

A Semi-Empirical Study of $(B_3H_3N_3H_3)Cr(CO)_3$

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(Received 4th November, 1998, revised 6th August, 1999)

Summary: A semi-empirical molecular orbital calculation at the PM3 level has been done on the borazine chromium carbonyl complex, $(B_3H_3N_3H_3)Cr(CO)_3$. The results of our calculation show that the B_3N_3 ring atoms of borazine favour a nonplanar ring unlike the arene complex $(\eta^6-C_6H_6)Cr(CO)_3$ and $(\eta^6-C_6Me_6)Cr(CO)_3$. The Cr atom is pseudo octahedral having the six coordinate positions occupied by three-CO groups and three -N atoms with the CO group located trans to the nitrogen atoms. The puckered borazine ring gave a Cr-N distance of 2.14 Å and a Cr - B distance of 2.30 Å. Other data including the B-N distance, formal charge on B and N and the barrier to rotation will be presented and compared with experimental data taken on the hexaethylborazine chromium tricarbonyl complex.

Introduction

Molecular orbital calculations of the delocalization energies of various arene - and borazine - chromium tricarbonyl complexes have shown that the interaction energy of the borazine - chromium system is less than the corresponding benzene - chromium system [1]. These previous calculations were used to suggest that π -bonded complexes between borazine ring and $Cr(CO)_3$ were possible. The benzene complex, $(C_6H_6)Cr(CO)_3$, has been shown to have a planar benzene ring in which its bonding to chromium is described in terms of the donation of the benzene π orbitals to the metal atom [2,3]. Arene complexes of benzene such as $(\eta^6-C_6Me_6)Cr(CO)_3$ show C-C bond lengths that are usually equivalent with some small differences [4].

The photochemical reaction of $Cr(CO)_6$ with $B_3R_3N_3R_3$ was used to prepare the metal complex, $(B_3R_3N_3R_3)Cr(CO)_3$ [5]. These complexes have also been synthesized by displacement of ligands from the metal carbonyl, $(CH_3CN)_3Cr(CO)_3$ [6]. Initially, the bonding in these complexes was described in terms of a planar borazine ring similar to analogous benzene complexes [5(a), 6(b)]. An X-ray structure of the hexaethylborazine chromium tricarbonyl complex has shown that the nitrogen atoms are located trans to the carbonyl groups and the borazine ring is not planar [7]. Because the X-ray structure indicated a puckered ring with Cr-N and Cr-B distances of 2.22 Å and 2.31 Å, respectively, it was suggested that hexaethylborazine chromium

tricarbonyl is not a π -complex. Instead σ -bonding of the nitrogen atoms to the chromium atom was proposed. Thus the nitrogen atoms of the borazine ring act as tridentate ligand with sigma bonding to chromium. Other half sandwich complexes of $Cr(CO)_3$ moiety have been reported and based on their ¹H-NMR and electronic spectral data, a puckered borazine ring σ -bonded to Cr through the nitrogen atoms has also been suggested [6(c)]. This is in contrast to the original suggestion, based on similar carbonyl stretching frequencies, that the borazine and benzene chromium tricarbonyls were identical in the nature of their bonding [6(b)].

We now report a detailed semi-empirical MO calculation done at the PM3 level on the complex, $(B_3H_3N_3H_3)Cr(CO)_3$.

Results and Discussion

The results of our calculations show that the borazine B_3N_3 ring atoms are not planar. The chromium atom is pseudo octahedral having the six-coordinate positions occupied by three carbonyl groups located trans to three nitrogen atoms (Fig. 1a). The π -ring character of borazine is reduced in this complex as shown by the slightly longer B-N distance in the complex (1.50 Å) compared to borazine (1.44 Å) [8]. The lengthening of the B-N bond is probably due to the π -electron donation to the metal orbitals. This change from our calculations

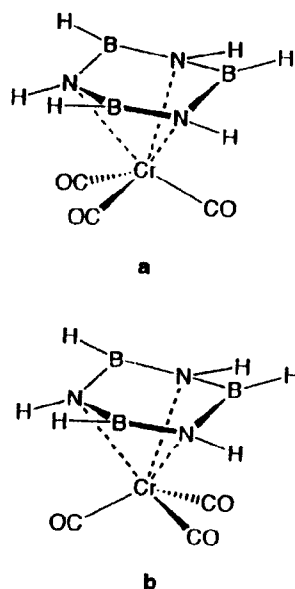


Fig. 1: $(B_3H_3N_3H_3)Cr(CO)_3$ conformations (a) BH over CO (b) NH over CO.

gave an increase in the nitrogen atom's formal charge by +0.16, whereas, the boron atom's charge changes only slightly (+0.06). This latter result is consistent with the small change in the B-CH₃ vibrations in hexamethylborazine upon complexation with $Cr(CO)_3$, [6(c)]. The large value for boron, 1/3 of the value for nitrogen, would make an argument for π -bonding in the complex.

Our calculations also gave Cr-N and Cr-B distance of 2.14 Å and 2.30 Å respectively. These values compare favourably with the experimental values noted above. The X-ray structure determination indicated that the plane of the nitrogen atoms was 0.07 Å closer to the chromium atom than was the plane of the boron atoms compared to our computed structure of 0.10 Å. The longer Cr-N distance (2.22 Å) in the reported X-ray structure of $B_3N_3(C_2H_5)_6Cr(CO)_3$ is probably due to an added steric interaction in which two of the N-C₂H₅ groups are bent towards the Cr atom [7]. The three B-C₂H₅ and one N-C₂H₅ groups are bent up from the puckered borazine ring for an experimental Cr-B distance (2.31 Å) similar to our value (2.30 Å).

A bond dissociation energy of the hexa-alkylborazines ($R-CH_3$, C_2H_5) from $Cr(CO)_3$ is about

25 kcal/mol with a corresponding value of 49 kcal/mole for the π -arene complex, $(\eta^6-C_6Me_6)Cr(CO)_3$ [9]. This data along with electronic spectral results support the poor π -acceptor character of the borazine ring compared to an arene ring, yet both have similar donor characteristics [6(c), 10].

Finally, we calculated the barrier to rotation by 60° to be + 18.3 kcal/mole for placing the N-H groups over the CO groups (transition state) compared to the B-H groups over the CO groups (ground state) (Figure 1b) which is in agreement with that reported earlier by Hoffmann [12]. A smaller 0.3 kcal/mole rotational barrier for the staggered geometry of $\eta^6-C_6H_6 Cr(CO)_3$ to the eclipsed geometry was done by EHT calculations [11] and this value compares favorably with our PM3 level calculations for $\eta^6-C_6H_6 Cr(CO)_3$, corrected for ZPE, as 0.35 kcal/mole.

Our calculations also have the one imaginary frequency required for the transition state (NH over CO). This larger activation energy value also provides good evidence for a puckered borazine ring in our complex. Indeed, a bond dissociation energy of 25 kcal/mole indicates that rotation of the puckered borazine ring is not favoured. An activation energy of 18.3 kcal/mole also indicates that a 60° rotation results in breaking most of the 25 kcal/mole bonding that holds the borazine ring to the $Cr(CO)_3$ fragments. One might expect that a π -bonded borazine to $Cr(CO)_3$ would have a much lower activation energy. NMR T₁ measurements at -100°C on crystalline $(C_6H_6)Cr(CO)_3$ give a higher activation energy of 4.2 kcal/mole than our calculated value (0.35 kcal/mole) which was mainly accounted for by packing forces [12]. More recent investigations give a rotational barrier of about 0.8 kcal/mole [13].

It is interesting to compare our calculated activation energy for the borazine- $Cr(CO)_3$ complex with that of the trimethylenemethane - $Fe(CO)_3$ complex. The three orbitals of $Fe(CO)_3$, assuming a pseudo-octahedral geometry, give a staggered geometry with the titled CH₂ groups over the bonding orbitals of iron [13]. Rotation of the $Fe(CO)_3$ by 60° reduces the delocalized overlap of the iron orbitals with the carbon 2p-orbitals at the methylene giving a rotational barrier from EHT to

be about 23.6 kcal/mole [14] compared to NMR data of 19-20 kcal/mole [15]. This is analogous to our rotational barrier for the borazine - Cr(CO)₃ complex where the Cr(CO)₃ group and the puckered ring bonding is reduced by locating the carbonyls over the nitrogens which places the metal bonding orbitals on chromium over the boron atoms.

All of our data taken as a whole is in agreement with a recent theoretical study of B₃H₃N₃H₃-Cr(CO)₃ done at a higher computational level which argues that the puckering of the borazine ring is due to repulsive interactions [16]. Similar bond lengths for Cr-N (2.25 Å), Cr-B (2.39 Å) and B-N (1.52 Å) are reported with a rotational barrier of 5.3 kcal/mol for the unsubstituted borazine ring. The data further shows that both nitrogen and boron are involved in ring to metal and metal to ring donations; indicating that borazine does not act as a triamine (sigma) ligand.

We have extended our calculations to include some preliminary data on the heats of formation of hexaethylborazine in various conformations of the ethyl group for an isolated molecule. The data ranges from 199 kcal/mol for the ethyl groups to have an alternate up down arrangement to 205 kcal/mol for an all up configuration. The actual configuration must in part be determined by packing forces as an X-ray study of hexaethyl borazine has alternating up and down ethyl groups [17]. For the hexaethylborazine - Cr(CO)₃ complex an all up ethyl group configuration has a heat of formation of 242 kcal/mol compared to an all down ethyl group configuration (231 kcal/mol). The X-ray structure of the complex has two N-Et down and four groups up (three B-Et, one N-Et) [7]. This configuration for the isolated molecule has a heat of formation of 238 kcal/mol again suggesting that packing forces are important. Substitution of ethyl groups on the borazine ring seems to have no appreciable change in the nature of its bond [7].

Likewise in a phenyl-borazine compound where a choice of a coordination site is available, ¹H and ¹¹B nmr spectral data indicates exclusive bonding of the chromium tricarbonyl moiety to the phenyl ring rather than the borazine ring [18].

Experimental

The molecular orbital calculations were performed on (B₃H₃N₃H₃)Cr(CO)₃ at the PM3 level

using PC Spartan Plus [19]. Geometry optimization resulted in the nitrogen atoms being staggered with respect to the carbonyl groups. A transition state calculation was done on the 60° rotamer with the boron atoms staggered with respect to the carbonyl groups. Frequency calculations showed the former structure to be an energy minimum; and the latter to be a first-order saddle point with one imaginary frequency. Zero point energy corrections were made in computing the activation energy.

Conclusions

Our calculations reproduce all of the features of the borazine chromium tricarbonyl complex, and it is in agreement with known experimental data and theoretical data. We intend to refine our energy calculations by doing large basis set ab initio computations on the hexaethylborazine chromium tricarbonyl complex.

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