Boron carbonyl complexes analogous to hydrocarbons

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Recent studies on boron carbonyl complexes show their intriguing structural and bonding properties, enriching our knowledge on main group coordination chemistry. The isolobal relationships between BCO and CH and the more generally applicable CO/H− and B=C analogies are employed to understand the structure and bonding of boron carbonyl complexes, bridging the boron carbonyl chemistry to the well-known hydrocarbon analogues.

Introduction

Chemical bonding in transition metal compounds is usually discussed with the donor–acceptor bonding model, which was first introduced by Dewar, Chatt and Duncanson (DCD model).1–3 The DCD bonding model considers synergic σ donation from a ligand to a transition metal center and π back-donation of electron density from the metal center to the ligand as the major components of chemical bonding.4,5 Although the covalent electron-sharing bonding model once dominated main group chemistry,6,7 the donor–acceptor model is increasingly employed to discuss the bonding of main group compounds.8–45 Recent investigations have shown that main group compounds mimic the bonding property and reactivity of transition metal complexes, effectively mediating and extending the DCD bonding model and catalytic reactions that were once thought to be only possible for transition metal complexes to the main group systems.29–45 This family of main group compounds is based on small molecular fragments supported by neutral ligands, in which the central fragment contains main group elements that can be considered in zero and low oxidation states. Among the neutral ligands, CO is the simplest one and the main group carbonyl complexes can thus serve as models in understanding the bonding properties and reactivities of these main group compounds.

Much progress has been made in the synthesis of heteroleptic and homoleptic boron carbonyl complexes. The electron deficient boron species are able to coordinate one CO ligand in forming the closed-shell carbonyl borane H3BCO and related derivatives,46–50 which are well-known stable boron carbonyl compounds. A boron dicarbonyl complex [RB(CO)2]64 (R being a bulky aryl group) with two terminal carbonyl ligands that is stable under ambient conditions has been synthesized recently.45 It can undergo decarbonylation to form reactive intermediates, showing features of carbonyl complexes that are known from transition metal carbonyls. Following this work, many stable carbonyl adducts of other borylenes have been synthesized,34,51–53 including [[CAAC]B(CO)Ar] (Ar = aromatic ring), three neutral ligands stabilized [[NHSi]3B(CO)]+ cations and the dicarbonyldihydridoborene complexes. The commonality of these carbonyl complexes is that they can undergo decarbonylation reactions to form transient intermediates or ligand exchange reactions to produce other complexes. Homoleptic boron carbonyl complexes are unstable species under ambient conditions. They have only been observed in low-temperature matrices or in the gas phase.54–64 The calculated dissociation energy of the binding carbonyl ligands varies from 10.5 (OC−B(CO)2) to 79.8 kcal mol−1 (OC−B(CO)3)51, some of which are even higher than those of typical stable transition metal carbonyls (41.5 kcal mol−1 for OC−Fe(CO)4).65

These homoleptic boron carbonyls show intriguing structural and bonding properties, enriching our understanding on the main group systems. The OCBCO molecule is characterized to be a boron–boron triple-bonded species.56 Both BBCO and B4(CO)2 are σ−π diradicals.57,59 The linear closed-shell B(CO)2− anion is considered as a donor–acceptor bonding complex rather than a cumulene OC==B(−)==CO molecule with electron sharing bonding.60 Tricarbonyl complex B(CO)3 possesses a tilled one electron donor carbonyl ligand.61 The B4(CO)3+ cation complex is determined to have a planar D3h structure featuring the smallest π aromatic cyclic B3+ moiety.62 B3(CO)4+ and B4(CO)5+ are identified to have a linear chain boron framework.64

An emerging issue is how to understand the structure and bonding of these boron carbonyl complexes. The isolobal analogy has been widely used in organometallic chemistry to...
relate the structure and bonding of organic and inorganic molecular fragments. The structure and bonding of a less-known organometallic compound can be predicted from that of a better known species, due to the similarity of frontier orbitals and valence electrons. We found that the isolobal principle can be applied to bridge boron carbonyl complexes and the well-known hydrocarbon molecules.

**Isolobal relationship between BCO and CH**

Based on the similarity of the electronic structures, an isolobal relationship between BCO and CH is proposed. The BCO molecule was determined by electron spin resonance (ESR) spectroscopy and theoretical calculations to have a \(^4\Sigma^-\) quartet ground state with the three spins predominantly located on the boron atom.\(^{54}\) Its electronic structure is similar to that of the quartet state of the CH radical. The CH radical has a doublet ground state, but the \(^4\Sigma^-\) quartet excited state lies only about 16.6 kcal mol\(^{-1}\) higher in energy above the ground state.\(^{56,67}\) On the basis of this isolobal relationship, the known boron carbonyl complexes have familiar counterparts (Fig. 1). For example, the carbonyl borane \(\text{H}_2\text{BCO}\) is isolobal to methane. The carbonyl adduct of phenylborylene \(\text{PhBCO}\) determined to have a triplet ground state is isoelectronic to the phenylcarbene \(\text{PhCH}\).\(^{41}\) The simplest diboron carbonyl complex \(\text{BBCO}\) is characterized to have a linear structure with a \(^3\Sigma^+\) ground state, suggesting a \(\sigma\)-\(\pi\) diradical, the same as the electronic structure of the well-studied \(\text{CCH}^+\) radical cation.\(^{68,69}\)

The isolobal relationship between \(\text{OCBBCO}\) and \(\text{C}_2\text{H}_2\) is illustrated by the chemical bonding analysis on the basis of the canonical molecular orbitals. The OCBBCO molecule was determined to have a linear singlet ground state. The B–B bonding molecular orbitals are shown in Fig. 2. The doubly degenerate highest occupied molecular orbital (HOMO, \(\text{HOMO}_2\)) is the B–B \(\pi\) bonding orbital, which comprises B\(_2\) to CO \(\pi^*\) backbonding. HOMO–1 is a B–B \(\sigma\) bonding orbital. The doubly degenerate HOMO–2 and HOMO–3 are primary C–O \(\pi\) bonding orbitals. The HOMO–4 and HOMO–5 comprise CO \(5\sigma\) to \(\text{B}_3\) donation, and are B–B antibonding and bonding in character, respectively. Therefore, singlet OCBBCO exhibits a boron–boron triple bond character. These molecular orbitals of OCBBCO are reminiscent of those in acetylene, as shown in Fig. 2.

The \(\text{B}_3(\text{CO})_3^+\) cation and the cyclopropyl cation serve as another prototypical example in demonstrating the isolobal relationship between BCO and CH. In this case, chemical bonding analyses are performed using the adaptive natural density partitioning (AdNDP) method.\(^{70}\) AdNDP is a theoretical tool for obtaining patterns of chemical bonding based on the concept of the electron pair as the main element of chemical bonding models. It achieves a seamless description of systems, featuring both localized and delocalized bonding without invoking the concept of resonance. The \(\text{B}_3(\text{CO})_3^+\) cation was produced in the gas phase and characterized to have a planar \(D_{3h}\) structure involving a cyclic \(\text{B}_3^+\) cation that is ligated by three CO ligands. The AdNDP pattern of \(\text{B}_3(\text{CO})_3^+\) is shown in Fig. 3, which contains three 2c–2e B–B \(\sigma\) bonds, three 2c–2e \(\sigma\) bonds between boron and the carbonyl ligand, and one delocalized \(\pi\) bond perpendicular to the molecular plane. Correspondingly, the cyclopropyl cation \(\text{C}_3\text{H}_3^+\) has three 2c–2e C–C \(\sigma\) bonds, three 2c–2e C–H \(\sigma\) bonds and one delocalized \(\pi\) bond. The only difference between \(\text{B}_3(\text{CO})_3^+\) and \(\text{C}_3\text{H}_3^+\) is that the \(\pi\) bond in \(\text{C}_3\text{H}_3^+\) is a 3c–2e bond, while that of \(\text{B}_3(\text{CO})_3^+\) is more delocalized (9c–2e) as it comprises weak \(\text{B}_3^+\) → CO back donation.

The \(\text{B}_3(\text{CO})_3^+\) cation and the bare \(\text{B}_3^+\) core cation each have two \(\pi\) electrons which are delocalized over the three-membered ring, and thus are aromatic. The bare \(\text{B}_3^+\) with only eight valence electrons represents the smallest 2\(\pi\)-aromatic system. The \(\text{B}_3^-\) anion has been claimed to be a \(\sigma\) and \(\pi\) double aromatic species.\(^{71,72}\) Its HOMO has been declared as the source of \(\sigma\) aromaticity. The \(\text{B}_3^+\) cation has two electrons shorter than the anion, and thus the HOMO of \(\text{B}_3^-\) is unoccupied in \(\text{B}_3^-\), where it becomes the LUMO. This LUMO of \(\text{B}_3^+\) is perfectly suited for CO → \(\text{B}_3^+\) \(\sigma\) donation. The \(\sigma\) donation interaction was predicted to be the largest contribution to the bonding interactions between \(\text{B}_3^+\) and three CO ligands according to the energy decomposition analysis with natural orbitals of chemical valence (EDA-NOCV). This suggests that \(\text{B}_3(\text{CO})_3^+\) might also possess some \(\sigma\) aromaticity, because the CO → \(\text{B}_3^+\)
σ donation interaction leads to partial occupation of the LUMO of B$_3^+$. The aromaticity in these molecules was estimated with the nuclear independent chemical shift (NICS) method and compared with the classical two π-electron aromatic cyclopropenyl cation C$_3$H$_3^+$. The calculated NICS(1) values, which were suggested as reliable indicators of aromaticity in non-fused cyclic systems, predicted that the boron cations possess a significant aromatic character with decreasing order B$_3^+$ (−18.4 ppm) > C$_3$H$_3^+$ (−14.6 ppm) > [B$_3$(CO)$_4$]$^+$ (−13.2 ppm).

**Boron carbonyls and hydrocarbons**

Although the isolobal relationship between BCO and CH works well for the boron carbonyl complexes containing stoichiometric (BCO)$_n$ fragments, this isolobal relationship cannot apply to the non-stoichiometric boron carbonyl complexes including highly coordinated carbonyl complexes such as B(CO)$_2$, B(CO)$_3^+$, and B$_3$(CO)$_4^+$. According to the DCD bonding model, the end-on bonded carbonyl ligand serves as a two-electron donor. Thus, the carbonyl ligand can be regarded as “isolobal” with the H$^-$ anion in electron counting. This isolobal relationship in conjunction with the B$^-$/C analogy provides a more generally applicable method to bridge the boron carbonyl complexes and the hydrocarbon species. Following this relationship, the boron dicarbonyl complexes B(CO)$_2$ are isoelectronic to the methylene anion CH$_2^-$, while the B(CO)$_3^+$ cation is isolobal to the methyl anion CH$_3^-$. The B$_3$(CO)$_4^+$ cation complex can be regarded as isolobal to the allene molecule (H$_2$CCCH$_2$), and the B$_3$(CO)$_5^+$ cation complex is the counterpart of the allyl anion C$_3$H$_5^-$. 

These isolobal relationships are supported by chemical bonding analyses using the AdNDP method. The B$_3$(CO)$_4^+$ cation was characterized by infrared photodissociation spectroscopy and theoretical calculations to have a $D_{2h}$ symmetry (OC)$_2$B=−B=−B(CO)$_2$ structure and an $^1A_1$ electronic ground state with a linear boron skeleton. AdNDP analysis shows that the B$_3$(CO)$_4^+$ cation involves two 2c–2e σ bonds between the boron skeleton, four 2c–2e σ bonds between boron and the carbonyl ligand, and two 6c–2e delocalized π bonds. Correspondingly, the allene molecule is well-known to have a $D_{2h}$ symmetry structure with a linear C=≡C skeleton. It possesses two 2c–2e C–C σ bonds, four 2c–2e C–H σ bonds, and two 2c–2e C–C π bonds (Fig. 3). The only difference in bonding between B$_3$(CO)$_4^+$ and the allene lies in the fact that the two C–C π bonds in the allene are localized, whereas the two B–B π bonds of B$_3$(CO)$_4^+$ are delocalized that comprise significant B$_2$ → CO π back bonding. Therefore, the two B=−B bonds in B$_3$(CO)$_4^+$ were calculated to have a bond distance of 1.573 Å, slightly longer than the value for a standard B=−B double bond (1.56 Å). Similar B$_3$ chains connected by two B=−B double bonds were recently found in the triminotriborane molecule, whose B–B bond length is reported to be 1.56 Å. The bonding pattern of B$_3$(CO)$_5^+$ is also shown in Fig. 3. It is determined to have a chain boron framework with $C_{2n}$ symmetry. The AdNDP analysis indicates that the B$_3$(CO)$_5^+$ cation involves two 2c–2e σ bonds between skeletal boron atoms, five 2c–2e bonds between boron and the carbonyl ligand, and two delocalized π bonds. This chemical bonding pattern is very similar to that of the allyl anion, which contains two C–C σ bonds, five C–H σ bonds, and two 3c–2e C–C π bonds (Fig. 3).

These isolobal relationships provide an intuitive rationale for understanding the relative stability and structural difference of the B$_3$(CO)$_4^+$ (n = 3, 4) cation complexes. The B$_3$(CO)$_4^+$ cation complex was determined to have a $D_{2h}$ symmetric structure involving a cyclic B$_3^+$ ring. It is isolobal to the cyclopropyl cation, which is the most stable structure for species with C$_3$H$_3^+$ stoichiometry. The B$_3$(CO)$_4^+$ cation complex was determined to have an open-chain boron skeleton structure. The structural isomer with a cyclic B$_3^+$ moiety that is isolobal to cyclopropyl is higher in energy than the chain structure that is isolobal to allene. Cyclopropyl is well known to be less stable than the allene isomer due to strong ring strain.

The experimental studies on boron carbonyl complexes containing more than three boron atoms are rare. A neutral B$_3$(CO)$_2$ molecule has been produced by the reaction of boron with carbon monoxide in a solid argon matrix. Infrared spectroscopic experiments combined with theoretical calculations confirm that the molecule has a planar $D_{2h}$ structure involving...
a rhombic B$_4$ ring. High level theoretical calculations predicted that it has an open-shell singlet ground state with the triplet state lying very close in energy. The B$_4$(CO)$_4$ molecule is a $\sigma$-$\pi$ diradical regardless of whether the ground state is an open-shell singlet or a triplet state. As shown in Fig. 4, one singly occupied molecular orbital (SOMO) has $\sigma$ symmetry and contributes to the diagonal B–B interaction. Another SOMO is a delocalized $\pi$ symmetry orbital that is involved with the B–C bonding. The counterpart B$_2$(CH)$_2$ was predicted to have a similar planar D$_{2h}$ structure involving a rhombic B$_2$C$_2$ ring with two SOMOs resembling those of B$_4$(CO)$_4$, as shown in Fig. 4.\textsuperscript{75}

The isolobal relationship of BCO and CH along with the more generally applicable CO/H$^-$ and B/C analogies provides a very useful tool in predicting many other interesting boron carbonyl compounds from the well-known hydrocarbon molecules for future experimental study.\textsuperscript{76,77} In this regard, a large number of boron carbonyl clusters in the form of (BCO)$_n$\textsuperscript{27} (n = 3–24) which are isolobal to the Hückel aromatic species or polyhedral hydrocarbons have been predicted by theory. These clusters such as (BCO)$_n$, the counterpart of benzene, are very interesting candidates for future experimental studies. The B$_4$(CO)$_2$$^+$ dication, a counterpart of ethylene, is another interesting candidate. As demonstrated in Fig. 5, the bonding patterns show that B$_2$(CO)$_4$$^+$ has one 2c–2e B–B $\sigma$ bond, four 2c–2e B–CO $\sigma$ bonds and one 10c–2e $\pi$ bond, indicating a B≡B double bond, similar to the C≡C double bond in the known C$_2$H$_4$ molecule. The B$_2$(CO)$_4$$^+$ monocation has been observed experimentally in the gas phase, which was identified to have a 2$^2$B$_2g$ ground state with planar D$_{2h}$ symmetry, similar to the C$_2$H$_4$$^+$ anion.\textsuperscript{63,78} Recently, an example of phosphine-supported terminal diborene complexes was also reported as an analogue of the vinylidene dication,\textsuperscript{40} showing an equable bonding property.

The CO ligand is not only a $\sigma$ donor but also a good $\pi$ acceptor. This causes a small bonding difference between boron carbonyl complexes and the hydrocarbon analogues. As has been mentioned above, the delocalized $\pi$ bonding orbitals are confined to the carbon skeleton in hydrocarbons. By contrast, the $\pi$ bonding orbitals of the carbonyl counterparts are more delocalized due to the B–CO $\pi$ backdonation interaction. Such $\pi$ backdonation interaction is generally weak in the cationic carbonyl species, but may have a strong contribution to the neutrals and anions, which could affect the validity of the isolobal relationship. The delocalized $\pi$ bonds can stabilize the planar geometries and make the 2D structures more favorable than the 3D structures, the same as previously reported for small boron clusters.\textsuperscript{79,80}

Conclusions

The isolobal relationship between BCO and CH and the CO/H$^-$ and B/C analogies are proven to be generally applicable methods in understanding the structure and bonding of known boron carbonyl complexes and predicting other interesting unknown boron carbonyl compounds from the well-known hydrocarbon molecules. Although these simple homoleptic boron carbonyl complexes are not stable under ambient conditions and can only be studied in low-temperature noble gas matrixes or in the gas phase, they serve as prototypical models in understanding the bonding properties and reactivities of other more complicated main group complexes. Other ligands including N-heterocyclic carbenes (NHCs), cyclic(alkyl) (amino)carbene (CAAC), 2,2,6,6-tetramethylpiperidino (TMP), etc. are well-known two-electron donors and $\pi$ acceptors,\textsuperscript{17,18,81,82} akin to the carbonyl ligand in the bonding structure. In this regard, the isolobal relationship can be extended to the boron complexes involving such large bulky ligands. The substitution of carbonyl ligands by bulkier ligands such as CAAC or NHCs would lead to the bulk synthesis of such boron complexes, as demonstrated by recent successful isolation of a boron–boron triple bonded (NHC) $\rightarrow$ B≡B $\rightarrow$ (NHC) compound.\textsuperscript{14} The boron centers in these complexes can donate electrons occupied in the delocalized $\pi$ orbitals to react as a boron-centered nucleophile and form dative-bonded complexes, like transition metal complexes.\textsuperscript{37–39} Such a strategy has been used in organic and inorganic synthesis to connect the boron center with other elements.

The advantage of the carbonyl ligand is its small size, which ensures the high coordination number of ligands and the possibility of forming long boron chains. The main properties of these boron carbonyl complexes are the tendency to form planar structures and delocalized $\pi$ bonds, indicating the potential $\pi$ donor ligands for these boron complexes. We hope that this study on boron carbonyl complexes can enrich the fundamental understanding on the main group coordination.
chemistry and reactions, especially for the boron element, and provide some new ideas for organic or inorganic synthesis under ambient conditions.

Conflicts of interest
The authors declare that there are no conflicts of interest.

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Notes and references
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