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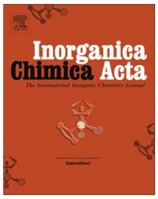

Research paper

Preference of three-electron donor boronyl groups over metal-metal multiple bonding in unsaturated binuclear manganese carbonyl boronyls: Comparison with isoelectronic binuclear chromium carbonyls

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ABSTRACT

The lowest energy structures for the unsaturated $Mn_2(BO)_2(CO)_n$ ($n = 8, 7$) are very different from those of the isoelectronic $Cr_2(CO)_{n+2}$ owing to the greater basicity of the oxygen atoms in BO groups relative to CO groups. Thus the lowest energy $Mn_2(BO)_2(CO)_n$ ($n = 8, 7$) structures have two bridging three-electron donor η^2—μ—BO groups bonded to the manganese atoms through both their boron and oxygen atoms. The long Mn···Mn distances in these structures indicate the lack of metal–metal bonding. These $Mn_2(BO)_2(CO)_n$ ($n = 8, 7$) structures thus differ from their $Cr_2(CO)_{n+2}$ analogues, which have normal two-electron donor CO groups and Cr—Cr bonds. The only example of manganese-manganese multiple bonding in the $Mn_2(BO)_2(CO)_n$ systems occurs in a high-energy triply bridged $Mn_2(BO)_2(CO)_7$ structure with a short ~2.3 Å Mn≡Mn distance suggesting a formal triple bond. This structure is completely analogous to the lowest energy $Cr_2(CO)_9$ structure.

1. Introduction

The binuclear metal carbonyls $Co_2(CO)_8$, $Fe_2(CO)_9$, and $Mn_2(CO)_{10}$ with the favored 18-electron configuration are all well-known stable species, available commercially and function as useful starting materials for the synthesis of other organometallic compounds of these metals [1]. The corresponding chromium derivative, $Cr_2(CO)_{11}$, also with the favored 18-electron configuration, is unknown. Reactions expected to form $Cr_2(CO)_{11}$ instead lead to decomposition to give the very stable mononuclear complex $Cr(CO)_6$. This is consistent with theoretical studies on $Cr_2(CO)_{11}$, which show $Cr_2(CO)_{11}$ to be disfavored relative to fragmentation giving $Cr(CO)_6$ and the unsaturated $Cr(CO)_5$ [2].

The synthesis of the boronyl complex $(Cy_3P)_2Pt(BO)Br$ (Cy = cyclohexyl) in 2010 [3,4], (Fig. 1) demonstrates that under certain circumstances stable metal boronyl complexes can be synthesized containing the BO^- ligand isoelectronic with the CO ligand. However, no metal complexes containing solely CO and BO ligands have been synthesized. Nevertheless, theoretical studies on metal carbonyl boronyls have included $Co(BO)(CO)_4$, [5] $Co_2(BO)_2(CO)_7$, [5] $Fe_2(BO)_2(CO)_8$, [6] and $Mn(BO)(CO)_5$ [7] systems isoelectronic with the well-known stable binary metal carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, $Mn_2(CO)_{10}$, and $Cr(CO)_6$. The BO ligands in these species can be considered as one-electron donor neutral ligands, bonding to the metal only throughout the boron atom. Syntheses of such metal boronyl complexes present major difficulties since monomeric BO, unlike monomeric CO, is only stable in low-temperature matrices under conditions not suitable for the synthesis of transition metal complexes [8]. Solid BO is a polymer with B—B bonds as well as B—O bonds and unreactive as a ligand in transition metal chemistry [9].

The oxygen atoms in such terminal BO ligands carry a higher negative charge than the oxygen atoms in terminal CO ligands. This appears to limit the viability of metal complexes with terminal BO ligands. Thus, the BO ligand in the experimentally known cation $[(Cy_3P)_2Pt(BO)]^+$, obtained by debromination of $(Cy_3P)_2Pt(BO)Br$ with silver ion, undergoes facile dimerization to give the dication $[[(Cy_3P)_2PtBr]_2(\mu\text{-}B_2O_2)]^{2+}$ [4]. The cyclic μ–B_2O_2 ligand bridges the two platinum atoms through Pt–B bonds (Fig. 1). A recent theoretical study predicts $Co(BO)(CO)_4$ to be similarly disfavored with respect to dimerization to $[(OC)_4Co]_2(\mu\text{-}B_2O_2)$ with a similar bridging cyclic μ-B_2O_2 ligand [10]. Analogous dimerizations of metal

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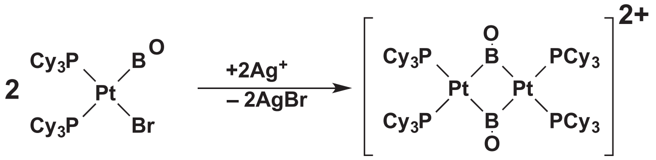
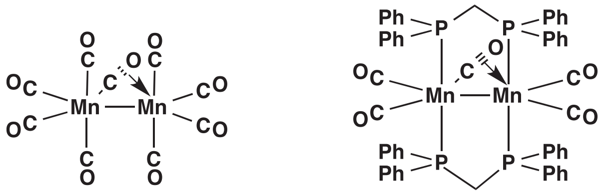


Fig. 1. The relationship between the experimentally known platinum boronyl complexes $(Cy_3P)_2Pt(BO)Br$ and $[[(Cy_3P)_2PtBr]_2(\mu\text{-}B_2O_2)]^{2+}$.

carbonyls with d-block transition metals to form binuclear metal complexes of a cyclic $\mu\text{–}C_2O_2$ ligand are unknown.

The CO ligands in almost all of the thousands of known metal carbonyl complexes, whether terminal or bridging, bond to the transition metal mainly only through the carbon atom. However, there are relatively rare examples of metal carbonyl complexes where a bridging CO group functions as a four-electron donor by bonding to an M_2 unit through both the carbon and oxygen atoms. The first example of such a metal carbonyl derivative with a four-electron donor carbonyl ligand using the oxygen atom as well as the carbon atom for metal-ligand bonding was the compound $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{–}\mu\text{–}CO)$ (Fig. 2), shown by Colton and collaborators [11,12] to have an unusual bridging CO group. Thus the short Mn–O distance of 2.29 Å in this complex suggests direct Mn–O bonding as well as the usual Mn–C bonding to both manganese atoms expected for a bridging carbonyl group. A bridging carbonyl group of this type can donate two electrons to one transition metal through a σ-bond and two electrons to another transition metal through the CO π-bond, bringing the carbonyl oxygen atom within bonding distance of the metal atom. The π-bonding lowers the effective carbon–oxygen bond order consistent with the very low bridging infrared $\nu(CO)$ frequency of 1645 cm^{-1} found experimentally for $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{–}\mu\text{–}CO)$. The larger negative charge on the boronyl oxygen compared with that on the carbonyl oxygen in analogous complexes would appear to make metal complexes with three-electron donor $\eta^2\text{–}\mu\text{–}BO$ groups more favorable than metal complexes with four-electron donor $\eta^2\text{–}\mu\text{–}CO$ groups. In this connection such $\eta^2\text{–}BO$ groups are predicted to occur in low-energy structures of the formally unsaturated binuclear iron carbonyl boronyls $Fe_2(BO)_2(CO)_n$ ($n = 7, 6$) [13].

This paper presents a density functional theory study on the unsaturated manganese carbonyl boronyls $Mn_2(BO)_2(CO)_n$ ($n = 8, 7$) which are isoelectronic with $Cr_2(CO)_n$ ($n = 10, 9$) [14,15], respectively. A frequently encountered feature in the low-energy $Mn_2(BO)_2(CO)_n$ structures is the presence of three-electron donor bridging $\eta^2\text{–}\mu\text{—}BO$ groups similar to those found in low-energy $Fe_2(BO)_2(CO)_n$ ($n = 7, 6$) structures [13] and analogous to four-electron donor $\eta^2\text{–}\mu\text{–}CO$ groups such as those found in the manganese carbonyl derivatives depicted in Fig. 2. Involvement of the B-O multiple bond in the bonding of a bridging $\eta^2\text{–}\mu\text{–}BO$ group to a central Mn_2 unit reduces the tendency of the BO ligands to couple to form B_2O_2 ligands similar to the bridging B_2O_2 group in the platinum dication $[[(Cy_3P)_2PtBr]_2(\mu\text{-}B_2O_2)]^{2+}$ mentioned above (Fig. 1) [4]. However, low-energy isomeric $Mn_2(B_2O_2)(CO)_n$ structures were also found with bridging B_2O_2 ligands of various types.



$Mn_2(CO)_8(\eta^2\text{-}\mu\text{-}CO)$ $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$

Fig. 2. Manganese carbonyl derivatives containing four-electron donor bridging carbonyl groups.

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 organometallic compounds [16–22]. Two DFT functionals (B3LYP and BP86) were used in this study. These two functionals are constructed in very different ways. B3LYP is a hybrid HF/DFT functional using a combination of the three-parameter Becke functional (B3) with the Lee-Yang-Parr (LYP) generalized gradient correlation functional [23,24]. It includes exact exchange and is calibrated by fitting three parameters to a set of experimental results. BP86 combines Becke's 1988 exchange functional (B) [25] with Perdew's 1986 gradient corrected correlation functional (P86) [26]. It does not include exact exchange and is mainly deduced by forcing the functional to satisfy certain exact constraints based on first principles. When these two very different DFT functionals agree, confident predictions can be made. For most of the compounds investigated in this work, both methods agree quite well.

For consistency 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, [27,28] designated as (9s5p1d/4s2p1d). The loosely contracted DZP basis set for manganese is the Wachters primitive set, [29] augmented by two sets of p functions and one set of d functions, and then contracted following Hood, Pitzer, and Schaefer, [30] 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.

The $\nu(CO)$ and $\nu(BO)$ frequencies reported in the present paper were obtained by the BP86 method, which has been shown to give values closer to experimental values without using any scaling factors [26,31]. This concurrence may be accidental, because the theoretical vibrational frequencies predicted by BP86 are harmonic frequencies, whereas the experimental fundamental frequencies are anharmonic. All of the computations were carried out with the Gaussian03 program package, [32] using the fine grid (75, 302) option as the default to evaluate integrals numerically.

A given $Mn_a(BO)_a(CO)_b$ structure is designated as **ab-cA** where **a** is the number of manganese 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 singlet $Mn_2(BO)_2(CO)_8$ structure is designated **28-1S**.

3. Results

Both singlet and triplet $Mn_2(BO)_2(CO)_7$ structures were optimized. The lowest energy triplet $Mn_2(BO)_2(CO)_n$ ($n = 8, 7$) structures were found to lie at least 30 kcal/mol above the corresponding global minima **28-1S** and **27-1S**. Therefore triplet $Mn_2(BO)_2(CO)_n$ ($n = 8, 7$) structures are not discussed in this paper.