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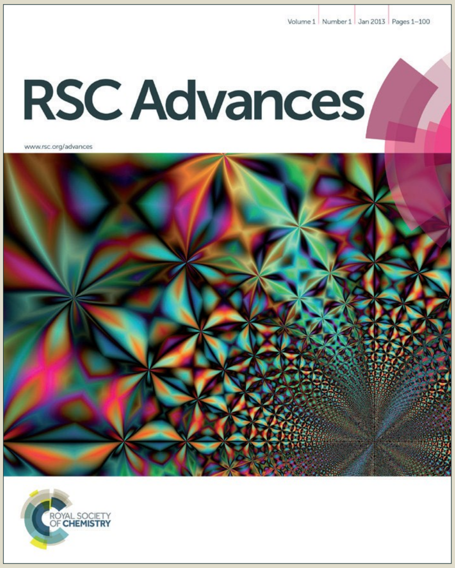

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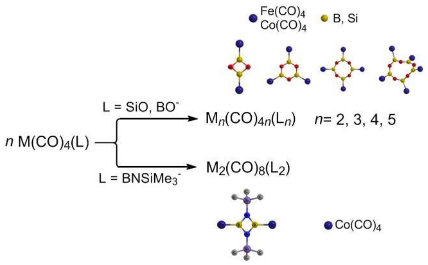
The Siliconyl, Boronyl, and Iminoboryl Ligands as Analogues of the Well-known Carbonyl Ligand: Predicted Reactivity towards Dipolar Cyclooligomerization in Iron/Cobalt Carbonyl Complexes

Zhong Zhang,*[a,b] Liang Pu,[a] Qian-shu Li,[b] and R. Bruce King*[c]

Graphical Abstract

The $Fe(CO)_4(SiO)$, $Co(CO)_4(BO)$, and $Co(CO)_4(BNSiMe_3)$, complexes analogous to the well-known $Fe(CO)_5$ are predicted by density functional theory to undergo exothermic oligomerization to give the oligomers $[Fe(CO)_4]_n(Si_nO_n)$, $[Co(CO)_4]_n(B_nO_n)$, and $[Co(CO)_4]_2(B_2N_2Si_2Me_6)$ containing Si_nO_n/B_nO_n/B_2N_2 rings with single bonds.



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Full ARTICLE

The Siliconyl, Boronyl, and Iminoboryl Ligands as Analogues of the Well-known Carbonyl Ligand: Predicted Reactivity towards Dipolar Cyclooligomerization in Iron/Cobalt Carbonyl Complexes

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The $Fe(CO)_4(SiO)$, $Co(CO)_4(BO)$, and $Co(CO)_4(BNSiMe_3)$ complexes analogous to the well-known $Fe(CO)_5$ are predicted by density functional theory to undergo exothermic oligomerization to give the oligomers $[Fe(CO)_4]_n(Si_nO_n)$, $[Co(CO)_4]_n(B_nO_n)$, and $[Co(CO)_4]_2(B_2N_2Si_2Me_6)$ containing $Si_nO_n/B_nO_n/B_2N_2$ rings with single bonds.

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),[1,2,3] 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]

The development of analogous coordination chemistry of ligands isoelectronic with CO containing either boron or heavier main group elements has lagged considerably owing to the instability of the free ligands. Such ligands include CE (E= S, Se, Te), BO^-, SiE (E= O, S), BX (X= F, Cl, Br), and BNR^-. The π bonds in the free ligands are extremely reactive leading to polymerization already at very low temperatures.[10,11] Thus the free ligands are not available as reagents for the direct synthesis of their metal complexes. However, theoretical studies predict strong ML bonding in their metal complexes owing to the stronger σ donation and comparable π* donation to the M-CO bond in analogous metal carbonyls.[12,13]

An early study [14] reported unstable $Fe(CO)_4(BX)$ and $Fe(CO)_4[BN(CH_3)_2]$ intermediates in the formation of the polymers $[Fe(CO)_4(BX)]_n$ and $\{Fe(CO)_4[BN(CH_3)_2]\}_n$ from reactions of $Fe_2(CO)_9$ with boron halides. However, this field then received relatively little attention until the synthesis of $(Cy_3P)_2BrM(BNSiMe_3)$ (Cy=cyclohexyl) by Braunschweig and coworkers [15] from the oxidative addition of $Br_2BN(SiMe_3)_2$ to $(Cy_3P)_2M$ (M= Pd, Pt) followed by elimination of $BrSiMe_3$. The first metal boronyl complex $(Cy_3P)_2Pt(BO)Br$ was subsequently synthesized by an analogous method.[16] A theoretical study of the mechanism of such reactions indicated that the rate limiting step is the $BrSiMe_3$ elimination.[17] The mixed carbonyl boronyl complex $(PR_3)_2MClBr(BO)(CO)$ (M = Ir, Rh) was suggested to be a good candidate for a stable boronyl complex. Most recently, $[Cp^*Ru(\mu_2\text{-}H)_3](\mu_3\text{-}CPh)(\mu_3\text{-}BO)$ was obtained by Suzuki and coworkers from direct reaction of $[Cp^*Ru(\mu_2\text{-}H)_3](\mu_3\text{-}CPh)(\mu_3\text{-}BH)$ with H_2O.[18]

The synthetic methods developed by Braunschweig and coworkers have thus led to the syntheses of several interesting metal boronyls and metal iminoboryls. The highly polarized boronyl group was found to act as a Lewis acid or electrophile at the electron-deficient boron atom and as a Lewis base or nucleophile at the electron-rich oxygen atom.[19,20,21] In addition, the labile Br^- anion in $(Cy_3P)_2Pt(BO)Br$ is reactive towards nucleophilic substitution by PhS^- and CH_3CN.[16,21] Furthermore, debromination of $(Cy_3P)_2Pt(BO)Br$ using the Ag^+ cation led to the cyclodimerization of the BO ligand to $[(Cy_3P)_2Pt_2(B_2O_2)]^{2+}$ containing a B_2O_2 ligand bridging the two Pt atoms.[22] This report shows how the reactivity of the boronyl group in metal complexes can be controlled using different metal centers, charges, and bulky ligands,[23] as indicated by the kinetic stabilization of $(Cy_3P)_2Pt(BO)Br$ in contrast to the easily dimerized cation $[(Cy_3P)_2Pt(BO)]^+$.

The chemical properties of the silicon monoxide (siliconyl) ligand, SiO, might be expected to resemble those of the BO^- ligand in view of the diagonal relationship between boron and silicon in the Periodic Table. However, metal siliconyls have not yet been synthesized despite the recent syntheses of metal boronyls and metal iminoboryls noted above. A recent density functional theory (DFT) study on neutral dimeric cobalt carbonyl boronyls $Co_2(BO)_2(CO)_n$ (n = 8, 7, 6) suggested that bridging boronyl groups rather than bridging carbonyl groups are preferred in binuclear complexes.[24] This paper presents preliminary results on $M_n(CO)_{4n}(L)_n$ (L = SiO, BO^-, $BNSiMe_3^-$) complexes using DFT methods to explore the following questions: (1) Are the mononuclear complexes $M(CO)_4(L)$ isoelectronic with the well-known stable $Fe(CO)_5$ likewise thermodynamically and kinetically viable with respect to dimerization or further oligomerization of the L ligands? (2) Are higher oligomers obtained by polymerization of the L ligands viable species? Our results predict reactivity of the SiO, BO^-, and $BNSiMe_3^-$ ligands in these simple metal carbonyl complexes towards dimerization and further polymerization. Thus complexation of these ligands L with simple $M(CO)_4$ units does not appear to be sufficient to eliminate their reactivity towards dimerization and polymerization reactions.

2. Theoretical Methods

Electron correlation effects were considered using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40] The functional used in this work is a hybrid *meta*-GGA DFT method, M06-L, developed by Truhlar's group.[41, 42] The studies in Truhlar's group suggest that M06-L is one of the best functionals for the study of organometallic and inorganic thermochemistry, and perhaps the best currently available functional for transition metal energetics.

Basis sets have been chosen to provide continuity with a body of existing research on organometallic compounds. Fortunately, DFT methods are less basis set sensitive than higher-level methods such as coupled cluster theory. In this work all computations were performed using double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for hydrogen, carbon, oxygen, nitrogen, and silicon add one set of pure spherical harmonic p(H)/d functions with orbital exponents $\alpha_p(H) = 0.75$, $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, $\alpha_d(N) = 0.80$, and $\alpha_d(Si) = 0.50$ to the standard Huzinaga-Dunning contracted DZ sets.[43, 44, 45] The loosely contracted DZP basis sets for iron and cobalt are the Wachters primitive set[46] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer and Schaefer,[47] and designated (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using the M06-L/DZP method. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. All of the computations were carried out with the Gaussian 09 program,[48] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,[49] while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

The optimized structures are depicted in Figures 1, 3, and 4. Each $M_n(CO)_{4n}(L)_n$ (M = Fe, Co; L= BO^-, BNR^-, SiO; n = 1, 2, 3, 4, 5) structure is designated as **Ln-X** where **L** is the ligands (L= BO^-, BNR^-, SiO), **n** is the number of metal atoms (M = Fe, Co), and **X** orders the structures according to their relative energies. The optimized transition state structures are indicated by **ts**.

3. Results and Discussion

3.1 Monomers

The global minima of $Fe(CO)_4(SiO)$, $Co(CO)_4(BO)$, and $Co(CO)_4(BNSiMe_3)$ (Figure 1) are derived from the trigonal bipyramidal $Fe(CO)_5$, and $[Co(CO)_5]^+$ structures by replacing an equatorial CO group with a neutral SiO group (**SiO1-I**) and an axial CO group with an anionic BO (**BO1-I**) or an anionic iminoboryl group (**BN1-I**). The Si≡O, B≡O, and B≡N distances are predicted to be 1.521, 1.218, and 1.264 Å (Fig. 2), respectively, suggesting multiple bonds as also indicated by the Wiberg bond indices of 1.47 (SiO), 1.81 (BO), and 1.83 (BN). The axially substituted $Fe(CO)_4(SiO)$ (**SiO1-II**) is predicted to be a transition state, lying 4.7 kcal/mol above **SiO1-I** (Figure S1). However, structure **SiO1-II** provides a good opportunity to compare the *trans* influence of the SiO, BO^-, and $BNSiMe_3^-$ ligands. Thus the *trans* Fe-C(O) and Co-C(O) bond lengths are found to be 1.795 Å (**SiO1-II** in Fig. S1), 1.819 Å (**BO1-I**), and 1.815 Å (**BN1-I**), respectively, indicating that the *trans* influence increases in the sequence siliconyl < iminoboryl < boronyl. The $(OC)_4Fe \leftarrow SiO$ bond dissociation energy (BDE) is predicted to be 46.0 kcal/mol, which is slightly stronger than the experimental value of 37.0 kcal/mol for the $(OC)_4Fe \leftarrow CO$ BDE.[50] The $(OC)_4Co \leftarrow L$ (L = BO^-, $BNSiMe_3^-$) BDE is predicted to be even higher at ~130 kcal/mol indicating electrostatic interaction between the $[Co(CO)_4]^+$ cation and the L^- anion in addition to the strong σ donation from L^- to $[Co(CO)_4]^+$. The bonding of $M(CO)_4$ units to the reactive ligands SiO, BO^-, and $BNSiMe_3^-$ is thus stronger than that to CO groups. However, the natural charges on these L ligands are predicted to be 1.84 for Si(O), –1.06 for O(Si), 1.09 for B(O), –0.83 for O(B), 0.97 for B(N), and –1.35 for N(B) (Figure S1 in ESI), indicating positive charges on the silicon or boron atom and negative charges on the nitrogen or oxygen atom. This significant polarization of the SiO, BO^-, and $BMSiMe_3^-$ ligands prepares them for dipolar cyclooligomerization processes by linking the positive boron or silicon atom to the negative nitrogen or oxygen atom of the ligand in another molecule.

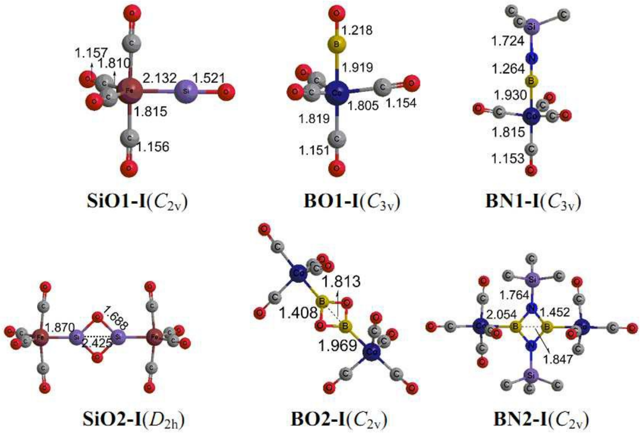
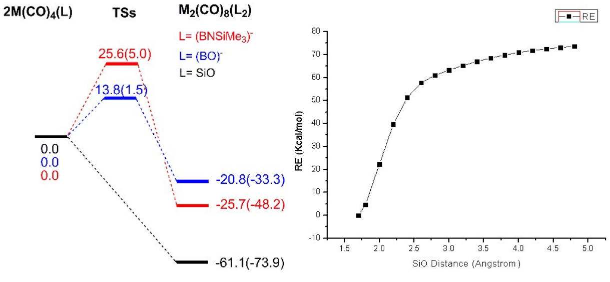


Figure 1. The predicted lowest energy $M_n(CO)_{4n}(L)_n$ (n =1, 2) structures. Bond distances are given in Å. Symmetries are given in parentheses. Hydrogen atoms are omitted for clarity. From Figure 1 to Figure 4, the SiO or BO^-/$BNSiMe_3^-$ ligands and the equivalent $Fe(CO)_4$ or $Co(CO)_4^+$ fragments provide the $M_n(CO)_{4n}(L_n)$ neutral molecules.

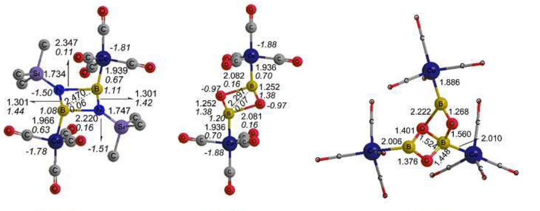
2.2 Dimers

The predicted structures for the [2+2] cyclodimerization products of the $M(CO)_4L$ complexes, namely **SiO2-I**, **BO2-I**, and **BN2-I**, contain a planar four membered $[Si_2O_2]$, $[B_2O_2]$, or $[B_2N_2]$ ring, respectively (Figure 1). The Si-O (**SiO2-I**), B-O (**BO2-I**), and B-N (**BN2-I**) distances in the dimers are predicted to be 1.688, 1.408, and 1.452 Å, respectively, which are ~0.2 Å longer than the corresponding distances in the corresponding monomers (Figure 1). In addition, the Wiberg bond indices of 0.60 (SiO), 0.76 (BO), and 0.79 (BN) bonds for the four-membered rings in these dimers are approximately one third of those in the corresponding monomers thereby suggesting Si–O, B–O, and B–N single bonds in the dimers. The Si···Si (**SiO2-I**), B···B (**BO2-I**), and B···B (**BN2-I**) distances are found to be 2.425 Å, 1.813 Å, and 1.847 Å, respectively, suggesting weak Si···Si and B···B interactions. Such Si···Si and B···B bonding originates from the lone-pair electrons repulsion between the oxygen atoms or nitrogen atoms. The negligible "unsupported π bond" was proposed by Schaefer [51] and Gordon. [52] These dimers are thermodynamically favored since the dimerizations of two monomer units are predicted to release Gibbs energies of 61.1, 20.8, and 25.7 kcal/mol for **SiO2-I**, **BO2-I**, and **BN2-I**, respectively (Figure 2**a**). This is consistent with the replacement of the π components of the polarized multiple bonds in Si≡O, B≡O, or B≡NSiMe$_3$ with energetically stronger σ bonds. Several organic compounds have been found containing Si_2O_2,[53] B_2O_2,[54] or B_2N_2[55] rings. Also note that our reported structure **BO2-I** is found to lie 56.5 kcal/mol below the earlier reported "global minimum" $Co_2(CO)_8(BO)_2$ structure.[24]



a **b**

Figure 2. The $Fe_2(CO)_8(Si_2O_2)$, $Co_2(CO)_8(B_2O_2)$, and $Co_2(CO)_8(B_2N_2Si_2Me_6)$ formation mechanisms (**a**), and the potential energy surface as a function of Si···O distance (**b**). The reaction Gibbs energies (*G*) and total relative electronic energies (Δ*E*) are given in kcal/mol, and the zero-point corrected electronic energies (E_{ZPE}) are given in parentheses in kcal/mol.



BN2-ts **BO2-ts** **BO3-ts**

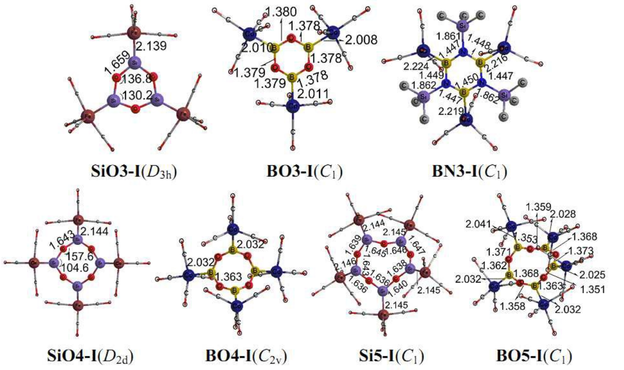
Figure 3. The predicted transition states for formation of $Co_2(CO)_8(B_2N_2Si_2Me_6)$, $Co_2(CO)_8(B_2O_2)$, and $Co_3(CO)_{12}(B_2O_2)$. Hydrogen atoms are omitted for clarity. The Wiberg bond indices (WBIs) as well as the Natural Charges are given in italics. The bond distances are given in Å. All the TSs are optimized without any symmetry.

The dimerization processes are also investigated in kinetics and shown in Figure 2**a**. The $Co_2(CO)_8(B_2O_2)$, and $Co_2(CO)_8(B_2N_2Si_2Me_6)$ formation processes are predicted to have activation Gibbs energies of 13.8 kcal/mol, and 25.6 kcal/mol (Figure 2), respectively. Moreover, the formation of dimers is entropy controlled, since the zero point corrected total electronic energies (E_{ZPE}) of the *TS*s are reported to lie more than 12.5 kcal/mol below the activation Gibbs energies, especially the E_{ZPE} of the structural complexes **BN2-ts** lying 20.6 kcal/mol below the activation Gibbs energy. The predicted transition states (**BO2-ts**, and **BN2-ts** in Figure 3) are generated from the $Co(CO)_4(BO)$, and $Co(CO)_4(BNSiMe_3)$ monomers by the vacant LUMO orbitals at the boron atom in one monomer accepting the electron pair from the occupied HOMO orbital at oxygen or nitrogen in the other monomer (See Figure S4 in the SI). Both the **BO1-I** and **BN1-I** monomers are found to have a LUMO with the same contribution (8%) localized on the boron atom, thus leading to the similar positively charged B(O) (1.09), and B(N) (0.97) atoms. However, the HOMO orbital of **BN1-I** is reported to have a contribution of 28% localized on the nitrogen atoms, which is obviously larger than the contribution of 4% in **BO1-I**, thus providing a larger negative charge on the nitrogen atom (–1.35) than the oxygen atom (–0.83). The **BO2-ts** and **BN2-ts** are found have nearly symmetric B_2O_2 and B_2N_2 rings with average long B···O and B···N distances of 2.08 Å and 2.28 Å. The longer B···N distances can be a consequence of steric hindrance from the bulky SiMe$_3$ group. In the B_2O_2 and B_2N_2 rings, a four-center π orbital is formed from two π orbitals perpendicular to the rings, and a four-center σ orbital is formed by using a pair of π orbitals parallel to the rings (See Figure S4 in the ESI). A search for the expected **SiO2-ts** failed, even by scanning the potential energy surface in terms of longer Si···O distances in a symmetric Si_2O_2 rhombus (Figure **2b**). In addition, an optimized **SiO2-I** structure with fixed Si···O distances of 2.2 Å shows two imaginary vibrational frequencies of 241*i* (corresponding to the Si_2O_2 ring formation) and 19*i* (corresponding to terminal carbonyl rotation), respectively. We therefore suspect that the dimerization of $Fe(CO)_4(SiO)$ to give $Fe_2(CO)_8(Si_2O_2)$ is highly favored kinetically without any transition state. This can be explained from the frontier orbitals of **SiO1-I**. Thus the LUMO of **SiO1-I** is greatly concentrated (43%) on the more positively charged silicon atom (natural charge of 1.84). In summary, these monomers are kinetically unstable with respect to [2+2] cyclodimerization. and The rate of cyclodimerization is predicted to increase in the sequence BNSiMe$_3$ < BO < SiO. This can be related to the successful syntheses and isolation of $[BrM(PCy_3)_2](BNSiMe_3)$ (M = Pd, Pt),[15] $[BrPt(PCy_3)_2](BN\textit{i}Bu)$,[19] and $[Br_2Rh(PMe_3)_3](BNSiMe_3)$,[19] possibly because of increased Gibbs energies for dimerization of the iminoboryl groups owing to the bulky phosphine ligands. enlarging activation. In contrast, the analogous boronyl complex $[BrPt(PCy_3)_2](BO)$, , still can be activated toward cyclodimerization into $\{[Pt(PCy_3)_2](B_2O_2)\}^{2+}$ using Ag^+.[16,22] Finally, we predict that isolation of related siliconyl complexes will be a great challenge because of their highly kinetic instability.

2.3 Larger Oligomers

The polarized Si-O, B-O, and B-N single bonds lead to significant positive charges on the silicon and boron atoms. Therefore, dipolar cyclooligomerization can be continued beyond the dimer to give trimers, tetramers, pentamers, etc. (Figure 4). All of the oligomers are found to be thermochemically viable except the iminoboryl complex **BN3-I** (Table S1 in ESI). Thus the formation of **BN3-I** from **BN2-I** and **BN1-I** is predicted to be endothermic by 15.1 kcal/mol. This appears to be a consequence of steric repulsion of the three bulky SiMe$_3$ groups in **BN3-I**. Furthermore, the Co-B interactions are weakened since the average Co-B distances increase to 2.20 Å, which is ~0.15 Å longer than the Co-B distances in **BN1-I** or **BN2-I**. The higher oligomer **BN4-I** and **BN5-I** structures are not expected to be viable because of the bulky $SiMe_3$ groups.

The trimers **SiO3-I** and **BO3-I**, contain planar six-membered Si_3O_3 and B_3O_3 rings, respectively. The singly bonded Si-O and B-O distances in these trimers are predicted to be 1.659 Å (**SiO3-I**) and 1.380 Å (**BO3-I**), which are ~0.025 Å shorter than the corresponding distances in the dimers. Such bond shortening is attributed to the lower steric strain in six-membered rings relative to four membered rings as well as the aromaticity of the B_3O_3/Si_3O_3 rings.[56] However, each trimer contains three $M(CO)_4$ fragments, which might lead to extra steric repulsion for kinetically inhibiting the cyclotrimerization proceesses. Thus, the trimerization mechanism was investigated for checking the kinetic accessibility of **BO3-I**. The Gibbs energy of activation for **BO3-ts** (Figure 3) is predicted to be only 8.2 kcal/mol, which is 5.6 kcal/mol less than that of **BO2-ts** (Figure 2). This discrepancy arises from the weakly π aromatic boroxine ring[57] as well as the increased positive charge on boron from 1.09 in **BO1-I** to 1.24 in **BO2-I** (See Figure S1 in the ESI). This leads to a stronger electrostatic attraction for opposing the increased steric repulsion. Unlike the **BO2-ts** with a nearly symmetric B_2O_2 ring, the **BO3-ts** is found to have a long B•••O distance of 2.222 Å and a particularly short B•••O distance of 1.560 Å. Such an unsymmetrical B_2O_2 ring in **BO3-ts** contributes significantly to the frontier orbitals of **BO2-I** since the unoccupied LUMO orbital is mainly located on the boron atoms (30% contribution) in **BO2-I**. The stronger attraction to the lone pair electrons of O(B) group in **BO-I** (Figure S4 in the ESI), thus leads to the particularly short B•••O distance. Although locating the **SiO3-ts** failed, we still can expect the corresponding activation Gibbs energy to be more negative than that for **SiO2-ts**, since the positive charge on the silicon atoms increase from 1.84 in **SiO-1** to 1.99 in **SiO-2** (See Figure S1 in ESI). Thus the trimers **SiO3-I** and **BO3-I** are kinetically more viable than the dimers. Similar Si_3O_3 rings have been found in a number of organosilicon compounds such as the chair conformations of $\{HC[SiMe_3(OH)Si(O)\}_3$ [58] and $\{R(OH)Si(O)\}_3$ (R = C_6H_5, $C_{12}H_7$) [59], [60] as well as the planar trimer precursor $[PhC(NtBu)_2Si(O)Cl]_3$ to the monomer $PhC(NtBu)_2Si{=}O$. [61] Theoretical work by Kudo and Nagase indicates considerable flexibility of the Si_3O_3 ring interconverting boat and chair conformations.[62]


SiO3-I(D_{3h}) **BO3-I**(C_1) **BN3-I**(C_1)

SiO4-I(D_{2d}) **BO4-I**(C_{2v}) **Si5-I**(C_1) **BO5-I**(C_1)

Figure 4. Optimized lowest energy $M_n(CO)_{4n}(L_n)$ (n = 3 to 5) oligomer structures. Bond distances are given in Å. Symmetries are given in parentheses. Hydrogen atoms are omitted for clarity.

The trimers $[Fe(CO)_4]_3(Si_3O_3)$ (**SiO3-I**) and $[Co(CO)_4]_3(B_3O_3)$ (**BO3-I**) can combine further with another $Fe(CO)_4(SiO)$ and $Co(CO)_4(BO)$ monomer, respectively, leading to the tetramers **SiO4-I** and **BO4-I** (Figure 4). The Gibbs energies of formation for the tetramers (Table S1 in the SI) are predicted to be 38.0 kcal/mol (**SiO4-I**) and 16.0 kcal/mol (**BO4-I**), indicating the thermodynamic instability with respect to addition of the monomers to the trimers. Structures **SiO4-I** are **BO4-I** are predicted to have bent eight-membered Si_4O_4/B_4O_4 rings with Si_4/B_4 dihedral angles of 40.0º/19.7º to relieve the steric repulsion of four $Fe(CO)_4$/$[Co(CO)_4]^-$ fragments in the tetramers. A similar Si_4O_4 ring is found experimentally in the tetramer of dimethylsiloxane $[(CH_3)_2SiO]_4$.[63] Further addition of $Fe(CO)_4(SiO)$ and $Co(CO)_4(BO)$ to **SiO4-I** or **BO4-I** gives the pentamer $[Fe(CO)_4]_5(Si_5O_5)$ (**SiO5-I**) or $[Co(CO)_4]_5(B_5O_5)$ (**SiO5-I**), respectively, containing a cardioid ten-membered Si_5O_5/B_5O_5 ring with a cusp *trans* to a silicon or boron vertex. Such addition processes are found to release Gibbs energies of 40.7 kcal/mol (**SiO5-I**) and 21.8 kcal/mol (**BO5-I**) (Table S1 in the SI), which are somewhat larger than the corresponding values for formation of tetramers. This might be attributed to the extra stability of the pentamers, since the pentamers are more distordered than the tetramers with larger Si_4/B_4 dihedral angles of 67.7º/67.4º.

3. Conclusions

The little-known chemistry of siliconyl, boronyl, and iminoboryl derivatives, including both monomer stabilization and oligomer preparation is of interest for further chemical applications. Thus the highly polarized and energetic multiply bonded siliconyl, boronyl, and iminoboryl groups might be used to activate small molecules. For example, the organic B=N double bond was reported to react reversibly with CO_2.[64] Our reported oligomers with highly positively charged boron or silicon atoms can act as strong Lewis acids for interaction with Lewis bases. Our DFT study on $L_nM_n(CO)_{4n}$ (n = 1 to 5) derivatives provide insight into these issues. First of all, the triply bonded monomeric siliconyl, boronyl, and iminoboryl groups in their simple transition metal carbonyl complexes $LM(CO)_4$ are predicted to be disfavored relative to oligomerization to $[Fe(CO)_4]_n(Si_nO_n)$, $[Co(CO)_4]_n(B_nO_n)$, and $[Co(CO)_4]_2(B_2N_2Si_2Me_6)$ containing cyclic Si_nO_n/B_nO_n/B_2N_2 rings with alternating single bonds. However, the trimer $[Co(CO)_4]_3(B_3N_3Si_3Me_9)$ is disfavored owing to the extra steric repulsion from the bulky $SiMe_3$ groups. The polarized triple bonds in these ligands analogous to the CO group makes these ligands in metal complexes susceptible to dipolar cyclooligomerization processes. The rate of cyclodimerization is predicted to increase in the sequence $BNSiMe_3$ < BO < SiO. This is likely to limit the range of stable complexes that can be synthesized containing such ligands. In this connection, several iminoboryl complexes, including $[BrM(PCy_3)_2](BNR)$ (M= Pd, Pt; R = $SiMe_3$, *i*Bu),[15,19] and $[Br_2Rh(PMe_3)_3](BNSiMe_3)$,[19] have been prepared as stable species, possibly owing to the bulky phosphine ligands increasing the Gibbs free energies of activation for stabilizing the iminoboryl group. Furthermore, the oligomers of iminoboryl complexes can be obtained by choosing a suitable host [M] as well as smaller R groups for replacing the bulky $SiMe_3$/*i*Bu group. In contrast, the complexes $(Cy_3P)_2Pt(BO)Br$ and $[(Cy_3P)_2Pt_2(B_2O_2)]^{2+}$ synthesized by the Braunschweig group provide a good example of using bulky ligands, in this case tricyclohexylphosphine ligands, to kinetically block the oligomerization of the boronyl ligand.[22] Furthermore, isolating the siliconyl complexes will be a great challenge because of their predicted high kinetic instability towards intermolecular siliconyl cycloligomerization. Thus, numerous metal complexes of inorganic Si_nO_n, B_nO_n, and B_nN_n rings are likely to be synthesized by using suitable chosen metal fragments.[65]

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Notes and references

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†Electronic Supplementary Information (ESI) available: [Theoretical methods; complete list of monomer and oligomer structures; Thermochemistry; Electronic structure and bonding nature; Tables S4-S17: theoretical Cartesian coordinates for $Fe_n(CO)_{4n}(SiO)_n$ (6 structures), $Co_n(CO)_{4n}(BO)_n$ (n = 1 to 5) (5 structures), $Co_m(CO)_{4m}(BNSiMe_3)_m$ (n = 1 to 3) (3 structures), and complete Gaussian 09 reference.

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