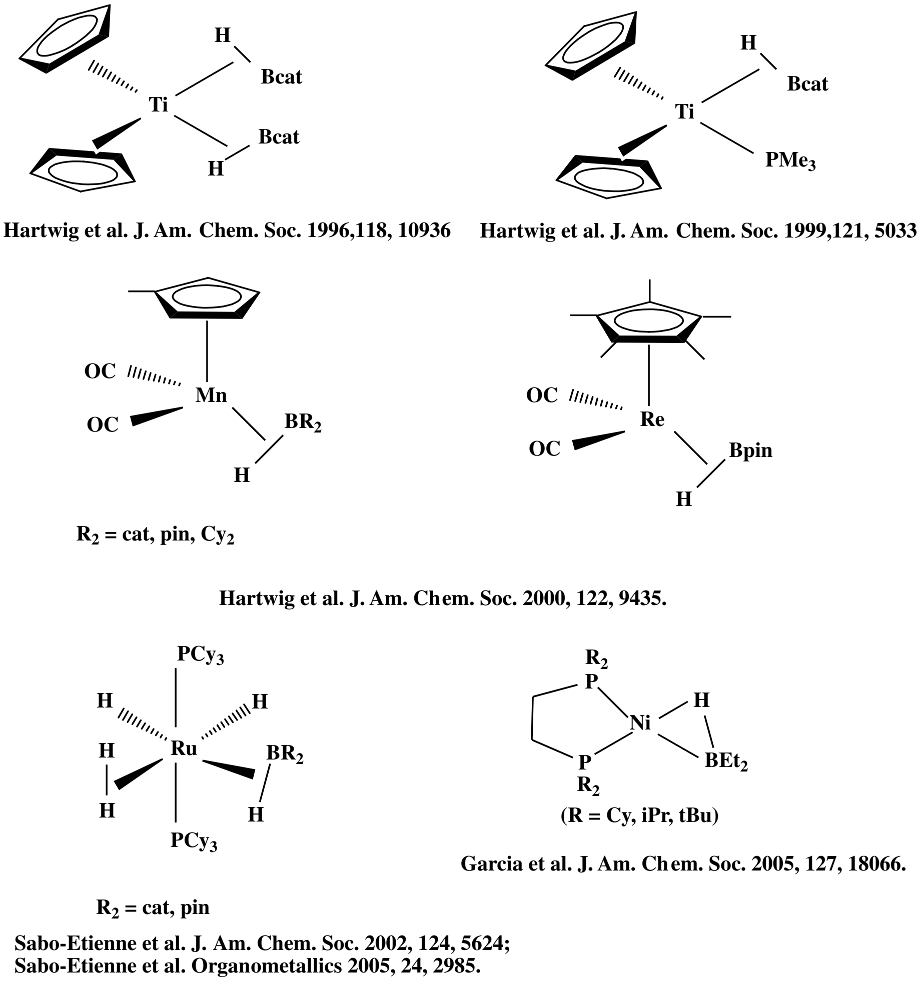

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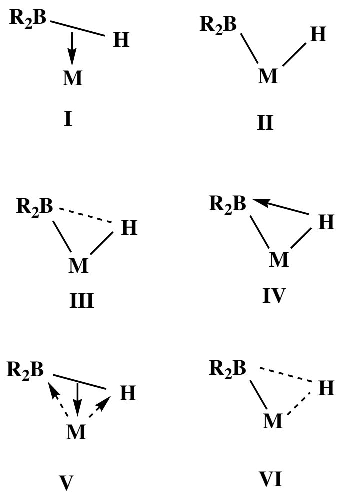
Chart 1. Overview of experimentally known metal-*s*-borane complexes.

The possible valence bond representations for M-HBR$_2$ moiety is presented in Chart 2. A main question concerns whether the bonding tends more towards the σ-borane complex **I** or to the classical oxidative addition product hydride boryl complex **II**. Structures **III** and **IV** are consistent with structure **II** with some residual B–H interaction. Structure **V** favors appreciable retention of B–H bond as in structure **I** with substantial donation of metal electron density to the borane by M → B back bonding. Structure **VI** represents the hydride as bridging between the M and B centers with a three center-two electron bond. The three center-two electron bond in M–H–B bridge may be regarded as a "protonated π-bond". This description is in accord with the 3c–2e bond study of Lammertsma and Ohwada [46]. Many factors can affect the relative stabilities of structures I and II, such as behavior of the ancillary ligands, substitutions on the boron atom and the replacement of one metal center by other. A number of elongated dihydrogen complexes with the H···H distances between 1 and 1.5 Å (representing structures **III** and **IV**) have been reported [11,47–49].



R = Me, Et; M = Ni, Pd, Pt

Chart 2.

In this paper, six complexes [(dmpe)M(HBR$_2$)] (dmpe = 1.2-bis(dimethylphosphino)ethane; **1NiEt**, M = Ni, R = Et;**1PdEt**, M = Pd, R = Et; **1PtEt**, M = Pt, R = Et; **2NiMe**, M = Ni, R = Me; **2PdMe**, M = Pd, R = Me;