Structure and Bonding of Transition Metal−Boryl Compounds. Theoretical Study of $[(PH_3)_2(CO)ClOs-BR_2]$ and $[(PH_3)_2(CO)_2ClOs-BR_2]$ ($BR_2 = BH_2, BF_2, B(OH)_2$, B(OCH═CHO), Bcat)†

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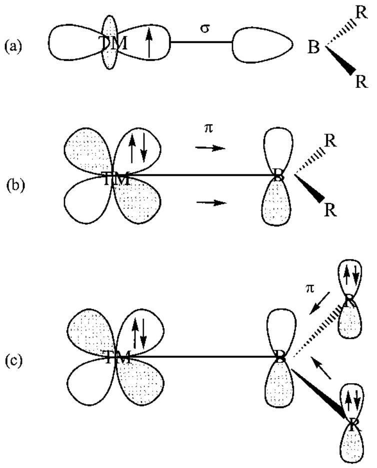
Quantum chemical DFT calculations using the B3LYP functionals have been carried out for the electronically unsaturated 16 VE five-coordinate osmium boryl−complexes $[(PH_3)_2(CO)ClOs-BR_2]$ and the 18 VE six-coordinate complexes $[(PH_3)_2(CO)_2ClOs-BR_2]$ with $BR_2 = BH_2, BF_2, B(OH)_2$, B(OHC═CHO), and Bcat (cat = catecholate $O_2C_6H_4$). The bonding situation of the Os−BR$_2$ bond was analyzed with the help of the NBO partitioning scheme. The Os−B bond dissociation energies of the 16 VE complexes are very high, and they do not change very much for the different boryl ligands. The 18 VE complexes have only slightly lower bond energies than the 16 VE species. The Os−B bond in both classes of compounds is provided by a covalent σ-bond which is polarized toward osmium and by strong charge attraction. Os→B π-donation is not important for the Os−B binding interactions, except for the Os−BH$_2$ complexes. The stability of the boryl complexes [Os]−BR$_2$ comes mainly from B←R π-donation, which is clearly higher than the Os→B π-donation. The intraligand charge distribution of the BR$_2$ group changes little when the Os−B bond is formed, except for BH$_2$. The CO ligand in $[(PH_3)_2(CO)_2ClOs-BR_2]$ which is trans to BR$_2$ has a relatively weak bond to the osmium atom.

Introduction

Transition metal−boryl (TM−BR$_2$) complexes received much attention by experimental chemists in the past few years, because the compounds may be used as versatile catalysts in various boration reactions.[1] Two recent reviews summarized the progress which has been made in the field.[2,3] Both reviews pointed out that the impressive knowledge about the synthesis, structure, and reactivity of boryl complexes which has been gained by experiment stands in contrast to the vague knowledge about the binding situation and the factors which influence the metal−boryl bond. The nature of the TM−BR$_2$ bonding is usually discussed in terms of a covalent two-electron, two-center σ-bond, which may be additionally stabilized by TM→BR π-donation (Scheme 1). The boron atom may also become electronically stabilized by B←R π donation if the substituents R have lone-pair π-electrons.

A major point of discussion has been the extent of π-interactions between the metal d(π) and the boron p(π) orbitals and its influence on the metal−boron bond strength. Some experimental results have been interpreted in favor of weak TM−BR$_2$ π-interactions,[4] while other studies led to the conclusion that π-interactions in boryl complexes are negligible.[5] Several theoretical studies have been published about the mechanism of TM−boryl catalyzed reactions,[5,6] but only few investigations addressed the question about the bonding situation in boryl complexes.[7−9] Sakaki and Kikuno (SK) calculated the bond

Scheme 1. Schematic Representation of the Most Important Orbital Interactions in TM−Boryl Complexes: (a) Metal−Boron σ-Bond; (b) TM→B π-Donation; (c) B←R π-Donation



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† Theoretical Studies of Inorganic Compounds. XI. For part X, see: Uddin, J.; Boehme, C.; Frenking, G. *Coord. Chem. Rev.* **2000**, *197*, 249.

[1] (a) Brown, H. C.; Singaram, B. *Pure Appl. Chem.* **1987**, *59*, 879. (b) Burgess, K.; Ohlmeyer, M. *Chem. Rev.* **1991**, *91*, 1179. (c) Iverson, C. N.; Smith, M. R. *Organomet.* **1996**, *15*, 5155.

[2] Irvine, G. A.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

[3] Braunschweig, H. *Angew. Chem.* **1998**, *110*, 1882; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1787.

[4] (a) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908. (b) Hartwig, J. F.; Gala, S. R. D. *J. Am. Chem. Soc.* **1994**, *116*, 3661.

[5] Braunschweig, H.; Kollann, C.; Müller, M. *Eur. J. Inorg. Chem.* **1998**, 291.

[6] (a) Musaev, D. G.; Mebel, A. M.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10693. (b) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355. (c) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 742. (d) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 1383. (e) Dorigo, A. E.; Schleyer, P. v. R. *Angew. Chem.* **1995**, *107*, 108; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 115.

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energies of Pd and Pt boryl complexes with BH_2 and $B(OH)_2$ as ligands and found that the $Pd-BR_2$ and $Pt-BR_2$ bond energies for R = H and R = OH are very similar, while the H_2B-BH_2 bond is clearly weaker than the $(OH)_2B-B(OH)_2$ bond.[7] This finding was interpreted in terms of easier TM→B π-delocalization compared to HO→B π-donation. The electronic structure of the compounds was not analyzed, however.

An important contribution which is pertinent to the present paper was made by Rablen, Hartwig, and Nolan (RHN), who investigated theoretically and experimentally the bond dissociation energies of X−B bonds where X is either a main-group element or a transition metal.[8] The authors estimated that the Ir−B bond energy in *trans,cis*-$[(Cl)(H)(CO)(PPh_3)_2Ir(Bcat)]$ (cat = catecholate $O_2C_6H_4$) has a rather large value of 66 kcal/mol. RHN concluded that π-interactions do not play a role for explaining the large Ir−B bond energy. The opposite conclusion was made in a theoretical study of neutral and positively charged $TM-BH_2$ and $TM-B(OH)_2$ (TM = Sc, Co, Rh, Ir) compounds by Musaev and Morokuma (MM).[9] A comparison of the TM−B bond energies with the TM−H and $TM-CH_3$ dissociation energies led MM to conclude that the TM−B π-interactions are an important factor for the bond strength. The NBO analysis showed that the p(π) orbital of boron is indeed populated by TM→B π-donation, but the population analysis was restricted to $TM-BH_2$ complexes only.[9]

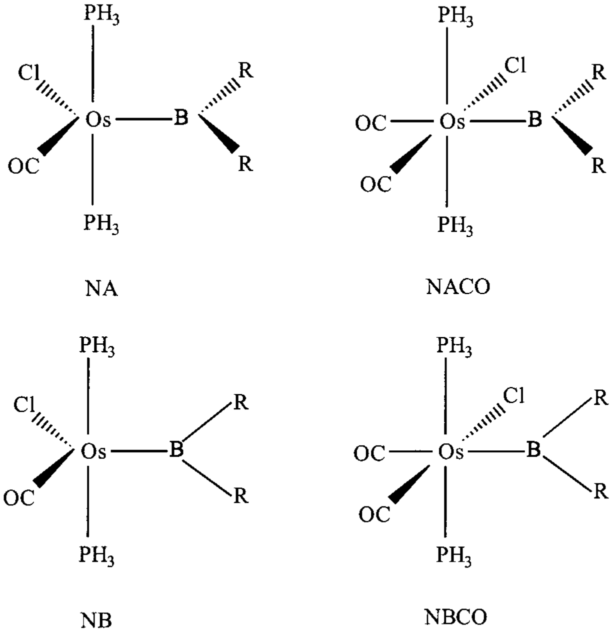
Another theoretical study which is relevant for the present work focused on the factors which influence the bond strength in boranes. Rablen and Hartwig (RH) found that the B−H and B−C bonds were essentially independent of the electronegativity, π-donating ability, and conjugative ability of the other substituents at boron.[10] A detailed study of substituted boranes pointed out, however, that lithiation weakens the π-bonding interactions between boron and π-donor substituents.[11]

The conflicting results about the importance of the $TM-BR_2$ π-interactions and the complete lack of information about the influence of the B←R π-donation on the bonding situation led us to carry out a theoretical study of the electronic structure of the osmium−boryl complexes $[(PH_3)_2(CO)ClOs-BR_2]$ and $[(PH_3)_2(CO)_2ClOs-BR_2]$ with $BR_2 = BH_2, BF_2, B(OH)_2$, B(OHC═CHO), and Bcat which are depicted in Scheme 2. The choice was made because the X-ray structures of the related five-coordinate complex $[(PPh_3)_2(CO)ClOs-BR_2]$ and the six-coordinate complex $[(PPh_3)_2(CO)_2ClOs-BR_2]$ with $BR_2 = B(OH)_2$ and Bcat have been reported in the literature.[2,12] A comparison of the results of the electronically unsaturated 16 VE complexes **1A**−**5B** with the 18 VE complexes **1ACO**−**5BCO** gives the opportunity to study the effect of attaching a CO ligand trans to the boryl group on the osmium−boron bond in the latter compounds. The present work complements our previous studies of transition metal complexes with group-13 ligand atoms which focused on diyl ligands ER.[13]

Theoretical Methods

All calculations were performed using the program package Gaussian98.[14] The geometry optimizations and the vibrational frequency analysis were carried out at the B3LYP level of theory.[15] We used our standard basis set II[16] for the calculations, which consists of a quasirelativistic small-core effective-core potential[17] with a (441/2111/

Scheme 2. Osmium Complexes Studied in This Investigation



NA

NACO

NB

NBCO

BH_2	N = 1
BF_2	N = 2
$B(OH)_2$	N = 3
B(OHC =CHO)	N = 4
Bcat	N = 5

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(7) Sakaki, S.; Kikuno, T. *Inorg. Chem.* **1997**, *2*, 2226.

(8) Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121.

(9) Musaev, D. G.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 6509.

(10) Rablen, P. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4648.

(11) Wagner, M.; Hommes, N. J. R. v. E.; Nöth, H.; Schleyer, P. v. R. *Inorg. Chem.* **1995**, *34*, 607.

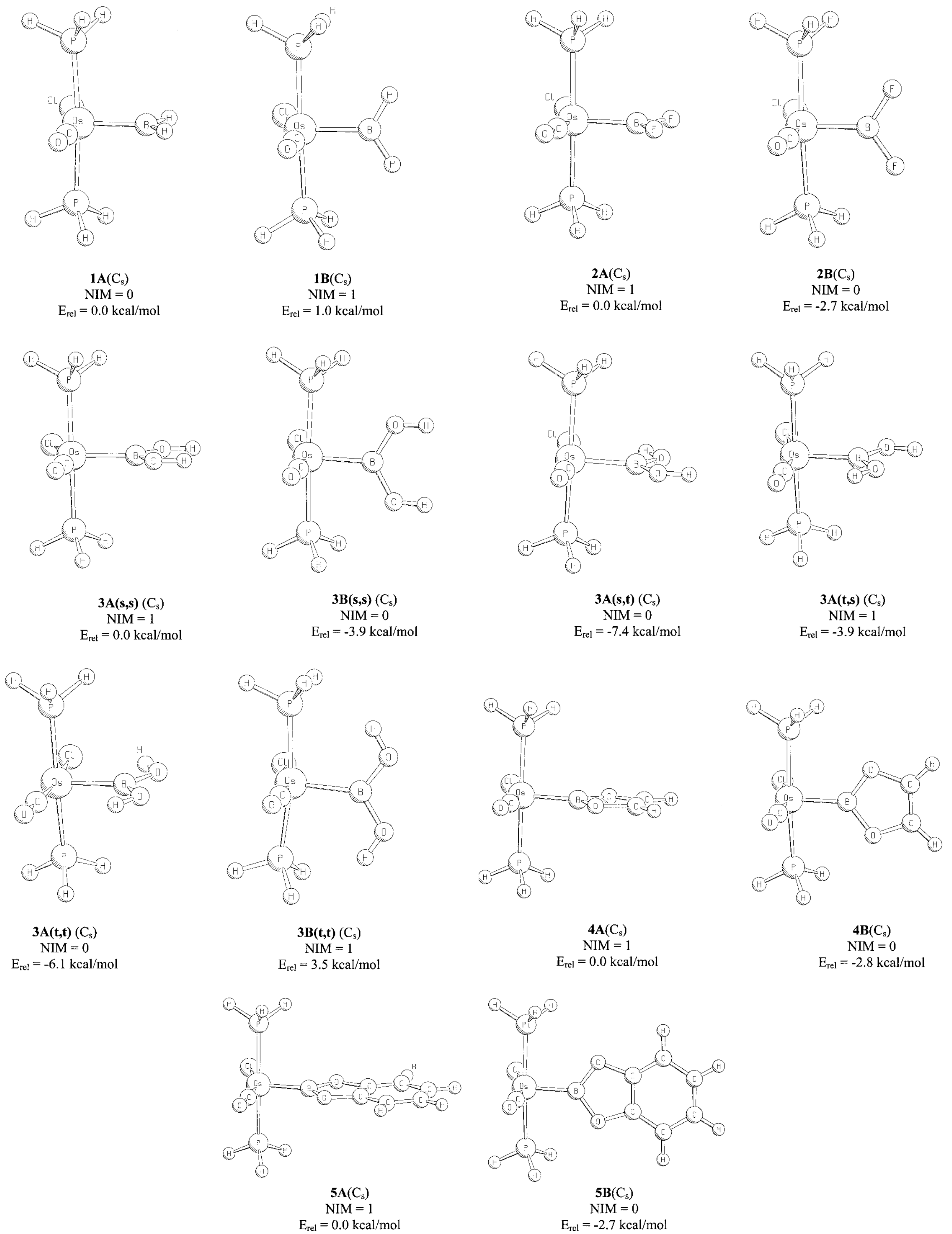
(12) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **1998**, *17*, 4869.

(13) (a) Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem.* **1997**, *109*, 95; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70. (b) Fischer, R. A.; Schulte, M. M.; Weiss, J.; Zsolnai, L.; Jacobi, A.; Huttner, G.; Frenking, G.; Boehme, C.; Vyboishchikov, S. F. *J. Am. Chem. Soc.* **1998**, *120*, 1237. (c) Boehme, C.; Frenking, G. *Chem. Eur. J.* **1999**, *5*, 2184. (d) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571. (e) Uhl, W.; Benter, M.; Melle, S.; Saak, W.; Frenking, G.; Uddin, J. *Organometallics* **1999**, *18*, 3778. (f) Bickelhaupt, F. M.; Radius, U.; Ehlers, A. W.; Hoffmann, R.; Baerends, E. J. *New J. Chem.* **1998**, 1. (g) Radius, U.; Bickelhaupt, F. M.; Ehlers, A. W.; Goldberg, N.; Hoffmann, R. *Inorg. Chem.* **1998**, *37*, 1080. (h) Ehlers, A. W.; Baerends, E. J.; Bickelhaupt, F. M.; Radius, U. *Chem. Eur. J.* **1998**, *4*, 210.

(14) Gaussian 98, Revision A.3; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Pair, R. G. *Phys. Rev.* **1988**, *37*, 785. (c) Vosko, S. H.; Wi1k, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 8, 1200. (d) Stephens, P. J.; Delvin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(16) Frenking, G.; Antes, I.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboishchikov, S. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, pp 63−144.



1A(C_s)
NIM = 0
E_{rel} = 0.0 kcal/mol

1B(C_s)
NIM = 1
E_{rel} = 1.0 kcal/mol

2A(C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

2B(C_s)
NIM = 0
E_{rel} = -2.7 kcal/mol

3A(s,s) (C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

3B(s,s) (C_s)
NIM = 0
E_{rel} = -3.9 kcal/mol

3A(s,t) (C_s)
NIM = 0
E_{rel} = -7.4 kcal/mol

3A(t,s) (C_s)
NIM = 1
E_{rel} = -3.9 kcal/mol

3A(t,t) (C_s)
NIM = 0
E_{rel} = -6.1 kcal/mol

3B(t,t) (C_s)
NIM = 1
E_{rel} = 3.5 kcal/mol

4A(C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

4B(C_s)
NIM = 0
E_{rel} = -2.8 kcal/mol

5A(C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

5B(C_s)
NIM = 0
E_{rel} = -2.7 kcal/mol

Figure 1. Optimized equilibirum structures and transition states (B3LYP/II) of the 16 VE five-coordinate complexes **1A**−**5B**. The geometrical variables are shown in Table 1.

21) valence basis set for Os and all electron 6-31G(d,p) basis sets[18] for the other atoms. Open-shell compounds were calculated with the restricted DFT formalism. All of the structures reported here are either minima (number of imaginary frequencies NIM = 0) on the potential energy surfaces, or they are transition states (NIM = 1) for the rotation of the boryl group. The bonding situation of the molecules has been

Table 1. Calculated Bond Lengths (Å) and Bond Angles (deg) at B3LYP/II Level for **1A**−**5B** (Experimental Values Are Given in Italics)

	1A	**1B**	**2A**	**2B**	**3A(s,s)**	**3B(s,s)**	**3A(s,t)**	**3A(t,s)**	**3A(t,t)**	**3B(t,t)**	**4A**	**4B**	**5A**	**5B**
Os−B	2.023	2.049	2.056	2.054	2.089	2.082	2.091	2.104 *2.046*[a]	2.115	2.130	2.066	2.060	2.058	2.053 *2.019*[b]
Os−P	2.367	2.360	2.363	2.366	2.354	2.361	2.354	2.358	2.359	2.359	2.359	2.362	2.361	2.364 *2.364*[b]
Os−Cl	2.452	2.420	2.433	2.420	2.440	2.431	2.465	2.436	2.462	2.434	2.432	2.425	2.429	2.422 *2.406*[b]
Os−C_{cis}	1.857	1.878	1.863	1.871	1.860	1.864	1.864	1.849	1.855	1.866	1.864	1.866	1.865	1.868 *1.798*[b]
C−O_{cis}	1.168	1.166	1.166	1.166	1.168	1.169	1.167	1.174	1.172	1.169	1.167	1.168	1.166	1.167 *1.173*[b]
B⋯C_{cis}	2.688	2.604	2.687	2.638	2.717	2.646	2.780	2.694	2.805	2.670	2.682	2.646	2.681	2.637
B⋯Cl	3.643	3.755	3.731	3.715	3.792	3.723	3.486	3.779	3.509	3.769	3.757	3.737	3.749	3.730
P−Os−B	93.7	89.7	91.7	89.9	90.6	90.0	90.8	90.6	90.7	95.5	90.7	90.0	91.0	90.2 *94.7*[b]
P−Os−Cl	85.3	86.3	85.5	86.0	86.0	86.2	86.6	85.3	86.2	84.2	85.9	86.4	85.8	86.2 *87.7*[b]
P−Os−C_{cis}	93.8	94.1	94.2	94.2	94.1	94.0	93.2	94.9	93.7	94.7	94.1	93.9	94.2	94.0 *88.3*[b]
Cl−Os−B	108.6	114.0	112.2	112.3	113.6	111.4	99.2	112.4	99.8	111.1	113.1	112.6	113.1	112.5 *105.0*[b]
C_{cis}-Os−B	87.6	82.9	86.4	84.4	86.4	84.0	89.1	85.6	89.7	83.6	85.9	84.6	86.1	84.4 *90.9*[b]
R−B−R	119.4	116.1	113.6	113.0	120.8	120.4	116.9	115.2	114.9	111.1	108.0	107.8	109.0	108.7

[a] Reference 2. [b] Reference 12.

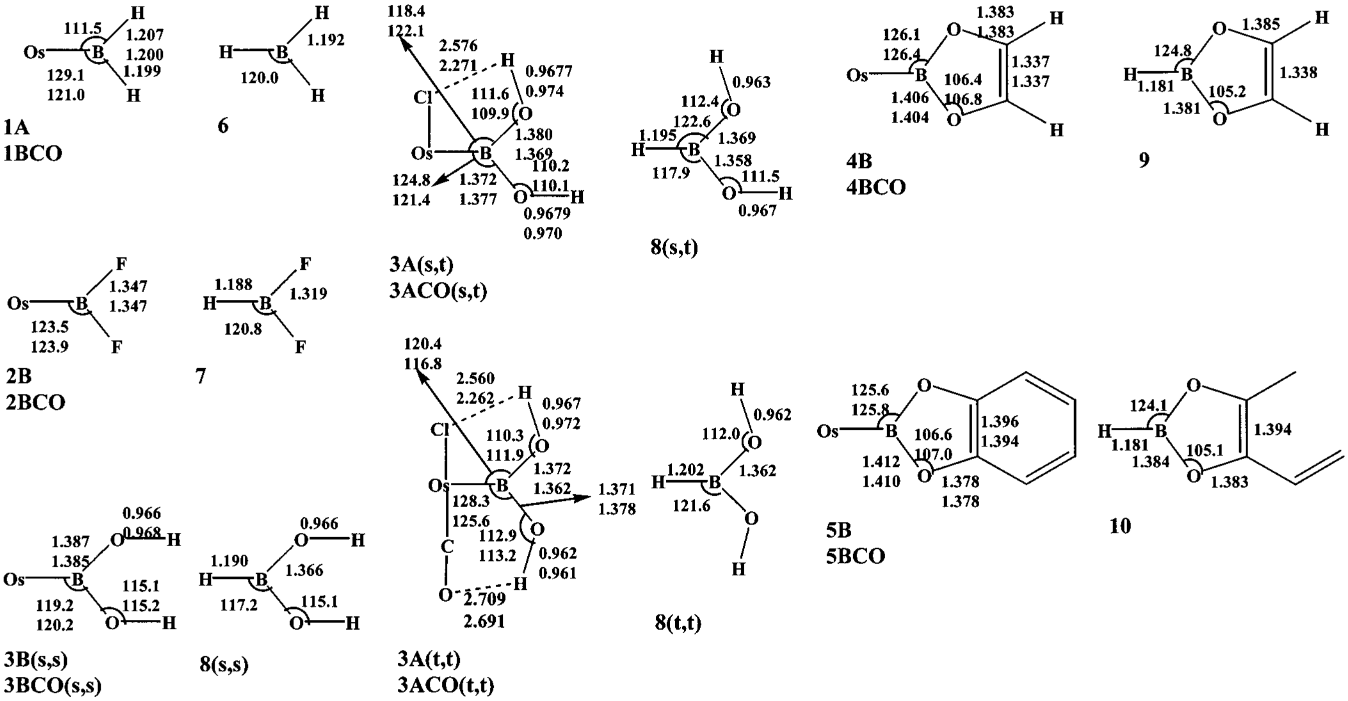


Figure 2. Optimized geometries (B3LYP/II) of the boryl ligands of the equilibrium structures **1A**−**5B** and **1BCO**−**5BCO** and calculated geometries of the respective HBR_2 molecules **6**−**10**. Interatomic distances are given in angstroms and angles in degrees.

analyzed using the NBO method.[19] The σ- and π-donation between Os and B has been calculated from the differences of the charge and orbital population. Details are given as a footnote in Table 6.

Results and Discussion

The presentation of the result is given in the following order. We first discuss the geometries and bond energies of the calculated molecules. Then, we present the results of the NBO analysis of the bonding situation in the boryl complexes. In each section, we discuss first the 16 VE complexes $[(PH_3)_2(CO)ClOs-BR_2]$ **1A**−**5B** and then the 18 VE complexes $[(PH_3)_2(CO)_2ClOs-BR_2]$ **1ACO**−**5BCO**.

Geometries and Bond Energies. Figure 1 shows the optimized geometries of the five-coordinate complexes **1**−**5**. The calculated bond lengths and bond angles are given in Table 1. The optimized geometries of the boryl ligands and the parent compounds HBR_2 are shown for comparison in Figure 2. Table 2 gives the theoretically predicted $Os-BR_2$ bond dissociation energies.

We calculated only structures where the phosphane ligands are in a trans position to each other, and where the remaining

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(17) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(18) (a) Hehre, W. J.; Ditchfeld, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 1063.

(19) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1985**, *88*, 899.

Table 2. Total Energies (au), ZPE (kcal/mol), Number of Imaginary Frequencies (NIM), Lowest Value of Vibrational Imaginary Frequency (in parentheses), Relative Energies (E_{Rel}, kcal/mol), Bond Dissociation Energies (kcal/mol) of the Boryl Ligands and the *trans*-CO Ligand at B3LYP/II Level

	symmetry	TE	ZPE	NIM	E_{rel}	D_e (D_o)	$D_{e(co)}$ ($D_{o(co)}$)
1A	C_s	−1377.05277	54.8	0	0.0	90.0 (85.6)	
1B	C_s	−1377.05045	54.3	1 (126i)	1.0		
2A	C_s	−1575.67446	48.0	1 (45i)	0.0		
2B	C_s	−1575.67922	48.3	0	−2.7	90.8 (88.3)	
3A(s,s)	C_s	−1527.61999	62.9	1 (55i)	0.0		
3B(s,s)	C_s	−1527.62670	63.2	0	−3.9	84.7 (81.9)	
3A(s,t)	C_s	−1527.63296	63.6	0	−7.4	84.6 (81.9)	
3A(t,s)	C_s	−1527.62730	63.6	1 (45i)	−3.9		
3A(t,t)	C_s	−1527.63103	63.7	0	−6.1	83.3 (80.7)	
3B(t,t)	C_s	−1527.61447	62.9	1 (121i)	3.5		
4A	C_s	−1603.80031	71.0	1 (40i)	0.0		
4B	C_s	−1603.80522	71.3	0	−2.8	88.1 (86.1)	
5A	C_s	−1757.46308	100.6	1 (29i)	0.0		
5B	C_s	−1757.46778	100.8	0	−2.7	87.1 (85.3)	
1ACO	C_s	−1490.39501	60.0	1 (144i)	0.0		
1BCO	C_s	−1490.40267	61.2	0	−3.6	78.1 (72.7)	26.8 (22.2)
2ACO	C_s	−1689.02600	53.7	1 (56i)	0.0		
2BCO	C_s	−1689.03177	53.8	0	−3.5	80.5 (77.9)	27.0 (24.7)
3ACO(s,s)	C_s	−1640.97241	68.7	1 (60i)	0.0		
3BCO(s,s)	C_s	−1640.98051	68.9	0	−4.9	75.2 (72.1)	27.8 (25.3)
3ACO(s,t)	C_s	−1640.99050	69.3	0	−10.7	77.4 (74.4)	30.2 (27.7)
3ACO(t,s)	C_s	−1640.97750	69.2	1 (63i)	−2.7		
3ACO(t,t)	C_s	−1640.98564	69.5	0	−7.5	74.2 (71.2)	28.3 (25.7)
3BCO(t,t)	C_s	−1640.96198	68.6	1 (152i)	6.4		
4ACO	C_s	−1717.15465	76.8	1 (45i)	0.0		
4BCO	C_s	−1717.16016	76.9	0	−3.4	79.3 (77.1)	28.5 (26.1)
5ACO	C_s	−1870.81661	106.4	1 (29i)	0.0		
5BCO	C_s	−1870.82196	106.4	0	−3.4	77.8 (75.8)	28.1 (25.7)

three ligands CO, Cl, and BR_2 are in a plane which is orthogonal to the P−Os−P axis. This is the ligand arrangement that has experimentally been found for the related osmium boryl complexes.[2,12] The optimized geometries look like an octahedral structure where one ligand trans to the boryl group is missing (Figure 1). Alternatively, they can be considered as square-based pyramidal forms with the boryl ligand in the apical position.

For each complex **1**−**5** we optimized two different conformations **A** and **B** with regard to the rotation about the Os−B bond. Conformations **A** have the BR_2 plane coplanar with the Cl−Os−CO plane and orthogonal to the P−Os−P plane, while the conformations **B** have the BR_2 ligand rotated by 90° about the Os−B bond. Different conformations are possible for the $B(OH)_2$ ligand, where the OH groups may be syn (s) or trans (t) to each other. This leads to conformations with (s,s), (s,t), (t,s), and (t,t) forms for **3A** and **3B**.

The calculations show that conformation **A** is a minimum on the potential energy surface for **1A**, **3A(s,t)**, and **3A(t,t)**, while the other boryl complexes have the conformation **B** as energy minima. The reason **3A(s,t)** and **3A(t,t)** are energy minima lies in the hydrogen bonding between chlorine and the proton of one OH group. The (s,s) form of the $B(OH)_2$ ligand, which cannot establish a hydrogen bonding with the chlorine ligand in **3A(s,s)** has conformation **3B(s,s)** as energy minimum (Figure 1). The theoretically predicted energy minimum structure for **3A(s,t)** with a Cl···HO bond is in agreement with the experimentally observed geometry for the complex $(PPh_3)_2(CO)ClOs-B(OH)_2$, which has a cis,trans arrangement of the hydroxyl group where one OH group points toward the chlorine atom.[2] Geometry optimization of a possible conformation **3B-(s,t)** led to **3A(s,t)** as energy minimum structure.

The energy barriers for rotation about the Os−B bond are not very high. The conformational profile for the complex **3** is rather complex because of the Cl···H hydrogen bonding, which makes it difficult to estimate the rotational barrier. The activation barriers for the other complexes **1**, **2**, **4**, and **5** is < 3 kcal/mol (Table 2). The energy difference between **3A(t,t)** and **3B(t,t)** is 9.6 kcal/mol. This means that the strength of the hydrogen bonding in **3A(s,t)** and **3A(t,t)** may be estimated as ∼6.6 kcal/mol, if a value of 3 kcal/mol is used as upper limit for the rotational barrier about the Os−B bond. We did not make a complete search for the conformational profile of complex **3**, because we are mainly interested in the nature of the Os−B bonding in the energy minimum structures. We believe that **3A(s,t)** is the global energy minimum of the $[Os]-B(OH)_2$ complex.

The theoretically predicted bond lengths and bond angles are in good agreement with experiment (Table 1). The calculated Os−B distances of **3A(s,t)** (2.091 Å) and **5B** (2.053 Å) are slightly longer than the experimental values for the related complexes (2.046 and 2.019 Å). Note that the theoretical and experimental differences between the two complexes are nearly the same. The difference between theory and experiment may partly be caused by solid-state effects which tend to shorten donor−acceptor bonds.[20] The effect of Cl···HO hydrogen bonding in **3A(s,t)** and **3A(t,t)** becomes obvious by the calculated Cl−Os−B bond angles (99.2° in **3A(s,t)** and 99.8° in **3A(t,t)**), which are significantly smaller by 9−15° than in the other complexes (Table 1). A comparison of the geometries of the boryl ligands BR_2 in the energy minimum structures of **1**−**5** with the respective boranes HBR_2 shows that the B−R bond becomes longer in the complexes and that the Os−B−R angles are larger than the H−B−R angles.

The calculated Os−B bond dissociation energies (Table 2) show remarkably similar values for the different boryl ligands BR_2. This is in agreement with previous theoretical studies of platinum boryl complexes, which gave comparable bond energies for $Pt-BH_2$ and $Pt-B(OH)_2$ bonds.[7] The highest bond energy is predicted for **2B** (D_e = 90.8 kcal/mol) and the lowest

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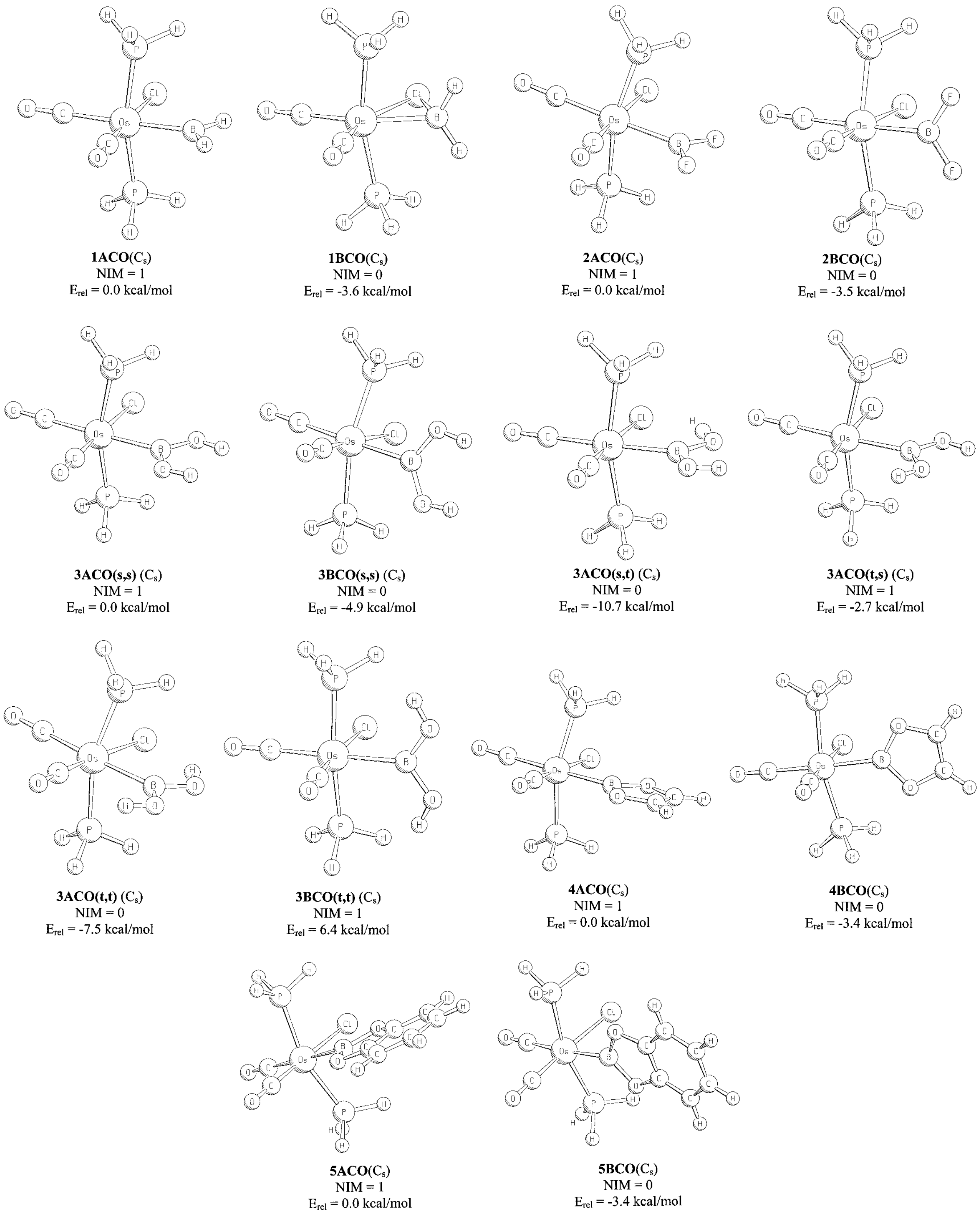
(20) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.



1ACO(C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

1BCO(C_s)
NIM = 0
E_{rel} = -3.6 kcal/mol

2ACO(C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

2BCO(C_s)
NIM = 0
E_{rel} = -3.5 kcal/mol

3ACO(s,s) (C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

3BCO(s,s) (C_s)
NIM = 0
E_{rel} = -4.9 kcal/mol

3ACO(s,t) (C_s)
NIM = 0
E_{rel} = -10.7 kcal/mol

3ACO(t,s) (C_s)
NIM = 1
E_{rel} = -2.7 kcal/mol

3ACO(t,t) (C_s)
NIM = 0
E_{rel} = -7.5 kcal/mol

3BCO(t,t) (C_s)
NIM = 1
E_{rel} = 6.4 kcal/mol

4ACO(C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

4BCO(C_s)
NIM = 0
E_{rel} = -3.4 kcal/mol

5ACO(C_s)
NIM = 1
E_{rel} = 0.0 kcal/mol

5BCO(C_s)
NIM = 0
E_{rel} = -3.4 kcal/mol

Figure 3. Optimized equilibirum structures and transition states (B3LYP/II) of the 18 VE six-coordinate complexes **1ACO**−**5BCO**. The geometrical variables are shown in Table 1.

for **3A(t,t)** (D_e = 83.3 kcal/mol). It is interesting to note that the Os−B bond length does not always correlate with the bond energy. The Os−B distance in **1A** (2.023 Å) is clearly shorter than in **2B** (2.054 Å), but the latter compound has a slightly higher bond energy. The $Os-BR_2$ bond energies are slightly lower than the $H-BR_2$ dissociation energies, which have been calculated at the CBS-4 level as 104.0, 107.1, 105.7, 110.4, and 109.9 kcal/mol for BR_2 = BH_2, BHF_2, $BH(OH)_2$, BH(OHC═CHO), and HBcat, respectively.[10]

Now we discuss the geometries and bond energies of the six-coordinate 18 VE complexes [$(PH_3)_2(CO)_2ClOs{-}BR_2$]. Figure 3 exhibits the optimized geometries of **1ACO**−**5BCO** which have a CO ligand in a trans position to the boryl ligand. Table 3 shows the calculated geometrical parameters. The theoretically predicted Os−B and Os−CO_{trans} bond energies are given in Table 2.

The calculations show that the rotational isomers **1BCO**−**5BCO** are energy minima, while the isomeric forms **1ACO**−**5ACO** are transition states, except for compounds **3ACO(s,t)** and **3ACO(t,t)** which are stabilized by intramolecular OH···Cl hydrogen bonding (Table 2). The energy ordering of the conformational minima of the 16 and 18 VE species with $B(OH)_2$ ligand remains the same: (s,t) < (t,t) < (s,s). The BH_2 complex **1BCO** is stabilized by intramolecular Cl→B donation (Figure 3). The rotational barriers about the Os−B bond of the six-coordinate complexes are slightly higher than for the five-coordinate species (Table 2). The calculated bond lengths indicate that the Os−B bonds become 0.13−0.14 Å longer when a CO ligand is attached to Os trans to the boryl group. This is in agreement with experimental studies, which show that the osmium−boron distances in the PPh_3 analogues of **3ACO(s,t)** (2.20 Å) and **5BCO** (2.177 Å) are longer than in [$(PPh_3)_2(CO)$-$ClOs{-}B(OH)_2$] (2.046 Å).[2] The experimental values for the 18 VE complexes are in good agreement with the calculated data (Table 3). The Os−Cl bonds of the 16 VE complexes are clearly shorter than in the 18 VE species, while the Os−CO_{cis} bonds of the latter complexes are only slightly longer than in the former molecules. We want to point out that the Os−CO_{trans} bonds of the six-coordinate species are significantly longer by ∼0.1 Å than the Os−CO_{cis} bonds. Geometry optimization of a possible conformation **3BCO(s,t)** led to **3ACO(s,t)** as energy minimum structure.

Table 2 shows that the calculated Os−B bond dissociation energies of **1BCO**−**5BCO** are 7−12 kcal/mol lower than the bond energies of the respective 16 VE species, but the absolute values are still rather high. The very high bond energies of the boryl ligands in the osmium complexes are in agreement with the large bond energies in iridium−Bcat complexes that were estimated from thermochemical data.[8] The calculated Os−CO_{trans} bond dissociation energies are between $D_e = 26.8{-}30.2$ kcal/mol ($D_o = 22.2{-}27.7$ kcal/mol). This is lower than the first CO dissociation energy of $Os(CO)_5$, which has been calculated at the CCSD(T) level as $D_o = 40.3$ kcal/mol.[21] The rather weak Os−CO_{trans} bond in the 18 VE complex and the steric shielding of the $P(Ph)_3$ groups explains why the electronically unsaturated compounds [$(Cl)(CO)(PPh_3)_2Os(Bcat)$] and [$(Cl)(CO)(PPh_3)_2Os(BR_2)$] could become isolated.[2,12] It will be shown below that the reason for the weakness of the Os−CO_{trans} bond lies in the σ-donation of the boryl ligand, which partly compenstates the electron deficiency of the five-coordinate complexes.

We calculated also the difference between the B−R π-donor stabilization in the boryl groups of the complexes and that in HBR_2. Table 4 shows the results of isodesmic reactions. It becomes obvious that the π-donor groups F, OH, OCH═CHO, and cat stabilize the boranes HBR_2 more than the boryl osmium complexes, except for fluorine in the 18 VE complex **2BCO**, which becomes more stabilized than HBF_2. This means that the simultaneous stabilization of the boron atom by the [Os] fragment and the π-donor groups R in [Os]−BR_2 is less than the sum of the stabilization in [Os]-BH_2 and HBR_2. The calculated reaction energies of the isodesmic reactions indicate

Table 3. Calculated Bond Lengths (Å) and Bond Angles (deg) at B3LYP/II Level for **1ACO-5BCO** (Experimental Values Are Given in Italics)

	1ACO	1BCO	2ACO	2BCO	3ACO(s,s)	3BCO(s,s)	3ACO(s,t)	3ACO(t,s)	3ACO(t,t)	3BCO(t,t)	4ACO	4BCO	5ACO	5BCO
Os−B	2.168	2.243	2.193	2.184	2.226	2.209	2.234 *2.20*[a]	2.240	2.264	2.283	2.197	2.186	2.191	2.181 *2.177*[a]
Os−P	2.367	2.365	2.369	2.376	2.360	2.373	2.364	2.364	2.367	2.367	2.366	2.373	2.367	2.375
Os−Cl	2.520	2.530	2.509	2.515	2.514	2.519	2.531	2.513	2.529	2.517	2.512	2.518	2.510	2.515
Os−C_{cis}	1.885	1.879	1.890	1.890	1.888	1.885	1.887	1.876	1.876	1.888	1.890	1.887	1.890	1.886
Os−C_{trans}	2.011	1.974	1.995	1.996	1.988	1.990	1.989	1.993	1.992	1.987	1.988	1.990	1.990	1.992
C−O_{cis}	1.161	1.164	1.159	1.161	1.160	1.163	1.159	1.166	1.165	1.161	1.160	1.162	1.159	1.161
C−O_{trans}	1.151	1.156	1.151	1.151	1.152	1.153	1.152	1.151	1.152	1.153	1.152	1.152	1.151	1.151
B···C_{cis}	2.805	3.244	2.835	2.887	2.856	2.860	2.894	2.864	2.916	2.819	2.838	2.853	2.836	2.861
B···Cl	3.270	2.090	3.300	3.191	3.365	3.224	3.261	3.364	3.288	3.324	3.323	3.236	3.318	3.217
P−Os−B	84.9	82.1	84.9	84.5	83.6	84.6	83.0	83.2	82.8	89.1	84.1	84.5	84.4	84.7
P−Os−Cl	82.7	86.0	83.0	84.6	83.4	84.5	85.3	82.5	84.5	82.8	83.5	84.3	83.3	84.4
P−Os−C_{cis}	96.9	90.7	96.6	95.0	96.3	94.9	94.1	97.2	94.9	97.1	96.2	95.3	96.5	95.2
P−Os−C_{trans}	94.6	97.7	94.7	94.8	96.1	94.8	96.6	96.2	96.6	90.6	95.5	94.9	95.2	94.7
Cl−Os−B	88.1	51.5	88.9	85.2	90.3	85.7	86.1	89.9	86.5	87.5	89.5	86.6	89.5	86.2
Cl−Os−C_{trans}	88.0	104.4	87.7	88.1	86.7	88.6	88.7	86.2	87.7	90.5	87.0	87.9	87.2	88.1
C_{cis}-Os−B	87.3	103.5	87.6	89.9	87.5	88.3	88.8	87.7	89.0	84.5	87.6	88.6	87.7	89.0
R−B−R	115.6	116.0	112.8	112.1	120.0	119.5	116.5	113.9	113.9	108.7	107.5	107.3	108.6	108.3

[a] Reference 2.

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(21) Ehlers, A. W.; Frenking, G. *Organometallics* **1995**, *14*, 423.

Table 4. Reaction Energies (ZPE corrected, kcal/mol) and [Os] = Os(Cl)(CO)$(PH_3)_2$ or Os(Cl)$(CO)_2(PH_3)_2$ at B3LYP/II Level

		BH_2F	→	1/3 BF_3	+	2/3 BH_3	0.8
		BHF_2	→	2/3 BF_3	+	1/3 BH_3	3.0
[Os]-BH_2 (**1A**)	+	BHF_2	→	[Os]-BF_2 (**2B**)	+	BH_3	1.5
[Os]-BH_2 (**1A**)	+	$BH(OH)_2$ (**8(s,s)**)	→	[Os]-$B(OH)_2$ (**3B(s,s)**)	+	BH_3	6.3
[Os]-BH_2 (**1A**)	+	$BH(OH)_2$ (**8(s,t)**)	→	[Os]-$B(OH)_2$ (**3A(s,t)**)	+	BH_3	6.0
[Os]-BH_2 (**1A**)	+	$BH(OH)_2$ (**8(t,t)**)	→	[Os]-$B(OH)_2$ (**3A(t,t)**)	+	BH_3	5.9
[Os]-BH_2 (**1A**)	+	$BH(OCH)_2$	→	[Os]-$B(OCH)_2$ (**4B**)	+	BH_3	5.6
[Os]-BH_2 (**1A**)	+	$BH(OC_3H_2)_2$	→	[Os]-$B(OC_3H_2)_2$ (**5B**)	+	BH_3	6.4
[Os]-BF_2 (**2B**)	+	$BH(OH)_2$ (**8(s,s)**)	→	[Os]-$B(OH)_2$ (**3B(s,s)**)	+	BHF_2	4.7
[Os]-BF_2 (**2B**)	+	$BH(OH)_2$ (**8(s,t)**)	→	[Os]-$B(OH)_2$ (**3A(s,t)**)	+	BHF_2	4.4
[Os]-BF_2 (**2B**)	+	$BH(OH)_2$ (**8(t,t)**)	→	[Os]-$B(OH)_2$ (**3A(t,t)**)	+	BHF_2	4.1
[Os]-BF_2 (**2B**)	+	$BH(OCH)_2$	→	[Os]-$B(OCH)_2$ (**4B**)	+	BHF_2	4.1
[Os]-BF_2 (**2B**)	+	$BH(OC_3H_2)_2$	→	[Os]-$B(OC_3H_2)_2$ (**5B**)	+	BHF_2	4.8
[Os]-BH_2 (**1BCO**)	+	BHF_2	→	[Os]-BF_2 (**2BCO**)	+	BH_3	−1.0
[Os]-BH_2 (**1BCO**)	+	$BH(OH)_2$ (**8(s,s)**)	→	[Os]-$B(OH)_2$ (**3BCO(s,s)**)	+	BH_3	3.1
[Os]-BH_2 (**1BCO**)	+	$BH(OH)_2$ (**8(s,t)**)	→	[Os]-$B(OH)_2$ (**3ACO(s,t)**)	+	BH_3	0.5
[Os]-BH_2 (**1BCO**)	+	$BH(OH)_2$ (**8(t,t)**)	→	[Os]-$B(OH)_2$ (**3ACO(t,t)**)	+	BH_3	2.3
[Os]-BH_2 (**1BCO**)	+	$BH(OCH)_2$	→	[Os]-$B(OCH)_2$ (**4BCO**)	+	BH_3	1.7
[Os]-BH_2 (**1BCO**)	+	$BH(OC_3H_2)_2$	→	[Os]-$B(OC_3H_2)_2$ (**5BCO**)	+	BH_3	2.9
[Os]-BF_2 (**2BCO**)	+	$BH(OH)_2$ (**8(s,s)**)	→	[Os]-$B(OH)_2$ (**3BCO(s,s)**)	+	BHF_2	4.1
[Os]-BF_2 (**2BCO**)	+	$BH(OH)_2$ (**8(s,t)**)	→	[Os]-$B(OH)_2$ (**3ACO(s,t)**)	+	BHF_2	1.5
[Os]-BF_2 (**2BCO**)	+	$BH(OH)_2$ (**8(t,t)**)	→	[Os]-$B(OH)_2$ (**3ACO(t,t)**)	+	BHF_2	3.3
[Os]-BF_2 (**2BCO**)	+	$BH(OCH)_2$	→	[Os]-$B(OCH)_2$ (**4BCO**)	+	BHF_2	2.7
[Os]-BF_2 (**2BCO**)	+	$BH(OC_3H_2)_2$	→	[Os]-$B(OC_3H_2)_2$ (**5BCO**)	+	BHF_2	3.9

the thermodynamic stabilization of the boryl group by the osmium fragment relative to its stabilization by hydrogen.

Analysis of the Bonding Situation. Table 5 shows the calculated partial charges and the population of the π-orbitals of the boron atom and the boryl ligands [B] in the complexes and in the free boryl ligands, which were calculated with the frozen geometry of the complexes. Table 6 gives the amount of total charge donation, π-charge donation, and σ-charge donation between the boryl ligand and the osmium fragment. We calculated also the change in the intraligand charge transfer in BR_2 between the free ligand and the complex. Note that positive numbers indicate a charge transfer in the direction of the arrow, while negative numbers indicate a reverse charge transfer. Table 7 shows the calculated Wiberg bond orders[22] and the results of the NBO analysis of the Os−B bond orbitals.

We begin our discussion with the 16 VE complexes **1**−**5**. Table 5 shows that the boron atom carries always a large positive charge, except in the BH_2 complex **1** which has only a slightly positively charged boron atom. The osmium atom is always negatively charged. It follows that the Os−B bonding has a significantly ionic character. The total charge transfer between the boryl ligand and the osmium fragment, which may go in either direction depending on the nature of the boryl ligand is very small (Table 6). The small amount of total charge transfer is partly caused by the opposite directions of σ- and π-charge donation, which have a similar magnitude. It becomes obvious, however, that the [Os] → [B] π-donation into the p(π) AO of boron is not very large when the BR_2 ligand carries a π-donor substituent R. A comparison of the [Os] → [B] π-donation with the B ← R_2 π-donation shows that the latter is clearly larger except when R = H (Table 6). A significant [Os] → [B] π-donation is only found for **1A**, where the free BH_2 ligand has a vacant p(π) AO. Thus, [Os] → [B] π-donation is important for the electronic stabilization of boryl complexes with ligands BR_2 with substituents R which are poor π-donors. Table 6 shows also that the intraligand charge transfer within the boryl ligand in the complexes is very small, with the exception of the change in the σ-charge of the BH_2 ligand in **1A**. The calculated changes in the charge distribution suggest that the groups R_2 strongly

Table 5. Natural Charges q on Os, B, and Boryl Fragment [B], and π-Occupancies Only on B and on Boryl Fragment [B] of **1A**−**5BCO** at B3LYP/II Level

	q			π-occupancies	
	Os	B	[B]	B	[B]
1A	−0.24	0.13	−0.03	0.22	0.22
1B	−0.27	0.17	−0.04	0.27	0.27
2A	−0.32	1.04	0.04	0.36	4.11
2B	−0.32	1.05	0.04	0.36	4.12
3A(s,s)	−0.28	0.93	0.03	0.41	4.09
3B(s,s)	−0.28	0.96	0.04	0.40	4.08
3A(s,t)	−0.33	0.95	0.09	0.42	4.09
3A(t,s)	−0.27	0.93	0.06	0.41	4.08
3A(t,t)	−0.33	0.95	0.13	0.42	4.08
3B(t,t)	−0.33	0.97	0.13	0.40	4.08
4A	−0.25	0.88	−0.04	0.44	6.10
4B	−0.26	0.89	−0.03	0.44	6.04
5A	−0.25	0.89	−0.06	0.43	10.12
5B	−0.26	0.91	−0.05	0.41	10.10
1ACO	−0.33	0.02	−0.14	0.09	0.09
1BCO	−0.27	−0.25	−0.36	0.76	0.76
2ACO	−0.38	0.92	−0.09	0.32	4.05
2BCO	−0.39	0.94	−0.09	0.35	4.11
3ACO(s,s)	−0.33	0.79	−0.11	0.38	4.04
3BCO(s,s)	−0.33	0.83	−0.11	0.40	4.01
3ACO(s,t)	−0.34	0.78	−0.10	0.40	4.04
3ACO(t,s)	−0.32	0.78	−0.09	0.39	4.04
3ACO(t,t)	−0.33	0.78	−0.06	0.40	4.03
3BCO(t,t)	−0.34	0.81	−0.05	0.43	4.09
4ACO	−0.33	0.72	−0.17	0.42	6.04
4BCO	−0.33	0.76	−0.17	0.40	6.02
5ACO	−0.33	0.74	−0.19	0.40	10.05
5BCO	−0.33	0.77	−0.18	0.37	10.04
BH_2 (**1A**)[a]		0.32	0.00	0.00	0.00
BF_2 (**2B**)[a]		1.01	0.00	0.25	4.00
$B(OH)_2$ (**3B(s,s)**)[a]		0.96	0.00	0.31	4.00
$B(OH)_2$ (**3A(s,t)**)[a]		0.89	0.00	0.32	4.00
$B(OH)_2$ (**3A(t,t)**)[a]		0.83	0.00	0.32	4.00
$B(OCH)_2$ (**4B**)[a]		0.92	0.00	0.37	6.00
$B(OC_3H_2)_2$ (**5B**)[a]		0.95	0.00	0.34	10.00
BH_2 (**1BCO**)[a]		0.33	0.00	0.00	0.00
BF_2 (**2BCO**)[a]		1.01	0.00	0.25	4.00
$B(OH)_2$ (**3BCO(s,s)**)[a]		0.96	0.00	0.31	4.00
$B(OH)_2$ (**3ACO(s,t)**)[a]		0.89	0.00	0.32	4.00
$B(OH)_2$ (**3ACO(t,t)**)[a]		0.83	0.00	0.32	4.00
$B(OCH)_2$ (**4BCO**)[a]		0.92	0.00	0.37	6.00
$B(OC_3H_2)_2$ (**5BCO**)[a]		0.95	0.00	0.34	10.00

[a] Corresponding to geometries of **1A**−**5BCO**.

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(22) (a) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083. (b) Mayer, I. *Theor. Chim. Acta* **1985**, *67*, 315.

Table 6. π and σ Contributions between Os and B Fragments Based on Natural Population Analysis at B3LYP/II Level[a,b]

	$[\mathrm{Os}]\leftarrow[\mathrm{B}]\ q$	$[\mathrm{Os}]\rightarrow[\mathrm{B}]\ (\pi)$	$[\mathrm{Os}]\leftarrow[\mathrm{B}]\ (\sigma)$	$\mathrm{B}\leftarrow\mathrm{R}_2\ (\pi)$	$\mathrm{B}\rightarrow\mathrm{R}_2\ (\Delta q)$	$\mathrm{B}\leftarrow\mathrm{R}_2\ (\Delta\pi)$	$\mathrm{B}\rightarrow\mathrm{R}_2\ (\Delta\sigma)$
1A	−0.03	0.22	0.19	0.00	−0.16	0.00	−0.16
2B	0.04	0.12	0.16	0.24	0.00	−0.01	−0.01
3B(s,s)	0.04	0.08	0.12	0.33	−0.04	0.01	−0.03
3A(s,t)	0.09	0.09	0.18	0.33	−0.03	0.01	−0.02
3A(t,t)	0.13	0.08	0.21	0.34	−0.01	0.02	0.01
4B	−0.03	0.04	0.01	0.40	0.00	0.03	0.03
5B	−0.05	0.10	0.05	0.31	0.01	−0.03	−0.02
2BCO	−0.09	0.11	0.02	0.24	0.02	−0.01	0.01
3BCO(s,s)	−0.11	0.01	−0.10	0.39	−0.02	0.08	0.06
3ACO(s,t)	−0.10	0.04	−0.06	0.36	−0.01	0.04	0.03
3ACO(t,t)	−0.06	0.03	−0.03	0.37	0.01	0.05	0.06
4BCO	−0.17	0.02	−0.15	0.38	0.01	0.01	0.02
5BCO	−0.18	0.04	−0.14	0.33	0.00	−0.01	−0.01

[a] $[\mathrm{Os}]\leftarrow[\mathrm{B}]\ q = [\mathrm{B}]\ q$; $[\mathrm{Os}]\rightarrow[\mathrm{B}]\ (\pi) = [\mathrm{B}]\ (\pi)_{\mathrm{Complex}} - [\mathrm{B}]\ (\pi)_{\mathrm{Ligand}}$; $[\mathrm{Os}]\leftarrow[\mathrm{B}]\ (\sigma) = [\mathrm{Os}]\leftarrow[\mathrm{B}]\ q + [\mathrm{Os}]\rightarrow[\mathrm{B}]\ (\pi)$; $\mathrm{B}\leftarrow\mathrm{R}_2\ (\pi) = \mathrm{B}(\pi)_{\mathrm{Complex}} - [\mathrm{Os}]\rightarrow[\mathrm{B}]\ (\pi)$; $\mathrm{B}\rightarrow\mathrm{R}_2\ (\Delta q) = \{(\mathrm{B}(q)_{\mathrm{Complex}} - \mathrm{B}(q)_{\mathrm{Ligand}}\} - \{[\mathrm{B}]\ (q)_{\mathrm{Complex}}\}$; $\mathrm{B}\leftarrow\mathrm{R}_2\ (\Delta\pi) = \{\mathrm{B}(\pi)_{\mathrm{Complex}} - \mathrm{B}(\pi)_{\mathrm{Ligand}}\} - \{[\mathrm{Os}]\rightarrow[\mathrm{B}]\ (\pi)\}$; $\mathrm{B}\rightarrow\mathrm{R}_2\ (\Delta\sigma) = \mathrm{B}\rightarrow\mathrm{R}_2\ (\Delta q) + \mathrm{B}\leftarrow\mathrm{R}_2\ (\Delta\pi)$. [b] Positive numbers indicate a charge transfer in the direction of the arrow, negative numbers indicate a reverse charge transfer.

Table 7. Results of the NBO Analysis and Wiberg Bond Indices (WBI) at the B3LYP/II Level

						Os−B						
	WBI					Os				B		
	Os−B	Os−P	Os−Cl	Os−C$_{\mathrm{cis}}$	Os−C$_{\mathrm{trans}}$	%	%*s*	%*p*	%*d*	%*s*	%*p*	%*d*
1A	1.074	0.519	0.391	1.200		60.9	27.2	0.2	72.6	28.6	71.2	0.2
2B	0.910	0.519	0.428	1.169		57.9	28.1	0.5	71.4	55.5	44.4	0.1
3B(s,s)	0.856	0.520	0.415	1.199		60.2	30.8	0.3	68.9	38.4	61.5	0.1
3A(s,t)	0.864	0.528	0.370	1.189		60.5	27.1	0.3	72.5	38.4	61.5	0.1
3A(t,t)	0.845	0.527	0.373	1.241		61.4	27.0	0.5	72.5	38.7	61.2	0.1
4B	0.889	0.517	0.425	1.184		57.6	31.1	0.1	68.8	39.4	60.5	0.1
5B	0.901	0.515	0.428	1.174		55.6	28.3	0.1	71.6	47.1	52.8	0.1
1BCO	0.461	0.489	0.289	1.065	0.763	69.4	7.4	0.3	92.3	28.4	71.4	0.2
2BCO	0.537	0.490	0.365	1.037	0.662	69.9	16.9	1.1	82.0	45.5	54.4	0.1
3BCO(s,s)	0.494	0.487	0.357	1.049	0.696	54.9	31.3	0.6	68.2	49.8	50.2	0.0
3ACO(s,t)	0.484	0.489	0.341	1.040	0.699	74.9	11.8	0.3	87.9	24.2	75.6	0.2
3ACO(t,t)	0.481	0.487	0.344	1.086	0.688	73.6	11.5	0.4	88.1	19.4	80.4	0.2
4BCO	0.510	0.484	0.359	1.038	0.696	51.9	32.1	0.4	67.5	49.9	50.1	0.0
5BCO	0.517	0.483	0.360	1.034	0.690	81.0	14.9	0.1	85.0	35.8	62.7	1.5

influence the electropilic character the boryl ligand mainly through B←R π-donation.

Our finding that the Os→B π-donation is much weaker than the B←R$_2$ π-donation does not agree with the suggestion of SK[6] that the d(π) electrons of Pt and Pd more easily delocalize to the p(π) orbital of BX$_2$ than do the p(π) orbitals of OH. This was given as explanation for the smaller difference between the Pt−BH$_2$ and Pt−B(OH)$_2$ bond energies compared to the difference between the H$_2$B−BH$_2$ and (OH)$_2$B−B(OH)$_2$ bond energies. It is possible, of course, that the Pt→B and Pd→B π-donation is much larger than the Os→B π-donation. However, the stronger B−B bond in (OH)$_2$B−B(OH)$_2$ compared with that in H$_2$B−BH$_2$ may also be explained in terms of the different hybridization at boron, which according to Bent's rule[23] should have a higher percent s character in the former molecule thereby yielding a stronger σ-bond. We calculated (OH)$_2$B−B(OH)$_2$ and H$_2$B−BH$_2$ at B3LYP/6-31G(d,p). The NBO analysis showed that the B−B bond in the former compound has 41.2% s character, while the latter has only 37.7% s at boron. The conclusion is that the hybridization of the B−B σ-bond already leads to a stronger B−B bond in (OH)$_2$B−B(OH)$_2$ than in H$_2$B−BH$_2$.

Table 7 shows that the calculated bond orders for the Os−B bonds of **1A**−**5B** are quite high. The data suggest that the Os−B bond should be considered as a covalent single bond, while the Os−P and Os−Cl bonds have bond orders that are much lower. These data and the calculated atomic partial charges (Table 5) indicate that the Os−BR$_2$ bonds are held together by strong covalent σ-bonding and by strong Coulombic interactions, which explains why the calculated bond dissociation energies are rather high. The Os−B bond of the 16 VE complexes is only slightly polarized toward the osmium end. The Os part of the Os−B bond orbital is between 55% and 61% (Table 7). The hybridization at Os is between sd^2 and sd^3, and at boron it is between sp and sp^2. The BH$_2$ ligand has a much higher percent p character at the boron end of the Os−B bond in **1A** than the other BR$_2$ ligands in the complexes.

The analysis of the Os−B bonding situation suggests that π-interactions between osmium and boron are not very important, with the possible exception of the BH$_2$ complexes. This is in agreement with the conclusions that were made by RHN[8] about the bonding in iridium−Bcat complexes. RHN compared the Ir−X bond dissociation energies in Vaska-type iridium complexes with X = CH$_3$, H, and BCat with the corresponding H−X bond strengths and concluded "that π-interactions need not be invoked to explain the large metal−boron BDE".[24] The osmium−boron bond is mainly held together by a covalent σ-bond and by electrostatic attraction. Only the Os−BH$_2$ bonds appear to have a significant Os→B π-donation, which compensates for the weaker charge attraction and thus, leads to similar bond energies as for the other Os−BR$_2$ bonds. The latter finding is in agreement with the work of MM.[9] The reason **1A**

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(23) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(24) One referee pointed out that the comparison of the iridium and osmium Bcat complexes is not strictly valid, because the metals have a different number of d- lone pairs.

is an energy minimum and not **1B**, whereas for the other boryl complexes the conformation **B** is the energy minimum is probably caused by weak interligand interactions between the BR_2 group and the axial and equatorial groups.

Now we turn to the 18 VE complexes **1ACO−5BCO**. Table 5 shows that the addition of a CO ligand enhances the negative charge of the boryl ligand [B]. The osmium atom is also more negatively charged, and boron is less positively charged in the six-coordinate complexes than in the respective five-coordinate species. The charge distribution of **1BCO** is different from the other six-coordinate complexes because of the different bonding situation of the boryl ligand. Therefore we did not include it in the list of compounds that is given in Table 6. The breakdown of the σ- and π-contributions shows that the [Os] → [B] π-donation is even lower in **2BCO−5BCO** than in **2B−5B** (Table 6). This is in agreement with the common bonding model for metal−ligand interactions, which predicts that the strong π-acceptor CO lowers the π-donation of the metal to a ligand trans to CO. The 18 VE complexes **3BCO(s,s)−5BCO** show σ-donation in the direction [Os] → [B], while the opposite direction was calculated for the respective 16 VE complexes. This means that the boryl ligands in the 16 VE complexes become significantly stronger σ-donor ligands than in the 18 VE complexes, thereby compensating in part for the electron deficiency at the osmium atom. A comparison of the valence electron configuration of the osmium atom in the 16 and 18 VE complexes shows very small differences (Table 2 in Supporting Information). This becomes also obvious by the partial charge at Os in the 16 and 18 VE complexes (Table 5), which are not very different. The intraligand charge rearrangement in the boryl ligands remains rather small in the six-coordinate species.

Table 7 shows that the additional CO ligand leads to significantly smaller values for the bond order of the Os−BR bond. The covalent bond order is now only ~0.5, while it is nearly a single bond in the 16 VE complexes. This explains why the Os−B bond dissociation energies of the 18 VE complexes are smaller than those of the 16 VE species. The large drop in the covalent bond order cannot be caused by less Os→B π-donation, because the π-contribution to the Os−B bond in the 16 VE complexes is already quite small. The change in the bond order is rather caused by a stronger polarization of the Os−B σ-bond toward the osmium atom in the 18 VE complexes. The osmium side has 69−85% of the bond orbital (Table 7). Although the six-coordinate complexes have significantly lower Os−B bond orders than the five-coordinate species, the bond energies of the former complexes are only slightly lower than in the latter compounds. This indicates that the covalent contributions to the Os−B bond are probably less important than the electrostatic interactions. There is a large difference in the bond order between the cis and trans Os−CO bonds (Table 7). The Os−CO bond trans to BR_2 has a much lower bond order than the cis Os−CO bond.

Summary and Conclusion

The results of this work can be summarized as follows. The calculated geometries of the five-coordinate 16 VE complexes $[(PH_3)_2(CO)ClOs-BR_2]$ and the six-coordinate 18 VE complexes $[(PH_3)_2(CO)_2ClOs-BR_2]$ are in very good agreement with the experimental data of related compounds. The Os−B bond dissociation energies are quite high and do not change very much for different boryl ligands. The 16 VE complexes have slightly higher Os−B bond energies (D_e = 83.3−90.8 kcal/mol) than the 18 VE species (D_e = 75.2−80.5 kcal/mol). The osmium−boron bonds are held together mainly by a covalent σ-bond which is polarized toward osmium, and by strong charge attraction. Os→B π-donation is not important for the Os−B binding interactions, except for the Os−BH_2 complexes. The stabilization of the boryl ligands BR_2 against nucleophilic attack comes mainly from the B←R π-donation, which is clearly higher than the Os→B π-donation except when R = H. The intraligand charge distribution of the BR_2 group changes little when the Os−B bond is formed, except for BH_2. The CO ligand in $[(PH_3)_2(CO)_2ClOs-BR_2]$ which is trans to BR_2 has a relatively low metal−ligand bond dissociation energy.

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Supporting Information Available: Two tables which contain the calculated total energies of the molecules and the valence natural electron configurations at Os and B in the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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