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Boronyl Ligand as a Member of the Isoelectronic Series $BO^{-} \rightarrow CO \rightarrow NO^{+}$: Viable Cobalt Carbonyl Boronyl Derivatives?

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Recently the first boronyl (oxoboryl) complex $[(c\text{-}C_6H_{11})_3P]_2Pt(BO)Br$ was synthesized. The boronyl ligand in this complex is a member of the isoelectronic series $BO^{-} \rightarrow CO \rightarrow NO^{+}$. The cobalt carbonyl boronyls $Co(BO)(CO)_4$ and $Co_2(BO)_2(CO)_7$, with cobalt in the formal d^8 +1 oxidation state, are thus isoelectronic with the familiar homoleptic iron carbonyls $Fe(CO)_5$ and $Fe_2(CO)_9$. Density functional theory predicts $Co(BO)(CO)_4$ to have a trigonal bipyramidal structure with the BO group in an axial position. The tricarbonyl $Co(BO)(CO)_3$ is predicted to have a distorted square planar structure, similar to those of other 16-electron complexes of d^8 transition metals. Higher energy $Co(BO)(CO)_n$ (n = 3, 2) structures may be derived by removal of one (for n = 3) or two (for n = 2) CO groups from a trigonal bipyramidal $Co(BO)(CO)_4$ structure. Structures with a CO group bridging 17-electron $Co(CO)_4$ and $Co(BO)_2(CO)_3$ units and no Co−Co bond are found for $Co_2(BO)_2(CO)_8$. However, $Co_2(BO)_2(CO)_8$ is not viable because of the predicted exothermic loss of CO to give $Co_2(BO)_2(CO)_7$. The lowest lying $Co_2(BO)_2(CO)_7$ structure is a triply bridged (2BO + CO) structure closely related to the experimental $Fe_2(CO)_9$ structure. However, other relatively low energy $Co_2(BO)_2(CO)_7$ structures are found, either with a single CO bridge, similar to the experimental $Os_2(CO)_8(\mu\text{-CO})$ structure; or with 17-electron $Co(CO)_4$ and $Co(BO)_2(CO)_3$ units joined by a single Co−Co bond with or without semibridging carbonyl groups. Both triplet and singlet $Co_2(BO)_2(CO)_6$ structures are found. The lowest lying triplet $Co_2(BO)_2(CO)_6$ structures have a $Co(CO)_3(BO)_2$ unit coordinated to a $Co(CO)_3$ unit through the oxygen atoms of the boronyl groups with a non-bonding ~4.3 Å Co···Co distance. The lowest lying singlet $Co_2(BO)_2(CO)_6$ structures have either two three-electron donor bridging η^2-μ-BO groups and no Co···Co bond or one such three-electron donor BO group and a formal Co−Co single bond.

1. Introduction

Simple diatomic ligands containing only first row elements have played important roles in the development of transition metal coordination chemistry. Thus, metal complexes of the cyanide (CN),[1−3] nitrosyl (NO),[4,5] and carbonyl (CO)[6] ligands were already known by the end of the 19th century, and an extensive coordination chemistry of each of these ligands has developed during the 20th century. In addition, the first metal complex of the dinitrogen ligand, namely, $[Ru(NH_3)_5N_2]^{+2}$, was discovered by Allen and Senoff in 1965,[7] and the coordination chemistry of dinitrogen has developed extensively since then.[8,9]

Development of the chemistry of simple diatomic ligands containing boron has lagged until very recently. The fluoroborylene ligand (BF) is isoelectronic with the carbonyl ligand (CO) and thus might be predicted to form extensive series of fluoroborylene metal complexes similar to the metal carbonyls. However, synthesis of BF metal complexes has been hindered by instability of free BF.[10] Thus at the present time there are only two examples of BF complexes in the literature. This includes an unconfirmed report in a 1968 conference proceedings[11] of the synthesis of the terminal fluoroborylene

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complex $Fe(BF)(CO)_4$ isoelectronic with $Fe(CO)_5$ from the reaction of $Fe(CO)_5$ with B_2F_4. Much more recently (2009) the bridging fluoroborylene complex $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4(\mu\text{-}BF)$ was synthesized by Vidović and Aldridge via the reaction of $NaRu(CO)_2(\eta^5\text{-}C_5H_5)$ with BF_3 and structurally characterized by X-ray diffraction.[12] Despite the paucity of transition metal BF complexes, numerous transition metal complexes of other BR ligands have been synthesized.[13−16] These include the terminal borylene complexes $(\eta^5\text{-}Me_5C_5)B\rightarrow Fe(CO)_4$ (ref 17) and $(Me_3Si)_2NB\rightarrow M(CO)_5$ (M = Cr, W[18]) that are simple substitution products of the homoleptic metal carbonyls $Fe(CO)_5$ and $M(CO)_6$, respectively. In addition, the analogous complexes $(CO)_nM\text{-}E(X)L_2$ (E = Ga, Al), as Lewis base adducts of the transition metal, have been reported experimentally.[19]

Another potentially important diatomic boron-containing ligand is the boronyl ligand, BO. In this connection, the first metal boronyl complex, $(Cy_3P)_2Pt(BO)Br$ (Cy = cyclohexyl) was synthesized only very recently by the reaction of $(Cy_3P)_2Pt$ with $Me_3SiOBBr_2$.[20] The coordinated BO ligand in $(Cy_3P)_2Pt(BO)Br$ is of interest since its oxygen atom is shown to have significant basic properties leading to adducts of the type $(Cy_3P)_2Pt(Br)(BO\rightarrow BR^f_3)$ ($R^f = C_6H_3\text{-}3,5\text{-}(CF_3)_2$).[21]

The instability of free monomeric BO, unlike monomeric CO and NO, has limited the possible synthetic approaches to metal boronyls. The first report of BO was its spectroscopic detection in 1924 by Robert Mulliken[22] in a gaseous mixture obtained from an electrical discharge in a BCl_3/O_2 mixture. Solid BO was synthesized in 1955 by Wartik and Apple[23] by the dehydration of $B_2(OH)_4$, itself obtained by the hydrolysis of B_2Cl_4 or $B_2(NMe_2)_4$. However, solid BO is a polymer with B−B bonds as well as B−O bonds and unreactive as a ligand in transition metal chemistry. Thus the problem of the synthesis of transition metal boronyl (BO) derivatives is similar to problems encountered in the successful synthesis of transition metal thiocarbonyl (CS) and fluoroborylene (BF) complexes, where the free ligand is unstable as a monomer and only available as an unreactive polymer. For the synthesis of the platinum complex $(Cy_3P)_2Pt(BO)Br$ noted above,[20] the BO source is $Me_3SiOBBr_2$, which generates the BO group by elimination of Me_3SiBr. Boron oxychloride, OBCl, might be another possible source of the BO ligand by reactions with transition metal nucleophiles such as $Co(CO)_4^-$. However, OBCl is an unstable molecule found only in small concentrations after applying an electrical discharge to a BCl_3/O_2 mixture.[24] Recent advances in the synthesis of other types of complexes with transition metal−boron bonds[25−27] may provide suitable starting materials for preparing boronyl metal complexes by conversion of another type of boron ligand to a boronyl group.

The possibility of transition metal complexes of the BO^- ligand isoelectronic with the CO ligand was first recognized as part of a comprehensive theoretical study by Baerends and co-workers[28] of transition metal complexes comparing the isolobal ligands BF, BNH_2, $BN(CH_3)_2$, and BO^-. Their study was limited to analogues of the well-established mononuclear metal carbonyls $Cr(CO)_6$, $Mn(CO)_5^-$, $Fe(CO)_5$, $Co(CO)_4^-$, and $Ni(CO)_4$, as well as the binuclear derivatives $Fe_2(CO)_9$ and $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4(\mu\text{-}CO)$ in which one of the carbonyl groups is replaced by the isoelectronic BO^- ligand leading, in all cases, to monoanions or dianions. No neutral BO derivatives were considered in their work. Their general conclusion is that the BO ligand is an unusually strong σ donor but a very poor π-acceptor because of the very high energy of its π^* LUMO.

This paper presents the first theoretical study of an extensive series of neutral transition metal boronyl derivatives. Isoelectronic analogues of the homoleptic iron carbonyls were chosen for this study since $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ have been known for more than 70 years as stable compounds and have very rich chemistry. Furthermore, the preferred structures for the unsaturated derivatives of the types $Fe_2(CO)_n$ (n = 8, 7, 6)[29] and $Fe_3(CO)_n$ (n = 11, 10, 9)[30] have been identified using density functional theory. Since the CoBO fragment is isoelectronic to FeCO, our attention naturally turns to cobalt in the context of the BO ligand. This paper reports studies on the cobalt carbonyl boronyls including $Co(BO)(CO)_4$, which is isoelectronic with both $Fe(CO)_5$ and the likewise known[31,32] $Mn(NO)(CO)_4$, as well as $Co_2(BO)_2(CO)_7$, which is isoelectronic with $Fe_2(CO)_9$. In addition the unsaturated derivatives $Co(BO)(CO)_n$ (n = 3, 2, 1) and $Co_2(BO)_2(CO)_6$ have also been investigated. Furthermore, the existence of the stable $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4(\mu\text{-}BF)$ with a bridging μ-BF group and no Ru−Ru bond[12] makes $Co_2(BO)_2(CO)_8$ of interest. Thus simple electron counting and the 18-electron rule suggests the possibility of $Co_2(BO)_2(CO)_8$ structures with one or two bridging μ-BO groups and no Co−Co bond.

2. Theoretical Methods

Electron correlation effects were considered by employing density functional theory (DFT), which has evolved as a practical and effective computational tool, especially for

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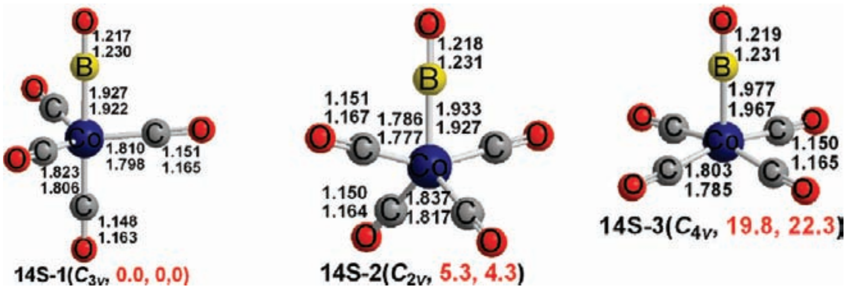

Figure 1. Three optimized structures for $Co(BO)(CO)_4$ showing the relative energies in kcal/mol (B3LYP, BP86) in parentheses.

organometallic compounds.[33−41] Two DFT methods were used in this study, namely, the B3LYP and BP86 methods. The popular B3LYP method combines the three-parameter Becke functional (B3)[42] with the Lee−Yang−Parr generalized gradient correlation functional (LYP).[43] The BP86 method combines Becke's 1988 exchange functional (B)[44] with Perdew's 1986 gradient corrected correlation functional (P86).[45] The BP86 method has been found to be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper, especially for the prediction of vibrational frequencies.[46,47]

For comparison with our previous research, the same double-ζ plus polarization (DZP) basis sets were adopted in the present study. Thus one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(B) = 0.7$, $\alpha_d(C) = 0.75$, and $\alpha_d(O) = 0.85$ for boron, carbon, and oxygen, respectively, was added to the standard Huzinaga−Dunning contracted DZ sets,[48,49] designated (9s5p1d/4s2p1d). The loosely contracted DZP basis set for cobalt is the Wachters primitive set[50] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer, and Schaefer,[51] designated as (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using the two DFT methods. Harmonic vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All computations were performed with the Gaussian 03 program package.[52] The fine grid (75, 302) was the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation is the default for the self-consistent field energy convergence. All of the predicted triplet structures in the present study are found to have negligible spin contamination, with the $S(S + 1)$ values close to the ideal outcome of 2.0.

The results predicted by both B3LYP and BP86 methods agree fairly well. For the sake of brevity, only the BP86 results are discussed in the text, unless specifically noted. However, both the B3LYP and the BP86 results are shown in the figures and tables.

A given $Co_a(BO)_a(CO)_b$ structure is designated as **abA-c** where **a** is the number of cobalt atoms (the same as the number of BO groups), **b** is the number of CO groups, and **c** orders the structures according to their relative energies. **A** indicates whether the structure is a singlet (**S**) or triplet (**T**). Thus the lowest energy structure of singlet $Co_2(BO)_2(CO)_8$ is designated **28S-1**. The total energies (E, in hartree), relative energies (ΔE, in kcal mol^{-1}), and numbers of imaginary vibrational frequencies (N_{Imag}) for all of the optimized structures are listed in the Supporting Information. The relative energies (ΔE, in kcal mol^{-1}) are also listed in Figures 1 to 7 (in parentheses, in the order of B3LYP and BP86).

3. Results

3.1. Mononuclear Derivatives. 3.1.1. $Co(BO)(CO)_4$.

Both DFT methods predict three singlet structures for $Co(BO)(CO)_4$ (Figure 1). The global minimum **14S-1** is a C_{3v} symmetry singlet trigonal bipyramidal structure with the linear BO group in an axial position. A C_{2v} trigonal bipyramidal $Co(BO)(CO)_4$ structure **14S-2**, with the BO group in an equatorial position, lies energetically above **14S-1** by 4.3 kcal/mol. Structure **14S-2** is a transition state with a small imaginary vibrational frequency at $27i$ cm^{-1}. Following the corresponding normal mode leads to **14S-1**. Assuming that the BO ligand is a formal one-electron donor and the CO ligand is a formal two-electron donor, the cobalt atoms in **14S-1** and **14S-2** have the favored 18-electron configuration.

We also predict a C_{4v} singlet $Co(BO)(CO)_4$ structure with a linear BO group in the apical position of a square pyramid at 22.3 kcal/mol above the global minimum **14S-1** (Figure 1). However, this structure has a large imaginary vibrational frequency at $204i$ cm^{-1}. Following the corresponding normal mode leads to **14S-2.**

3.1.2. $Co(BO)(CO)_3$.

Four low-lying structures (two singlets and two triplets) were found for $Co(BO)(CO)_3$. These structures are predicted to be genuine minima with all real vibrational frequencies (Figure 2). The global minimum **13S-1** of $Co(BO)(CO)_3$ is a singlet square planar structure of C_{2v} symmetry (B3LYP) or a distorted square planar structure of C_s symmetry (BP86) with the pair of opposite CO ligands slightly tilted in the same direction. The cobalt atom in $Co(BO)(CO)_3$ has a 16-electron configuration, assuming that the BO ligand is a formal one-electron donor and the CO ligand is a formal two-electron donor.

Two triplet structures were found for $Co(BO)(CO)_3$ (Figure 2). The C_s structure **13T-1** lies at 21.6 kcal/mol above **13S-1**. This structure may be derived from the

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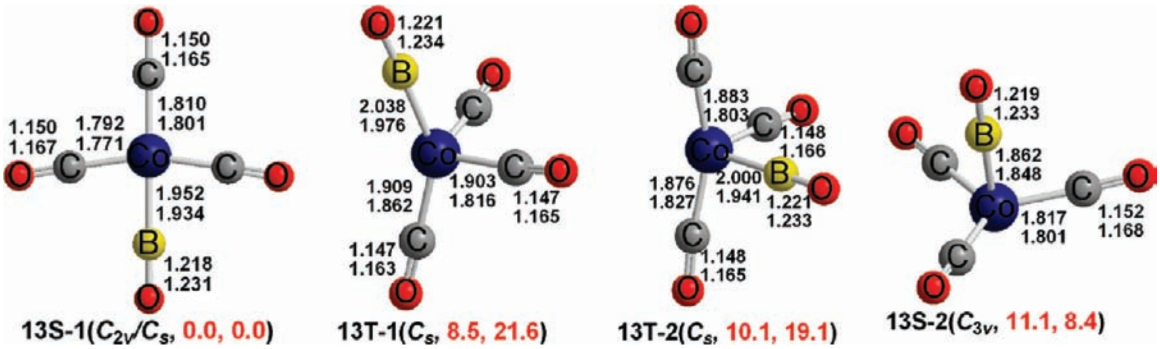


Figure 2. Four optimized structures for $Co(BO)(CO)_3$ showing the relative energies in kcal/mol (B3LYP, BP86) in parentheses.

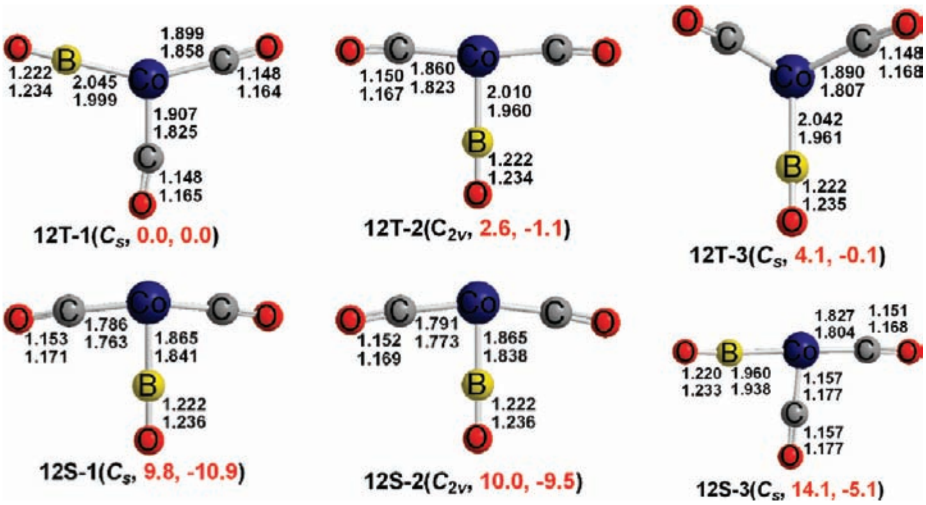


Figure 3. Six optimized $Co(BO)(CO)_2$ structures showing the relative energies in kcal/mol (B3LYP, BP86) in parentheses.

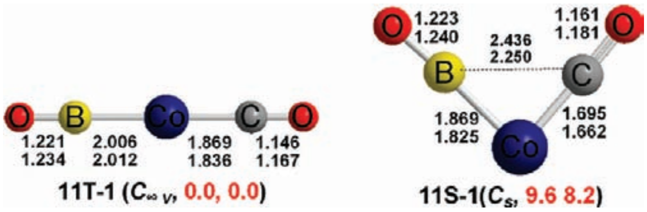


Figure 4. Two optimized Co(BO)(CO) structures showing the relative energies in kcal/mol (B3LYP, BP86) in parentheses.

$Co(BO)(CO)_4$ structure **14S-1** (Figure 1) by removal of an equatorial carbonyl group. The other triplet $Co(BO)(CO)_3$ structure **13T-2** is also a C_s structure and lies 19.1 kcal/mol above **13S-1**. This structure can be derived from the $Co(BO)(CO)_4$ structure **14S-2** (Figure 1) by removal of an equatorial carbonyl group.

The other singlet structure **13S-2** of $Co(BO)(CO)_3$ (Figure 2) has C_{3v} symmetry and is predicted to lie 8.4 kcal/mol in energy above **13S-1**. Structure **13S-2** can be derived from the $Co(BO)(CO)_4$ structure **14S-1** by removing a CO group from an axial position. In structure **13S-2** the three CO ligands are bent toward the BO ligand so all four ligands reside in the same hemisphere.

3.1.3. $Co(BO)(CO)_2$.

Three triplet structures and three singlet structures were found for $Co(BO)(CO)_2$ by each DFT method (Figure 3). Structures **12T-1**, **12T-2**, **12T-3**, **12S-1**, and **12S-3** are predicted to be genuine minima with all real vibrational frequencies. However, structure **12S-2** is predicted to have a small imaginary vibrational frequency. The B3LYP method predicts the C_s triplet structure **12T-1** to be the global minimum, at 9.8 kcal/mol below the singlet structure **12S-1.** However, the BP86 method predicts **12S-1** to be the global minimum, at 10.9 kcal/mol below **12T-1**. This sort of difference between B3LYP and BP86 is typical for singlet–triplet energy gaps. Structure **12T-1** for $Co(BO)(CO)_2$ is an unsymmetrical planar T-shaped structure, and **12S-1** for $Co(BO)(CO)_2$ is a distorted T-shaped structure.

The symmetrical planar T-shaped C_{2v} triplet structure **12T-2** and the pyramidal C_s triplet **12T-3** structure for $Co(BO)(CO)_2$ are nearly degenerate in energy within ~1.5 kcal/mol. The symmetrical planar T-shaped C_{2v} singlet $Co(BO)(CO)_2$ structure **12S-2** lies 10.0 kcal/mol above **12T-1** (B3LYP) or 9.5 kcal/mol below **12T-1** (BP86). The unsymmetrical planar T-shaped C_s singlet structure **12S-3** lies 14.1 kcal/mol above **12T-1** (B3LYP) or 5.1 kcal/mol (BP86) below **12T-1**. Structure **12S-2** is a transition state with an imaginary frequency of $62i$ cm^{-1}. Following the corresponding normal mode leads to **12S-1**.

3.1.4. Co(BO)(CO).

One triplet structure and one singlet structure are predicted for Co(BO)(CO) by either DFT method (Figure 4). Both structures are predicted to be genuine minima with all real vibrational frequencies.

The global minimum **11T-1** is a triplet linear structure with $C_{\infty v}$ symmetry. The singlet Co(BO)(CO) structure **11S-1** is a V-shaped C_s structure lying 8.2 kcal/mol above **11T-1**. The predicted B···C distance in **11S-1** of 2.250 Å is too long to correspond to a direct bond.

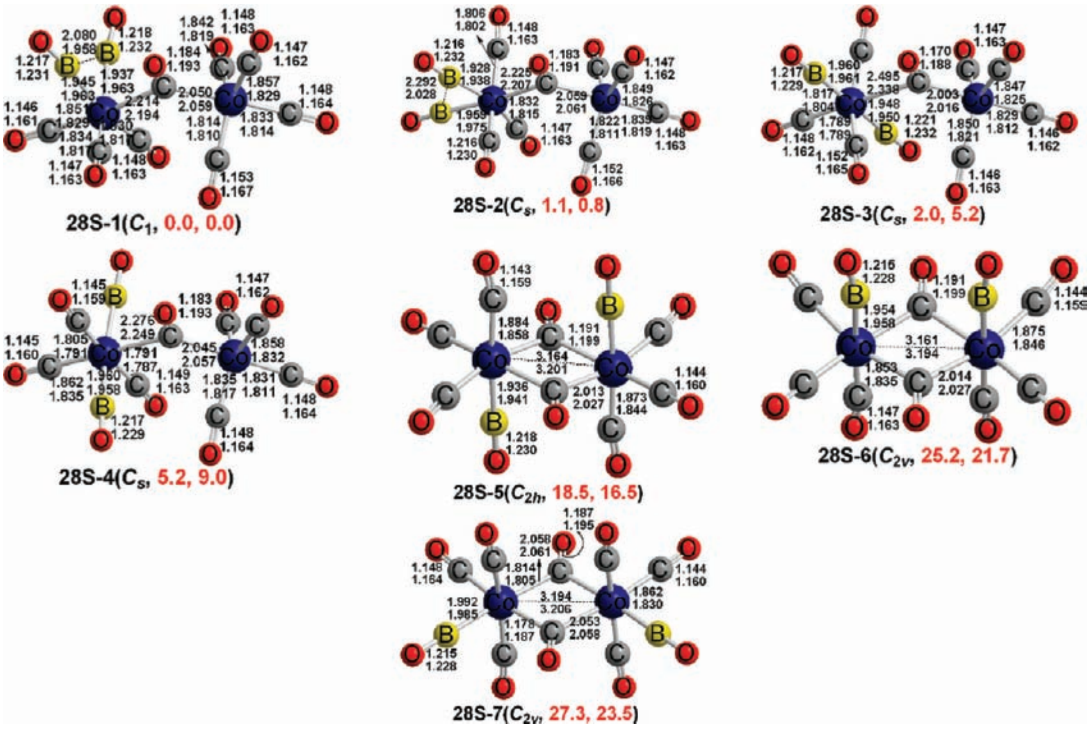


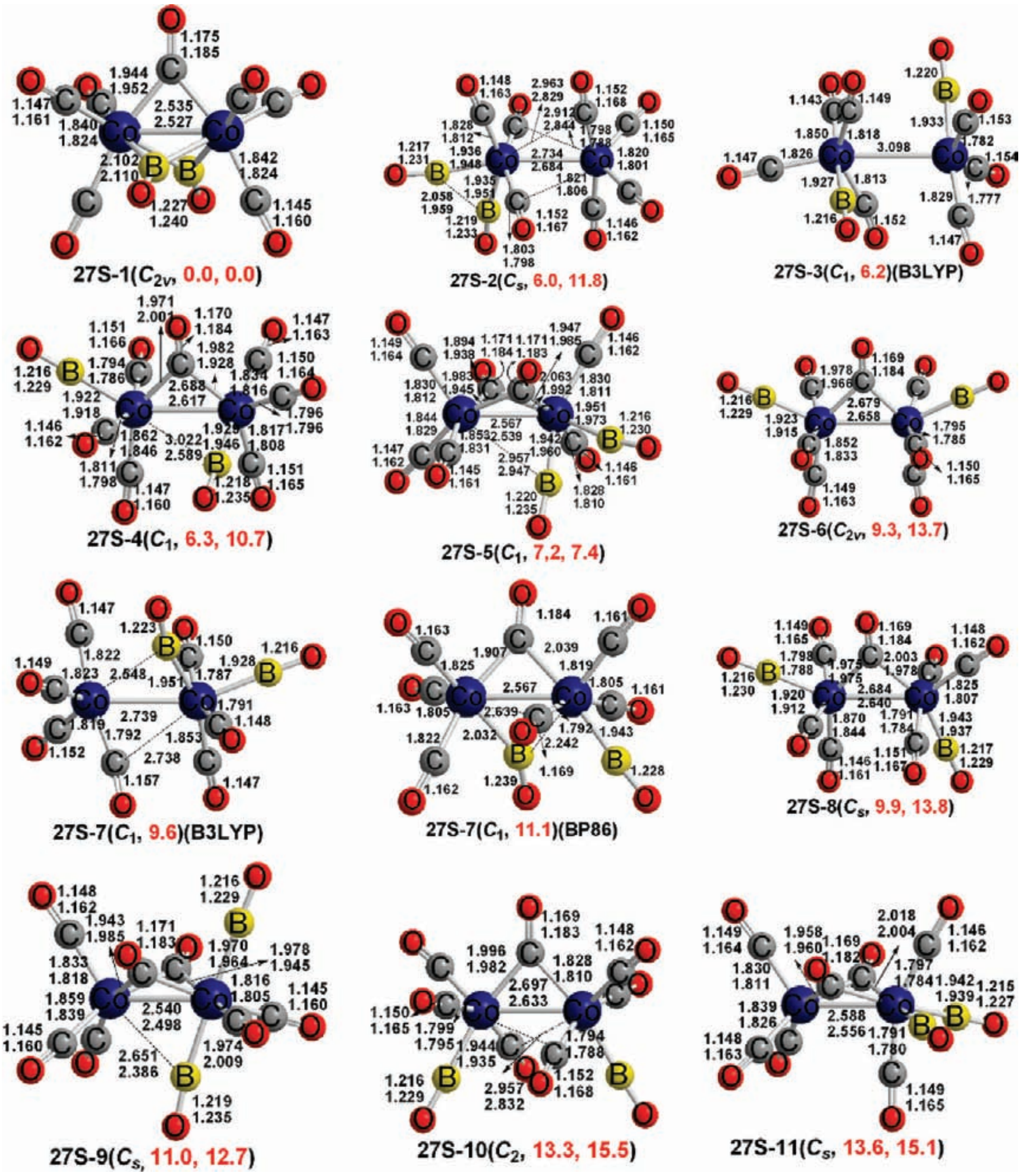
Figure 5. Optimized $Co_2(BO)_2(CO)_8$ structures, isoelectronic with the unknown $Fe_2(CO)_{10}$. The relative energies in kcal/mol (B3LYP, BP86) are shown in parentheses.

A singlet $C_{\infty v}$ linear Co(BO)(CO) structure similar to **11T-1** is predicted to lie 60.8 kcal/mol above **11T-1** in energy and thus is not likely to be chemically relevant. Attempted optimization of a triplet C_s V-shaped structure similar to **11S-1** collapsed to the linear triplet $C_{\infty v}$ structure **11T-1.**

3.2. Binuclear Derivatives. 3.2.1. $Co_2(BO)_2(CO)_8$. The cobalt atoms in a cobalt carbonyl boronyl derivative of stoichiometry $Co_2(BO)_2(CO)_8$ can have the favorable 18-electron configuration without a cobalt−cobalt bond. In view of the fact that $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4(\mu\text{-BF})$ has been synthesized with a bridging BF group but no ruthenium−ruthenium bond,[12] the cobalt carbonyl boronyls $Co_2(BO)_2(CO)_8$ were investigated even though their viability appeared to be questionable in view of the prospect of dissociation into 2 $Co(BO)(CO)_4$. In this connection seven singlet structures are found for $Co_2(BO)_2(CO)_8$ (Figure 5). Perhaps the most interesting feature of these structures is that none of them displays a bridging BO ligand. The four $Co_2(BO)_2(CO)_8$ structures **28S-1**, **28S-2**, **28S-3**, and **28S-4** have similar geometries, consisting of a $Co(BO)_2(CO)_3$ unit and a $Co(CO)_4$ unit joined by a bridging CO group. These four structures differ in the relative positions of the two BO groups. The remaining three singlet $Co_2(BO)_2(CO)_8$ structures, namely, **28S-5**, **28S-6**, and **28S-7**, have similar geometries consisting of two $Co(BO)(CO)_3$ units joined by two bridging CO groups. In all cases the Co···Co distances are too long to imply any direct cobalt−cobalt bonding.

The global minimum $Co_2(BO)_2(CO)_8$ structure **28S-1** (Figure 5) with one bridging CO group is predicted to be a genuine minimum by both the B3LYP and BP86 methods. The next low-lying C_s singlet $Co_2(BO)_2(CO)_8$ structure **28S-2**, also with one bridging CO group, lies only 0.8 kcal/mol above the global minimum **28S-1**. Thus structures **28S-1** and **28S-2** appear to be essentially degenerate. The geometries of **28S-1** and **28S-2** differ only by a rotation of the terminal BO groups. The $Co_2(BO)_2(CO)_8$ structures **28S-3** and **28S-4**, both with C_s symmetry, also have one bridging CO group, two terminal BO groups, and seven terminal CO groups. Structure **28S-3** is a genuine minimum by both the B3LYP and BP86 methods, lying 5.2 kcal/mol in energy above structure **28S-1**. The $Co_2(BO)_2(CO)_8$ structure **28S-4** is predicted to lie 9.0 kcal/mol in energy above **28S-1**. Structure **28S-4** is predicted to be a genuine minimum by B3LYP but has a small imaginary vibrational frequency of $10i$ cm^{-1} by BP86. This small imaginary frequency increases slightly to $13i$ cm^{-1} when a finer integration grid (120, 974) is used. The energy difference between **28S-3** and **28S-4** is 3.8 kcal/mol, and the geometries of these structures are very similar. The only difference between structures **28S-3** and **28S-4** is the location of the B···B axis relative to the CoCo(μ-CO) plane. Thus the B···B axis is parallel to the CoCo(μ-CO) plane in **28S-3** but perpendicular to the CoCo(μ-CO) plane in **28S-4**. The Co···Co distances of ~3.7 Å in the $Co_2(BO)_2(CO)_8$ structures **28S-1** through **28S-4** are too long for any direct cobalt−cobalt bonding. However, the cobalt atoms in these four structures all have the favored 18-electron configuration, even in the absence of any cobalt−cobalt bond.

Three $Co_2(BO)_2(CO)_8$ structures are found with two bridging carbonyl groups (Figure 5). All of these structures lie at significantly higher energies than the four singly bridged $Co_2(BO)_2(CO)_8$ structures discussed above. Among the three doubly bridged singlet $Co_2(BO)_2(CO)_8$ structures the two structures **28S-5** (C_{2h}) and **28S-6** (C_{2v}) are a *cis-trans* isomer pair. The *trans* isomer **28S-5** lies 16.5 kcal/mol in energy above **28S-1** and has no imaginary vibrational frequencies by either DFT method. The corresponding *cis* isomer **28S-6** lies 21.7 kcal/mol in energy above **28S-1** and has no imaginary vibrational frequency by B3LYP but a small imaginary vibrational frequency of



27S-1(C_{2v}, 0.0, 0.0) 27S-2(C_s, 6.0, 11.8) 27S-3(C_1, 6.2)(B3LYP)

27S-4(C_1, 6.3, 10.7) 27S-5(C_1, 7,2, 7.4) 27S-6(C_{2v}, 9.3, 13.7)

27S-7(C_1, 9.6)(B3LYP) 27S-7(C_1, 11.1)(BP86) 27S-8(C_s, 9.9, 13.8)

27S-9(C_s, 11.0, 12.7) 27S-10(C_2, 13.3, 15.5) 27S-11(C_s, 13.6, 15.1)

Figure 6. Optimized $Co_2(BO)_2(CO)_7$ structures showing the relative energies in kcal/mol (B3LYP, BP86) in parentheses.

$11i$ cm^{-1} by BP86. This small imaginary frequency becomes $9i$ cm^{-1} when the finer integration grid (120, 974) is used. The third doubly bridged $Co_2(BO)_2(CO)_8$ structure **28S-7** lies 23.5 kcal/mol above the singly bridged global minimum **28S-1**. The Co−Co bond distances in the three $Co_2(BO)_2(CO)_8$ structures **28S-5**, **28S-6**, and **28S-7** of ~3.2 Å are too long to indicate any direct cobalt−cobalt bonding. Nevertheless, each of the cobalt atoms in each of these three structures has the favored 18-electron configuration. For comparison the Co−Co formal single bond distance in $Co_2(CO)_8$ was found by X-ray crystallography[53−55] to be 2.530 Å.

3.2.2. $Co_2(BO)_2(CO)_7$.

Eleven singlet structures were found for $Co_2(BO)_2(CO)_7$ within 20 kcal/mol of the global minimum, thereby indicating a very complicated potential energy surface (Figure 6). All of these $Co_2(BO)_2(CO)_7$ structures are genuine minima by both DFT methods.

The global minimum $Co_2(BO)_2(CO)_7$ structure **27S-1**, predicted by both methods, (Figure 6) is a fascinating C_{2v} triply bridged singlet with two bridging BO groups, one bridging CO group, and six terminal CO groups. This geometry is related to the geometry of the known $Fe_2(CO)_9$, determined by X-ray crystallography.[56] The Co−Co bond distance in **27S-1** is predicted to be 2.527 Å, consistent with a single bond, giving each of the cobalt atoms the favored 18-electron configuration. Furthermore, this predicted Co−Co distance is very close to the experimental

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(54) Leung, P. C.; Coppens, P. *Acta Crystallogr*. **1983**, *B39*, 535.

(55) Braga, D.; Grepioni, F.; Sabatino, P.; Gavezzotti, A. *J. Chem. Soc., Dalton Trans*. **1992**, 1185.

(56) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans*. **1974**, 800.

Fe–Fe distance of 2.523 Å in $Fe_2(CO)_9$, determined by X-ray crystallography.

Two relatively low energy unbridged $Co_2(BO)_2(CO)_7$ structures were also found (Figure 6). Structure **27S-2** can be constructed by linking a 17-electron $Co(CO)_4$ unit to a 17-electron $Co(BO)_2(CO)_3$ unit with a cobalt–cobalt bond. This structure lies 11.8 kcal/mol above **27S-1**, without any imaginary vibrational frequencies by either method. The Co–Co bond distance in **27S-2** is 2.684 Å, corresponding to the formal single bond needed to give both cobalt atoms the favored 18-electron configurations. This unbridged Co–Co single bond distance is ~0.2 Å longer than the triply bridged Co–Co single bond distance found in the $Co_2(BO)_2(CO)_7$ structure **27S-1**, owing to the effect of the three bridging groups.

The second unbridged $Co_2(BO)_2(CO)_7$ structure **27S-3** lies 6.2 kcal/mol (B3LYP) in energy above the global minimum **27S-1**. Structure **27S-3** can be constructed by joining an 18-electron $Co(BO)(CO)_4$ unit to a 16-electron $Co(BO)(CO)_3$ unit through a very long (3.098 Å) Co→Co dative bond from the 18-electron unit to the 16-electron unit. Structure **27S-3** could only be optimized using the B3LYP method. Attempted optimization of **27S-3** by the BP86 method leads instead to **27S-1**. The $Co(BO)(CO)_4$ unit in the $Co_2(BO)_2(CO)_7$ structure **27S-3** is a square pyramidal isomer of the predicted 18-electron stable trigonal bipyramidal molecule **14S-1** (Figure 1) and thus can be considered as a "ligand" to the 16-electron $Co(BO)(CO)_3$ unit.

The four singly bridged singlet $Co_2(BO)_2(CO)_7$ structures **27S-4**, **27S-6**, **27S-8**, and **27S-10** (Figure 6) have similar geometries with a single bridging CO group, two terminal BO groups, and six terminal CO groups. All four structures are true minima with no imaginary vibrational frequencies by either B3LYP or BP86. The energies of the structures **27S-4**, **27S-6**, **27S-8**, and **27S-10** are 10.7 kcal/mol, 13.7 kcal/mol, 13.8 kcal/mol, and 15.5 kcal/mol higher, respectively, than that of the $[Fe_2(CO)_9]$-like global minimum **27S-1**. Structures **27S-6** and **27S-8** form a *cis-trans* isomer pair with essentially the same energies (within <1 kcal/mol). The Co–Co bond distances in the four structures **27S-4**, **27S-6**, **27S-8**, and **27S-10** fall in the range 2.64 ± 0.03 Å, corresponding to the formal single bond required to give both cobalt atoms in each structure the favored 18-electron configuration. These singly bridged structures of $Co_2(BO)_2(CO)_7$ are related to the known experimental structure of $Os_2(CO)_9$ with a single bridging carbonyl group and eight terminal carbonyl groups.[57,58]

The doubly bridged singlet $Co_2(BO)_2(CO)_7$ structures **27S-5**, **27S-9**, and **27S-11** have similar geometries with two bridging CO groups, two terminal BO groups, and five terminal CO groups (Figure 6). These three structures differ only in the locations of the terminal BO groups. All three structures are genuine minima, with no imaginary vibrational frequencies by either DFT method. The $Co_2(BO)_2(CO)_7$ structures **27S-5**, **27S-9**, and **27S-11** lie 7.4 kcal/mol, 12.7 kcal/mol, and 15.1 kcal/mol, respectively, above the global minimum **27S-1**. The Co–Co bond distances in the doubly bridged $Co_2(BO)_2(CO)_7$ structures **27S-5**, **27S-9**, and **27S-11** fall in the range 2.53 ± 0.03 Å, which is very similar to the triply bridged Co–Co single bond distance of 2.53 Å in the $Co_2(BO)_2(CO)_7$ structure **27S-1**. This corresponds to the formal single bonds required to give both cobalt atoms the favored 18-electron configurations.

The B3LYP and BP86 methods give slightly different structures for the final singlet $Co_2(BO)_2(CO)_7$ structure, namely, **27S-7** (Figure 6). Thus the **27S-7** structure predicted by the B3LYP method has two terminal BO groups and seven terminal CO groups and lies 9.6 kcal/mol above the global minimum **27S-1**. However, the **27S-7** structure by the BP86 method has one bridging CO group, one semibridging CO group, one bridging BO group, one terminal BO group, and five terminal CO groups and lies 11.1 kcal/mol in energy above the global minimum **27S-1**. Structure **27S-7** has no imaginary frequencies by either method. The Co–Co distance in **27S-7** is 2.567 Å, corresponding to the formal single bond required to give both cobalt atoms the favored 18-electron configuration. The shorter Co–Co distance in the BP86 **27S-7** structure of $Co_2(BO)_2(CO)_7$ relative to the B3LYP **27S-7** structure of $Co_2(BO)_2(CO)_7$ by ~0.17 Å may be related to the fact that the BP86 structure has two bridging groups (BO + CO) and one semibridging group (CO) whereas the B3LYP structure has no bridging groups.

3.2.3. $Co_2(BO)_2(CO)_6$.

A total of 18 singlet structures and 12 triplet structures within 43 kcal/mol of the global minimum are predicted for $Co_2(BO)_2(CO)_6$ indicating a very complicated potential energy surface. Only the 14 structures of $Co_2(BO)_2(CO)_6$ within 30 kcal/mol of the global minimum, namely, 9 singlet structures and 5 triplet structures, are discussed in the paper (Figure 7). The B3LYP and the BP86 methods differ significantly in the relative energy ordering of these structures. Thus, the B3LYP method predicts all five triplet structures to lie below the lowest lying singlet structure **26S-1**. However, the BP86 method predicts the energies of four of the singlet $Co_2(BO)_2(CO)_6$ structures to lie below that of the lowest lying triplet structure **26T-1**. The $Co_2(BO)_2(CO)_6$ structures, except for **26S-3** and **26S-9**, have no imaginary vibrational frequencies by BP86, implying that they are genuine minima. The designations for the $Co_2(BO)_2(CO)_6$ structures in Figure 7 are based on their relative energies, as determined by the B3LYP method.

The three triplet $Co_2(BO)_2(CO)_6$ structures **26T-1**, **26T-2**, and **26T-3** all have two $Co(CO)_3$ units linked by two bridging BO groups, bonded to one cobalt atom through the boron atom and bonded to the other cobalt atom through the oxygen atom (Figure 7). These structures can be dissected into a bidentate $Co(CO)_3(BO)_2$ "ligand" chelating to the cobalt atom of the other $Co(CO)_3$ group through the oxygen atoms of the two BO groups, thereby forming a six-membered $Co_2B_2O_2$ chelate ring. The Co–Co bond distances in these three $Co_2(BO)_2(CO)_6$ structures are ~4.3 Å, which is far too long for a direct Co–Co bond. Thus the cobalt atom in this bidentate $Co(CO)_3(BO)_2$ "ligand" has a 17-electron configuration, accounting for one of the two unpaired electrons of the triplet. The other $Co(CO)_3$ group in these three $Co_2(BO)_2(CO)_6$ structures receives two electrons from each of the BO oxygen atoms giving it a 19-electron configuration. The energy difference between **26T-1** and **26T-2** of only 0.4 kcal/mol suggests that these structures are

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(57) Moss, J. R.; Graham, W. A. G. *Chem. Commun.* **1970**, 835.
(58) Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.

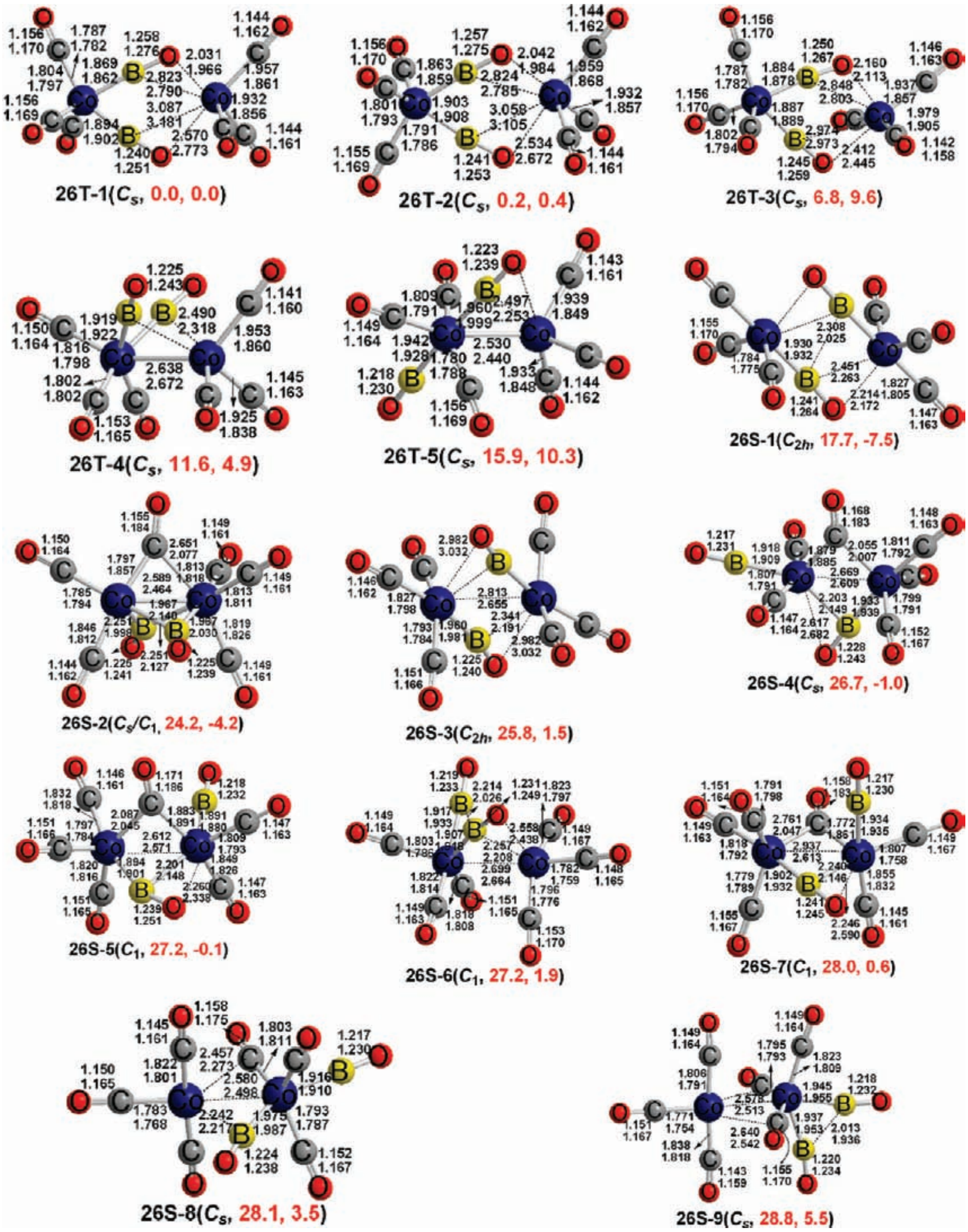

Figure 7. Optimized $Co_2(BO)_2(CO)_6$ structures showing the relative energies in kcal/mol (B3LYP, BP86) in parentheses.

essentially degenerate. The energy of **26T-3** is 9.6 kcal/mol higher than that of **26T-1**.

The *C*$_s$ triplet $Co_2(BO)_2(CO)_6$ structure **26T-4**, the *C*$_{2h}$ singlet structure **26S-1**, and the *C*$_{2h}$ singlet structure **26S-3** all have two bridging BO groups and six terminal CO groups (Figure 7). In **26T-4** the Co−Co bond distance is 2.672 Å corresponding to a formal single bond giving each cobalt atom the 17-electron configuration for a binuclear triplet. In the singlet structure **26S-1** the Co···Co distance is 3.689 Å, which is much too long for a direct bond. However, in **26S-1** the Co−O distances to the bridging BO groups are unusually short at 2.172 Å implying direct cobalt−oxygen bonds. The bridging BO groups, when considered as neutral ligands, are thus formal three-electron donors rather than the usual one-electron donors. This gives each cobalt atom in the $Co_2(BO)_2(CO)_6$ structure **26S-1** the favored 18-electron configuration.

The next lowest lying $Co_2(BO)_2(CO)_6$ structure **26S-2** is a bridged *C*$_s$ structure (B3LYP) or *C*$_1$ structure (BP86), lying 24.2 kcal/mol (B3LYP) above **26T-1** or 4.2 kcal/mol (BP86) below **26T-1** with no imaginary vibrational frequencies (Figure 7). Structure **26S-2** has two bridging BO groups, one semibridging CO group, and five terminal CO groups by B3LYP or two bridging BO groups, one bridging CO group, and five terminal CO groups by BP86. This $Co_2(BO)_2(CO)_6$ structure (BP86) can be derived from the triply bridged $Co_2(BO)_2(CO)_7$ structure **27S-1** by removing a terminal CO group. The Co−Co bond distance in **26S-2** is 2.464 Å.

The $Co_2(BO)_2(CO)_6$ structure **26S-3** (Figure 7) lies 9.0 kcal/mol above the lowest lying singlet structure **26S-1** with no imaginary vibrational frequencies (B3LYP) or one very small imaginary frequency of $27i$ cm^{-1} (BP86). The Co−Co bond distance in **26S-3** is 2.655 Å.

The doubly bridged singlet $Co_2(BO)_2(CO)_6$ structures **26S-4**, **26S-5**, and **26S-7**, all have one bridging BO group, one bridging CO group, one terminal BO group, and five terminal CO groups (Figure 7). Structure **26S-4** lies 26.7 kcal/mol higher than that of **26T-1** (B3LYP) or 1.0 kcal/mol lower than that of **26T-1** (BP86) with no imaginary vibrational frequencies. The energy difference between **26S-4** and **26S-5** of only 0.9 kcal/mol suggests that these structures are essentially degenerate. The bridging BO groups in these structures are three-electron donor ligands with short enough Co−O distances to suggest direct interactions. Thus in **26S-4** the predicted Co−O distances are 2.682 Å. In **26S-5** the predicted Co−O distances are significantly shorter at 2.338 Å. The Co−Co bond distances are 2.609 Å in **26S-4** and 2.571 Å in **26S-5** consistent with a formal single bond. This gives each of the cobalt atoms in **26S-4** and **26S-5** the favored 18-electron configurations after considering the fact that the bridging BO group donates three electrons rather than the usual single electron.

The $Co_2(BO)_2(CO)_6$ structure **26S-7** lies 0.6 kcal/mol above **26T-1** with no imaginary vibrational frequencies (Figure 7). The bridging BO group in **26S-7**, like that in the $Co_2(BO)_2(CO)_6$ structures **26S-4** and **26S-5**, is a formal three-electron donor η^2-μ-BO group as indicated by short Co−O distances of 2.590 Å. The Co−Co distances in **26S-7** predicted by the B3LYP and BP86 methods are distinctly different, namely, 2.937 Å by B3LYP but only 2.613 Å by BP86. However, structure **26S-7** has a semibridging CO group by B3LYP, which may account for the ~0.3 Å longer Co−Co distance by B3LYP than by BP86.

The $Co_2(BO)_2(CO)_6$ structure **26S-8** lies only 2.9 kcal/mol above **26S-7**, suggesting that these two structures are essentially degenerate. The Co−O distance to the bridging BO group in **26S-8** is too long for direct bonding, implying that the bridging BO group in **26S-8** is only a formal one-electron donor. The Co−Co distance in **26S-8** is 2.498 Å.

The singly bridged C_1 singlet $Co_2(BO)_2(CO)_6$ structure **26S-6** and C_s triplet structure **26T-5** both have one bridging BO group, one terminal BO group, and six terminal CO groups. Structures **26S-6** and **26T-5** lie 1.9 and 10.3 kcal/mol, respectively, above **26T-1** without any imaginary vibrational frequencies. The Co−O distance to the bridging BO group of 2.438 Å in **26S-6** suggests a three-electron donor bridging η^2-μ-BO group. However, the long Co−O distances to the bridging BO group in **26T-5** suggest the usual one-electron donor bridging BO group. The predicted Co−Co distances are 2.664 Å in **26S-6** and 2.440 Å in **26T-5**.

The singlet $Co_2(BO)_2(CO)_6$ structure **26S-9** (C_s) has two semibridging CO groups, two terminal BO groups on the same cobalt atom, and four terminal CO groups and lies 5.5 kcal/mol above **26T-1** with no imaginary vibrational frequencies (B3LYP) or a small imaginary vibrational frequency of $28i$ cm^{-1} (BP86). The predicted Co−Co distances in **26S-9** are 2.513 Å suggesting a formal single bond. This $Co_2(BO)_2(CO)_6$ structure can be generated by joining a $Co(BO)_2(CO)_3$ fragment to a $Co(CO)_3$ fragment through a Co−Co single bond followed by two of the originally terminal carbonyl groups moving to semibridging positions. This gives the cobalt atom in **26S-9** bearing the two BO groups the favored 18-electron configuration but the other cobalt atom only a 16-electron configuration. However, the cobalt atom in **26S-9** assigned a 16-electron configuration has essentially square planar coordination counting only the three terminal carbonyl groups and the Co−Co bond. Square planar metal complexes with a 16-electron configuration are rather well-known, as exemplified by numerous Rh(I), Ni(II), Pd(II), and Pt(II) complexes.

3.3. Dissociation Energies. Table 1 reports the dissociation energies for removing one carbonyl group from the global minima of the mononuclear $Co(BO)(CO)_m$ and binuclear $Co_2(BO)_2(CO)_n$ structures according to the following equations:

$$Co(BO)(CO)_m \rightarrow Co(BO)(CO)_{m-1} + CO \quad (m = 4, 3, 2)$$

$$Co_2(BO)_2(CO)_n \rightarrow CO_2(BO)_2(CO)_{n-1} + CO \quad (n = 8, 7)$$

The predicted dissociation energy for the loss of one CO group from mononuclear $Co(BO)(CO)_4$ is 41.4 kcal/mol. This is similar to the experimental dissociation energy[59] of 41 kcal/mol for the loss of one CO group from the isoelectronic $Fe(CO)_5$. The energy for the dissociation of $Co(BO)(CO)_3$ into $Co(BO)(CO)_2$ + CO is 58.0 kcal/mol. For the binuclear derivatives the carbonyl dissociation energy of $Co_2(BO)_2(CO)_8$ is predicted to be exothermic by −12.5 kcal/mol indicating instability with respect to the formation of $Co_2(BO)_2(CO)_7$. Such instability is typical for binuclear metal carbonyl derivatives without a formal metal−metal bond. The further dissociation of a carbonyl group from $Co_2(BO)_2(CO)_7$ is 28.6 kcal/mol suggesting that $Co_2(BO)_2(CO)_7$, unlike $Co_2(BO)_2(CO)_8$, is reasonably stable toward carbonyl dissociation to give $Co_2(BO)_2(CO)_6$.

Table 1 also reports the BO dissociation energies for the mononuclear $Co(BO)(CO)_m$ and binuclear $Co_2(BO)_2(CO)_n$ derivatives. All of the BO dissociation energies were found to be much higher than CO dissociation energies with even the lowest BO dissociation energy being greater than 65 kcal/mol. Therefore, BO dissociation is predicted not to be a factor in the chemistry of cobalt carbonyl boronyls.

The dissociation energies of the binuclear $Co_2(BO)_2(CO)_n$ into mononuclear fragments by the following reactions are also reported in Table 1:

$$Co_2(BO)_2(CO)_n \rightarrow Co(BO)(CO)_x + Co(BO)(CO)_y \quad (n = x + y)$$

The dissociation of $Co_2(BO)_2(CO)_8$ into two equivalent $Co(BO)(CO)_4$ fragments is seen to be an exothermic process by −31.7 kcal/mol. This is not surprising since

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[59] Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 12060.

Table 1. Dissociation Energies (kcal/mol) for $Co_2(BO)_2(CO)_m$ (m = 2, 3, 4) and $Co_2(BO)_2(CO)_n$ (n = 7, 8) Based on the Lowest Energy Structures[a]

	B3LYP	BP86
$Co(BO)(CO)_4$ (**14S-1**) → $Co(BO)(CO)_3$ (**13S-1**) + CO	31.7	41.4
$Co(BO)(CO)_4$ (**14S-1**) → $Co(CO)_4$ + BO	74.0	83.0
$Co(BO)(CO)_3$ (**13S-1**) → $Co(BO)(CO)_2$ (**12T-1**) + CO	32.0	58.0
$Co(BO)(CO)_3$ (**13S-1**) → $Co(CO)_3$ + BO	69.6	81.4
$Co(BO)(CO)_2$ (**12T-1**) → Co(BO)(CO) (**11T-1**) + CO	43.9	33.0
$Co(BO)(CO)_2$ (**12T-1**) → $Co(CO)_2$ + BO	67.4	62.9
Co(BO)(CO) (**11T-1**) → Co(CO) + BO	67.6	79.9
$Co_2(BO)_2(CO)_8$ (**28S-1**) → $Co_2(BO)_2(CO)_7$ (**27S-1**) + CO	−12.7	−12.5
$Co_2(BO)_2(CO)_8$ (**28S-1**) → $Co_2(CO)_8$ + 2BO	102.2	101.0
$Co_2(BO)_2(CO)_7$ (**27S-1**) → $Co_2(BO)_2(CO)_6$ (**26S-1**) + CO	16.0	28.6
$Co_2(BO)_2(CO)_7$ (**27S-1**) → $Co_2(CO)_7$ + 2BO	137.6	148.4
$Co_2(BO)_2(CO)_6$ (**26S-1**) → $Co_2(CO)_6$ + 2BO	144.5	142.8
$Co_2(BO)_2(CO)_8$ (**28S-1**) → $2Co(BO)(CO)_4$ (**14S-1**)	−37.8	−31.7
$Co_2(BO)_2(CO)_7$ (**27S-1**) → $Co(BO)(CO)_4$(**14S-1**) + $Co(BO)(CO)_3$(**13S-1**)	6.7	22.1
$Co_2(BO)_2(CO)_6$ (**26S-1**) → $2Co(BO)(CO)_3$ (**13S-1**)	22.4	35.0

[a] All results reported here refer to the global minima of reactant and products.

$Co(BO)(CO)_4$ is predicted to be a stable 18-electron complex (structure **14S-1** in Figure 1), which is isoelectronic with the well-known $Fe(CO)_5$. However, the energy required for dissociation of $Co_2(BO)_2(CO)_7$ into $Co(BO)(CO)_4$ + $Co(BO)(CO)_3$ is 22.1 kcal/mol. The dissociation of $Co_2(BO)_2(CO)_6$ into $2Co(BO)(CO)_3$ is seen to be endothermic with a predicted energy of 35.0 kcal/mol.

3.4. Vibrational Frequencies. The predicted ν(CO) and ν(BO) frequencies for the optimized structures of $Co(BO)(CO)_n$ (n = 4, 3, 2, 1) and $Co_2(BO)_2(CO)_n$ (n = 8, 7, 6) are reported in the Supporting Information, Tables S72 through S75 using the BP86 method, which has been shown to be more reliable for ν(CO) frequencies than the B3LYP method.[60,61] The predicted terminal ν(CO) frequencies for the $Co(BO)(CO)_n$ and $Co_2(BO)_2(CO)_n$ derivatives are seen to fall in the range 2101 to 1971 cm^{-1}, which is typical for terminal carbonyl groups. The ν(CO) frequencies for the bridging carbonyl groups in the binuclear $Co_2(BO)_2(CO)_n$ (n = 8, 7) derivatives are predicted to fall in the range of 1956 to 1789 cm^{-1}. The lower bridging ν(CO) frequencies relative to terminal ν(CO) frequencies are a typical feature of metal carbonyl spectra. It relates to the lower C=O bond order in the carbonyl group when bonded to two metal atoms rather than a single metal atom.

Supporting Information, Table S72 also compares the ν(CO) frequencies of the $Co(BO)(CO)_4$ global minimum **14S-1** (Figure 1) with those of the corresponding valence isoelectronic C_{3v} isomers of $Fe(CS)(CO)_4$ and $Mn(NO)(CO)_4$ predicted by using the same BP86 method. In accord with expectation, the predicted ν(CO) frequencies for the C_{3v} isomers of $Co(BO)(CO)_4$, $Fe(CS)(CO)_4$, and $Mn(NO)(CO)_4$ all follow the same pattern. Furthermore, the ν(CO) frequencies decrease in the sequence $Co(BO)(CO)_4 \gg Fe(CS)(CO)_4 > Mn(NO)(CO)_4$ indicating π-acceptor strengths in the sequence BO < CS < NO. This is in accord with the increased formal negative charges in the order $BO^- \rightarrow CS \rightarrow NO^+$ on these diatomic ligands functioning as actual electron pair donors, as well as the decrease in the corresponding formal metal oxidation states in the sequence Co(I) > Fe(0) > Mn(−I). A more negative metal formal oxidation state and a formal positive charge on the ligand are both likely to lead to increased ligand π-acceptor strength. The relatively low π-acceptor strength of the BO ligand is in accord with the previous observations of Baerends and co-workers.[28]

The terminal ν(BO) frequencies in the $Co(BO)(CO)_n$ and $Co_2(BO)_2(CO)_n$ are predicted to fall in the range 1878 to 1806 cm^{-1}. The ν(BO) frequencies for the normal one-electron donor bridging BO groups are significantly lower in the range 1788 cm^{-1} to 1724 cm^{-1} (see tables in the Supporting Information). The three-electron donor bridging η^2-μ-BO groups in the $Co_2(BO)_2(CO)_6$ structure **26S-1** are predicted to exhibit even lower ν(BO) frequencies at 1671 and 1664 cm^{-1} in accord with lowering the effective B−O bond order by π-electron donation from the B−O bond to the metal atom. The lowest ν(BO) frequencies in the range 1637 to 1597 cm^{-1} are predicted for the BO groups of the $Co(CO)_3(BO)_2$ "ligands" chelating to the $Co(CO)_3$ units in the low-lying triplet $Co_2(BO)_2(CO)_6$ structures **26T-1**, **26T-2**, and **26T-3**.

4. Discussion

4.1. Mononuclear Derivatives. The lowest energy $Co(BO)(CO)_4$ structure is the expected trigonal bipyramidal structure analogous to the isoelectronic $Fe(CO)_5$. However, only the $Co(BO)(CO)_4$ structure with the BO ligand in the axial position of the CoC_4B trigonal bipyramid, namely, **14S-1** (Figure 1), appears to be a genuine minimum. The isomeric $Co(BO)(CO)_4$ structure **14S-2** with the BO group in an equatorial position is also found at only 5 ± 1 kcal/mol above **14S-1**. However, this structure is not a genuine minimum since it has an imaginary vibrational frequency. Following the normal mode of this imaginary vibrational frequency converts the equatorially substituted isomer **14S-2** to the axially substituted isomer **14S-1**. This contrasts with the isovalent iron carbonyl complexes $Fe(CS)(CO)_4$ and $Fe(BF)(CO)_4$, for which the equatorially and axially substituted trigonal bipyramidal isomers are both genuine minima of similar energies. The square pyramidal isomer of $Co(BO)(CO)_4$ (**14S-3** in Figure 1) is also not a genuine minimum but has a large imaginary vibrational frequency. These observations suggest that $Co(BO)(CO)_4$ is a typical fluxional five-coordinate system capable of undergoing Berry pseudorotation.[62,63]

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The coordinately unsaturated Co(BO)$(CO)_3$ is an example of a four-coordinate complex of the d^8 Co(I) since the BO^- ligand is formally a monoanion. Such complexes are typically square planar with a 16-electron configuration for the central metal atom. The lowest energy Co(BO)$(CO)_3$ structure **13S-1** (Figure 2) is nearly square planar, but with the two CO groups *cis* to the BO group bent toward the BO group. The higher energy Co(BO)$(CO)_3$ structures can be derived from the trigonal bipyramidal Co(BO)$(CO)_4$ structure **14S-1** (Figure 1) by removal of an equatorial CO group (**13T-1**) or an axial CO group (**13S-2**). The final Co(BO)$(CO)_3$ structure **13T-2** is derived from a hypothetical equatorially substituted Co(BO)$(CO)_4$ structure by removal of an equatorial carbonyl group. Similarly, the structures for the more highly unsaturated Co(BO)$(CO)_2$ can be derived by removal of either two CO ligands from a trigonal bipyramidal Co(BO)$(CO)_4$ structure or one CO ligand from an approximate square planar Co(BO)$(CO)_3$ structure.

4.2. Binuclear Derivatives. The fundamental building blocks for many of the structures of the binuclear species $Co_2(BO)_2(CO)_n$ (n = 8, 7) are the 17-electron $Co(CO)_4$ and $Co(BO)_2(CO)_3$ units. The $Co(CO)_4$ unit is familiar in many cobalt carbonyl derivatives derived from $Co_2(CO)_8$ or obtained from reactions of the $Co(CO)_4^-$ anion. The $Co(BO)_2(CO)_3$ unit is isoelectronic with the $Mn(CO)_5$ unit prevalent in many manganese carbonyl derivatives derived from $Mn_2(CO)_{10}$ or obtained from reactions of the $Mn(CO)_5^-$ anion. Because of the stability of the 17-electron $Co(CO)_4$ and $Co(BO)_2(CO)_3$ units, many of the binuclear $Co_2(BO)_2(CO)_n$ (n = 8, 7) structures have an unsymmetrical distribution of BO groups, with two terminal BO groups on one cobalt atom and no terminal BO groups on the other cobalt atom.

The 18-electron rule suggests that $Co_2(BO)_2(CO)_8$ should have structures without any direct cobalt−cobalt bonds. Such structures were included in this study because of the recent discovery of stable $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4(\mu\text{-BF})$ with a bridging μ-BF group and no Ru−Ru bond.[12] In this connection, the lowest energy $Co_2(BO)_2(CO)_8$ structures (**28S-1**, **28S-2**, **28S-3**, and **28S-4** in Figure 5) are constructed by linking a $Co(CO)_4$ unit to a $Co(BO)_2(CO)_3$ unit by a bridging CO group without a cobalt−cobalt bond. Doubly carbonyl-bridged $Co_2(BO)_2(CO)_8$ structures with ~3.2 Å Co···Co distances too long for direct bonding (**28S-5**, **28S-6**, and **28S-7** in Figure 5) are found at higher energies, namely, >15 kcal/mol above the global minimum **28S-1**. Such 3.2 Å Co···Co distances are ~0.7 Å longer than the Co−Co single bond distance of 2.530 Å found by X-ray crystallography[53−55] in $Co_2(CO)_8$.

No $Co_2(BO)_2(CO)_8$ structures are found with bridging BO groups. Furthermore, the predicted exothermic CO dissociation energy of ~−12 kcal/mol of $Co_2(BO)_2(CO)_8$ (**28S-1**) to give $Co_2(BO)_2(CO)_7$ (**27S-1**) indicates that $Co_2(BO)_2(CO)_8$ is not viable. The driving force for the conversion of $Co_2(BO)_2(CO)_8$ (**28S-1**) to $Co_2(BO)_2(CO)_7$ (**27S-1**) + CO appears to be the energy gained by forming a Co−Co bond.

The heptacarbonyl $Co_2(BO)_2(CO)_7$ is strictly isoelectronic with $Fe_2(CO)_9$, which is a stable compound with a triply bridged $Fe_2(CO)_6(\mu\text{-CO})_3$ structure determined by X-ray crystallography.[56] It is also isovalent with $Os_2(CO)_9$, which has a different $Os_2(CO)_8(\mu\text{-CO})$ structure with only a single bridging carbonyl group.[57,58] The global minimum $Co_2(BO)_2(CO)_7$ structure is the triply bridged (2 μ-BO + μ-CO) structure **27S-1** (Figure 6), which is closely related to the experimental structure of $Fe_2(CO)_6(\mu\text{-CO})_3$. In fact, the predicted Co−Co distance of 2.53 Å in **27S-1** is very close to the experimental Fe−Fe distance of 2.523 Å in $Fe_2(CO)_6(\mu\text{-CO})_3$, determined by X-ray crystallography.[56] The triply carbonyl bridged $Co_2(BO)_2(CO)_4(\mu\text{-CO})_3$ structure **27S-10** is of significantly higher energy (14 ± 2 kcal/mol) than the 2 μ-BO + μ-CO triply bridged structure **27S-1**. The μ-BO + 2 μ-CO triply bridged structure **27S-7** lies in energy between the 2 μ-BO + μ-CO triply bridged global minimum **27S-1** and the triply carbonyl bridged structure **27S-10** at 10 ± 1 kcal/mol above **27S-1**. These observations suggest that bridging BO groups are more favorable than bridging CO groups.

Other relatively low energy $Co_2(BO)_2(CO)_7$ structures can be derived by joining a $Co(CO)_4$ unit to a $Co_2(BO)_2(CO)_3$ unit with a Co−Co bond, either with only terminal CO and BO groups (**27S-3** in Figure 6) or with two semibridging CO groups from the $Co(BO)_2(CO)_3$ unit to the $Co(CO)_4$ unit (**27S-2** in Figure 6). In addition singly carbonyl bridged $Co_2(BO)_2(CO)_6(\mu\text{-CO})$ isomers, namely, **27S-4**, **27S-6**, and **27S-8**, are found with structures analogous to the experimentally determined $Os_2(CO)_8(\mu\text{-CO})$ structure.[57,58] For $Fe_2(CO)_9$ the singly bridged isomer $Fe_2(CO)_8(\mu\text{-CO})$ has been shown by DFT[64] to be very close in energy to the experimentally known triply bridged isomer $Fe_2(CO)_6(\mu\text{-CO})_3$. Note that among the 11 $Co_2(BO)_2(CO)_7$ structures in Figure 6, the only structures with bridging BO groups are the structures **27S-1** and **27S-7**, in which two or one bridging μ-BO groups, respectively, form part of a triply bridging system.

Structures of the hexacarbonyl $Co_2(BO)_2(CO)_6$ are coordinately unsaturated and thus require a formal Co═Co double bond to give each cobalt atom the favored 18-electron configuration in a binuclear singlet structure. However, the lowest lying $Co_2(BO)_2(CO)_6$ structures are triplets. In fact, using the B3LYP method, five triplet structures (**26T-1** through **26T-5** in Figure 7) are found to lie in energy below the lowest lying singlet structure **26S-1**. The tendency for the B3LYP method to favor triplet structures relative to the BP86 method has been demonstrated by Reiher, Salomon, and Hess.[65,66] Using the BP86 method, four singlet structures (**26S-1**, **26S-2**, **26S-4**, and **26S-5** in Figure 7) are found to lie below the lowest lying triplet structure **26T-1**.

The low-lying triplet $Co_2(BO)_2(CO)_6$ structures exhibit a novel structural feature not found in homoleptic metal carbonyl derivatives, namely, a 17-electron $Co(BO)_2(CO)_3$ building block functioning as a bidentate ligand toward a $Co(CO)_3$ unit by bonding through the oxygen atoms of the two BO groups. Such a structure is represented schematically in Figure 8. Structures **26T-1**, **26T-2**, and **26T-3** are all of this type. In these structures the BO groups can be considered to be formal three-electron

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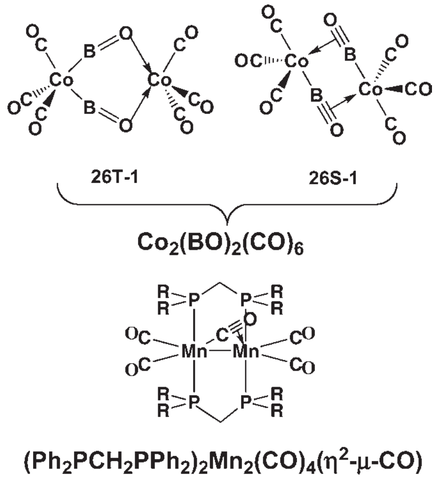

Figure 8. Comparison of η^2-μ-BO groups and η^2-μ-CO groups: (a) Two $Co_2(BO)_2(CO)_6$ structures with different types of three-electron donor bridging η^2-μ-BO groups; (b) The known $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4$-($\eta^2$-$\mu$-CO) structure with a four-electron donor bridging η^2-μ-CO group.

donors by donating one electron to one of the cobalt atoms (the "left" cobalt atoms in Figure 7) through the boron atom similar to a terminal BO group. The other two electrons come from a dative B=O→Co bond from the boronyl oxygen lone pair to the cobalt atom (the "right" cobalt atoms in Figure 7). Related B=O→M dative bonds were recently discovered in adducts of the known boronyl complex $(Cy_3P)_2Pt(BO)Br$ with fluorinated arylboranes.[21] In complexing with borane Lewis acids, the experimental B−O distance of 1.21 Å by X-ray crystallography in $(Cy_3P)_2Pt(Br)(BO)$ lengthens slightly to 1.23 Å in $(Cy_3P)_2Pt(Br)(BO{\rightarrow}BAr^f{}_3)$. Similarly the predicted terminal BO distances in the cobalt carbonyl boronyl compounds discussed in this paper fall in the range 1.21 to 1.22 Å (B3LYP) or 1.22 to 1.23 Å (BP86). However, the BO distances in the bridging boronyl groups in **26T-1**, **26T-2**, and **26T-3** are also somewhat longer in the range 1.25 to 1.27 Å. The Co···B distances from these bridging boronyl groups to the second cobalt atom in **26T-1**, **26T-2**, and **26T-3** fall in the range ~2.8 to ~3.2 Å (Figure 7), which are too long for direct Co−B bonds. Thus, the dative BO→Co bonds appear to involve an oxygen lone pair rather than a pair of π-electrons from a BO multiple bond. In this way this type of three-electron bridging η^2-μ-BO group differs from the four-electron donor η^2-μ-CO group found experimentally in structures such as $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$ (Figure 8).[67,68] The three **26T-1**, **26T-2**, and **26T-3** structures differ only in the relative arrangements of the terminal CO groups in the two $Co(CO)_3$ units. The Co···Co distances in these structures are very long at ~4.3 Å, indicating no bonding interaction. The lack of a cobalt−cobalt bond in the $Co(CO)_3(\mu\text{-}BO)_2Co(CO)_3$ structures **26T-1**, **26T-2**, and **26T-3** means that one cobalt atom in these structures has a 17-electron configuration and the other cobalt atom a 19-electron configuration consistent with a binuclear triplet.

The lowest lying singlet $Co_2(BO)_2(CO)_6$ structure **26S-1** also has two three-electron donor bridging η^2-μ-BO groups but of a type similar to the four-electron donor bridging η^2-μ-CO groups in metal carbonyl derivatives such as $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$.[67,68] In **26S-1** the Co−B−O units are linear, suggesting sp boron hybridization and a formal B≡O triple bond. The boron atoms of these two η^2-μ-BO groups each donate one electron to one of the cobalt atoms. An additional two electrons is donated to the other cobalt atom from one of the π orbitals of the formal B≡O triple bond of the boronyl group. Two three-electron donor bridging η^2-μ-BO groups of this type plus three terminal carbonyl groups on each cobalt atom gives each cobalt atom in **26S-1** the favored 18-electron configuration without a cobalt−cobalt bond. This is consistent with the predicted Co···Co distance of ~3.7 Å in **26S-1**, which is much too long for any direct cobalt−cobalt interaction. Two other low lying singlet $Co_2(BO)_2(CO)_6$ structures, namely, **26S-4** and **26S-5** (Figure 7), have only one three-electron donor bridging η^2-μ-BO group similar to either of the two bridging BO groups in **26S-1**, in addition to a normal type of two-electron donor bridging carbonyl group. However, in **26S-4** and **26S-5**, the Co−Co distances are predicted to be 2.6 to 2.7 Å, consistent with a formal single bond. The combination of one three-electron donor η^2-μ-BO group, one one-electron donor terminal BO group, all two-electron donor CO groups, and a Co−Co single bond gives both cobalt atoms in structures **26S-4** and **26S-5** the favored 18-electron configuration.

5. Conclusions

Our theoretical studies predict $Co(BO)(CO)_4$ to have a trigonal bipyramidal structure with the BO group in an axial position similar to the known structures of the isoelectronic compounds $Fe(CO)_5$ and $Mn(NO)(CO)_4$. The tricarbonyl $Co(BO)(CO)_3$ is predicted to have a distorted square planar structure, similar to those of other 16-electron complexes of d^8 transition metals. Higher energy $Co(BO)(CO)_n$ (n = 3, 2) structures may be derived by removal of one (for n = 3) or two (for n = 2) CO groups from a trigonal bipyramidal $Co(BO)(CO)_4$ structure.

The binuclear derivative $Co_2(BO)_2(CO)_7$ is isoelectronic with the known $Fe_2(CO)_9$. Thus the lowest lying $Co_2(BO)_2(CO)_7$ structure is a triply bridged (2BO + CO) structure closely related to the experimental $Fe_2(CO)_9$ structure. However, other relatively low energy $Co_2(BO)_2(CO)_7$ structures are found, either with a single CO bridge, similar to the experimental $Os_2(CO)_8(\mu\text{-}CO)$ structure; or with 17-electron $Co(CO)_4$ and $Co(BO)_2(CO)_3$ units joined by a single Co−Co bond with or without semibridging carbonyl groups. The stability of $Co(CO)_4$ and $Co(BO)_2(CO)_3$ units is also reflected in the lowest energy structures of $Co_2(BO)_2(CO)_8$. Thus structures with a CO group bridging 17-electron $Co(CO)_4$ and $Co(BO)_2(CO)_3$ units and no Co−Co bond are found for $Co_2(BO)_2(CO)_8$. However, $Co_2(BO)_2(CO)_8$ is not viable because of the predicted exothermic loss of CO to give $Co_2(BO)_2(CO)_7$.

Both triplet and singlet $Co_2(BO)_2(CO)_6$ structures are found. The lowest lying triplet $Co_2(BO)_2(CO)_6$ structures have a $Co(CO)_3(BO)_2$ unit coordinated to a $Co(CO)_3$ unit through the oxygen atoms of the boronyl groups with a nonbonding ~4.3 Å Co···Co distance. The basicity of the oxygen atoms in boronyl ligands has been discovered experimentally in fluorinated borane adducts of $(Cy_3P)_2Pt(BO)Br$. The lowest lying singlet $Co_2(BO)_2(CO)_6$ structures have

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either two three-electron donor bridging η^2-μ-BO groups and no Co···Co bond or one such three-electron donor BO group and a formal Co−Co single bond.

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Supporting Information Available: Tables S1 to S24: Theoretical harmonic vibrational frequencies for the 47 structures of $Co_2(BO)_2(CO)_n$ (n = 8, 7, 6) and $Co(BO)(CO)_m$ (m = 4, 3, 2, 1) using the BP86 and B3LYP method; Tables S25 to S71: Theoretical Cartesian coordinates for the 47 structures of $Co_2(BO)_2$-$(CO)_n$ (n = 8, 7, 6) and $Co(BO)(CO)_m$ (m = 4, 3, 2, 1) using the BP86/DZP method; Tables S72 to S75: ν(CO) and ν(BO) frequencies (cm^{-1}) for the $Co_2(BO)_2(CO)_n$ (n = 8, 7, 6) and $Co(BO)(CO)_m$ (m = 4, 3, 2, 1) using the BP86/DZP method; Tables S76−S82. Total energies (E, in hartree), relative energies (ΔE, in kcal mol^{-1}), and numbers of imaginary vibrational frequencies (N_{Imag}) for the optimized $Co_2(BO)_2(CO)_n$ (n = 8, 7, 6) and $Co(BO)(CO)_m$ (m = 4, 3, 2, 1) structures; complete Gaussian 03 reference (Reference 52). This material is available free of charge via the Internet at http://pubs.acs.org.