Group 11 Borataalkene Complexes: Models for Alkene Activation

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Abstract: A series of linear late transition metal (M = Cu, Ag, Au and Zn) complexes featuring a side-on \([B=\text{C}]^-\) containing ligand have been isolated and characterised. The \([B=\text{C}]^-\) moiety is isoelectronic with the \(\text{C=\text{C}}\) system of an alkene. Comparison across the series shows that in the solid-state, deviation between the \(\eta^2\) and \(\eta^1\) coordination mode occurs. A related zinc complex containing two \([B=\text{C}]^-\) ligands was prepared as a further point of comparison for the \(\eta^1\) coordination mode. The bonding in these new complexes has been interrogated by computational techniques (QTAIM, NBO, ETS-NOCV) and rationalised in terms of the Dewar–Chatt–Duncanson model. The combined structural and computational data provide unique insight into catalytically relevant linear \(d^{10}\) complexes of Cu, Ag and Au. Slippage is proposed to play a key role in catalytic reactions of alkynes through disruption and polarisation of the \(\pi\)-system. Through the preparation and analysis of a consistent series of group 11 complexes, we show that variation of the metal can impact the coordination mode and hence substrate activation.

Introduction

Alkene complexes of transition metals were among the first organometallic compounds reported.\(^{[1]}\) Coordination of alkene ligands typically occurs through a symmetric \(\eta^2\)-coordination mode involving a side-on approach to metal. Alkene binding is synonymous with the activation of this substrate during catalytic processes.\(^{[2–6]}\) For example, linear \(d^{10}\) of Cu, Ag and Au complexes have been reported for a wealth of synthetic transformations; including ring-expansions,\(^{[7]}\) cyclisations,\(^{[8,9]}\) hydroarylation,\(^{[10–12]}\) hydroamination,\(^{[13,14]}\) hydroalkoxylation,\(^{[15]}\) and carboxylation reactions.\(^{[16]}\) These reactions are believed to share a common mechanistic step in which binding of the alkene to the metal facilitates attack by a nucleophile.\(^{[17–20]}\) An earlier theoretical analysis suggested that symmetrically bound alkene complexes are actually deactivated toward external nucleophiles and that slippage from an \(\eta^2\) to \(\eta^1\) coordination mode is crucial to activate the \(\text{C=\text{C}}\) bond and facilitate orbital overlap in the transition state for nucleophilic attack.\(^{[21]}\)

Due to their relevance as potential catalytic intermediates, a number of linear Au alkene complexes have been isolated and structurally characterised.\(^{[22–33]}\) as have related three-coordinate trigonal planar species.\(^{[34]}\) In contrast, examples of crystallographically characterised linear Cu\(^{[1]}\) and Ag\(^{[1]}\) alkene complexes are extremely rare (Figure 1).\(^{[35,36]}\) The paucity of data has meant that the comparison of bonding in a complete series of alkene complexes of the group 11 triad has not been possible. There is limited experimental evidence to show how modulation of the metal influences alkene binding, including the ability to adopt \(\eta^2\) or \(\eta^1\) coordination modes believed to be so important in key bond making steps during catalysis.

In this paper, we consider the isoelectronic substitution of the \(\text{C=\text{C}}\) bond with a \([B=\text{C}]^-\) bond and the binding of this fragment to a series of group 11 and 12 metals. The \([B=\text{C}]^-\) moiety is found within borataalkene compounds of the form \([R,B=\text{C}]^-\). The synthesis of borataalkenes has been achieved by a number of methods, the principal approach involving the deprotonation of the parent boranes \([R,B=\text{C}]\).\(^{[37–40]}\) Crystallographically characterised examples of borataalkenes were first reported by Power and co-workers in the late 1980s, short \(B=\text{C}\) bond lengths of 1.4–1.5 Å were taken as an indication of double character.\(^{[41,42]}\) More recently a number of structurally characterised borataalkene compounds has been reported.\(^{[43–46]}\) Coordination of \([B=\text{C}]^-\) moieties to transition metals is limited. Pioneering examples include those of Nöth and co-workers who described the coordination of a fluorenylidene borane to transition metal carbonyl complexes,\(^{[47–50]}\) and those of Piers and co-workers who reported methylidene borane complexes of tantalum and...
titanium along with their alkene reactivity.\cite{51-57} Related coordination complexes of alkylidene boranes have also been reported.\cite{58} To the best of our knowledge, group 11 complexes of borataalkene ligands are limited to a single example involving coordination of a 9-borataphenanthrene anion to Au.\cite{59}

Recently Braunschweig and co-workers reported the lithium boryl compound \([cAAC\cdot BH_2]\)Li (1) which can be isolated and is stable under ambient conditions.\cite{60-62} An underappreciated characteristic of the anionic component \([cAAC\cdot BH_2]^-\) (A) is its potential for \(B=C\) \(\pi\)-bonding and borataalkene character (Figure 2). DFT calculations on this species (\(\omega B97XD/6-31G^{**}/SDD\)) demonstrate that the \(B=C\) bond length (1.45 \(\AA\)) is consistent with its assignment as a borataalkene. Natural bond orbital (NBO) calculations reveal that this is a polarised \(\pi\)-system. The \(B=C\) Wiberg bond index (WBI) is 1.64 and natural charges show localisation of more charge on the carbon atom (-0.32) relative to boron (-0.15). Key natural bond orbitals of the \(\pi\)-system are visualised in Figure 2. Despite the polarisation of the \(\pi\)-system, it should be noted that the contributions to the NBOs are relatively even: 66\% pAO carbon; 34\% pAO boron (bonding NBO) and 34\% pAO carbon; 66\% pAO boron (anti-bonding NBO).

\[\begin{align*}
\text{Dipp} &= 2,6-di\text{-iso-propyl phenyl} \\
\text{Dipp} &= \text{borataalkene moiety} \\
\text{B} &= \text{boron atom} \\
\text{C} &= \text{carbon atom} \\
\end{align*}\]

**Figure 2.** DFT optimised structure of Anion A. Calculated \((\pi)\) \(B=C\) and \((\pi^+)\) \(B=C\) natural bond orbitals (this work).

Herein we describe the side-on coordination of the \([B=C]^-\) bond of \([cAAC\cdot BH_2]^-\) to linear \(d^{10}\) metal fragments \((M = Cu, Ag, Au and Zn)\). The bonding has been interrogated by a combination of experimental (\(^1H, ^{11}B, ^{13}C\) NMR and IR spectroscopy) and computational techniques (QTAIM, NBO, ETS-NOCV). Comparison across the series of group 11 complexes shows that a spectrum of coordination between \(\eta^2\) and \(\eta^1\) is observed; with \(\eta^1\) coordination becoming more favorable for \(Au > Ag > Cu\). The data potentially provide new insight into catalytically relevant isoelectronic alkene complexes of \(Cu, Ag\) and \(Au\).

**Results and Discussion**

**Synthesis**

Reaction of 1 with the group 11 metal complexes \([M-(\text{IPr})\text{Cl}])\) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; \(M = Cu, Ag, Au\); 2a–c), in Et_2O at 25°C leads to a clean salt-metathesis reaction and the formation of the corresponding group 11 complexes (3a–c) in 73–80\% yield (Scheme 1). 3a–c are soluble in hydrocarbon and ether solvents. They are stable as solids at 25°C but decompose slowly (3a and 3c) or rapidly (3b) in solution under ambient light precipitating the metal from solution. The formation of 3a–c was confirmed by \(^{11}B\) NMR spectroscopy as demonstrated by a shift in the resonance from 1 (\(\delta_B = -3.6\) ppm) to higher field upon reaction to form 3a–c (\(\delta_B = -7.4\) to -13.5 ppm). Infrared spectroscopy of 3a–c reveal \(B-H\) stretches of \(\nu_{BH} = 2345-2411\) cm\(^{-1}\) which lie between reported stretching frequencies for \(sp^2(B-H)\), \(\nu_{BH} = 2467-2564\) cm\(^{-1}\)\cite{63,64} and \(sp^2(B-H)\), \(\nu_{BH} = 2273-2383\) cm\(^{-1}\)\cite{65}. The analogous Zn complex, \([\text{Zn}[\text{BH}_2(cAAC)]_2]\) (4, Scheme 1) can also be prepared by a salt-metathesis route and shows \(B-H\) stretches (\(\nu_{BH} = 2373, 2420\) cm\(^{-1}\)) that are marginally higher frequency than 3a–c.

**Solid-State Structures**

Complexes 3a–c can be described as linear \(d^{10}\)-metal centres with side-on coordination of the \([B=C]\) moiety. The molecular and structural formulae were confirmed by X-ray
The Au atom is only displaced from boron, implying the coordination is dominated by a post-transition metal, the metal centre is displaced 0.29(5) Å, as the group is ascended taking values of 89.0(7), 86.0(2), 82.2(7), 86.6(2), and 0.16(3) Å from boron, respectively. Conversely, in 3e the Au atom is only displaced 0.04(3) Å from B, implying the coordination is dominated by the B–Au interaction and an η1 coordination mode.

The zinc analogue 4 provides a further benchmark for the η1 coordination geometry. As a post transition metal, the filled d-orbitals of zinc are low in energy and expected to play a very limited role in bonding. The structure of 4 was found

diffraction analysis of single crystals grown form Et2O solutions (Figure 3a). The structures of 3b and 3c contain two molecules in the asymmetric unit, however the metrics are statistically identical accounting for standard deviation errors. The metal-boron distances in 3a–c (2.121(2)–2.23(1) Å) are directly comparable to the side-on bound diborane complexes of the coinage metals reported by Kinjo and co-workers (2.096(3)–2.220(4) Å).[66] These values are longer than those found in structurally related α-boryl complexes. For example, the metal-boron distances in [M-(IPr)(Bpin)] range from 2.002(3) to 2.063(5) Å (M = Cu, Au; Bpin = pinacoloborane).[67,68] The B–C bond distance for 3c (1.52(2) Å) is elongated slightly in comparison to 3a (1.469(3) Å) and 3b (1.473(5) Å), although the error of these measurements precludes definitive confirmation of this discrepancy. The M–B–C angle of 164.5(1)° is well beyond the sum of the covalent radii and an open Zn–B–C bond length ranging from 2.052(3) to 2.087(3) Å.[69] In contrast to the Cu analogue 3a, 4 contains a long Zn–C bond (> 2.8 Å) which is well beyond the sum of the covalent radii and an open Zn–B–C bond length ranging from 2.052(3) to 2.087(3) Å.[69] Both metrics are consistent with an η1 coordination mode in which the principal interaction between the ligand and metal is through a Zn–B bond. For comparison, related borataalkene complexes in which [CH2=BCl2] is coordinated to titanocene and tantocene have been shown to adopt both η2 and η1 coordination modes.[70] But in this case the borataalkene coordinates as the η1-C and not η1-B isomer with the M–C interaction dominating the bonding interaction, this differ-
ence is likely an effect of the very different steric profiles around the B and C atoms in A and [CH$_2$B(C$_6$F$_5$)$_2$].

**Calculations**

Theoretical calculations were conducted to gain insight into the bonding in 3a–c and 4. DFT calculations were conducted using Gaussian09. The oB97x-D functional with 6-31G** (C, H, N, B)/SDDAll(M) hybrid-basis set was applied, with single point PCM (THF) solvent corrections. The computationally optimised structures for 3a–c and 4 are in good agreement with the experimentally determined crystal structures and were used as inputs for a battery of methods for bonding analysis (QTAIM, NBO, ETS-NOCV).

QTAIM analysis of 3a–c identifies bond critical points (bcp) between boron and carbon, and boron and the coinage metal, but not from the coinage metal to carbon (Table 1). Nevertheless, the side-on binding mode and a non-negligible M–C interaction is supported by the curved bond paths identified in the contour plots from QTAIM analysis (Figure 5b). The curvature of the bond path is most marked for 3a (Cu) and least for 3c (Au). Virtually no curvature is seen in the bond paths for 4. In the free [(cAAC)BH$_2$]– anion (A), the electron density ($\rho(r)$) at the bcp between B and C is found to be 0.20. Upon complexation with a coinage metal, $\rho(r)$ decreases to 0.19 (Cu, Ag) and 0.18 (Au) implying a reduction in B=C bond order. For 3a–c, a small $\rho(r)$ at the bcp between the M and B (0.06–0.08) is found, consistent with a closed shell ionic interaction. Others have shown that ellipticity is not an accurate metric for evaluating the $\pi$-character of the B=C bond.[71]

A complementary picture emerges from NBO calculations. The WBIs are consistent with B–C multiple bonding character throughout the entire series of compounds, with coordination to the metals reducing the B=C WBI (Table 2). Further, comparison of M–B and M–C WBIs reveals that the covalent component of the metal ligand bonding is dictated by the M–B interaction as is expected for a side-on but slipped bonding interaction. This M–B value is largest for Au (compared with Ag and Cu) which could be interpreted as an indicator of a stronger binding interaction and a consequence of the greater radial extension of the AOs of Au relative to its lighter congeners.[72,73] The M–C interaction in the Zn analogue is the weakest of the series and consistent with very little interaction between the cAAC carbon atom and the metal. Based on the NPA charges, the polarisation of the B=C

| Tabelle 1: QTAIM parameters on 3a–c and 4. | | |
|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| M–B | $\rho(r)$ | M–B $\nabla^2\rho(r)$ | B–C $\rho(r)$ | B–C $\nabla^2\rho(r)$ |
| A | 0.20 | 0.23 | 0.19 | 0.33 |
| 3a | 0.07 | 0.08 | 0.19 | 0.32 |
| 3b | 0.06 | 0.04 | 0.19 | 0.32 |
| 3c | 0.08 | 0.01 | 0.18 | 0.34 |
| 4 | 0.05, 0.07 | 0.22, 0.37 | 0.18, 0.18 | 0.31, 0.36 |

| Tabelle 2: NPA charges and WBIs for complexes 3a–c and 4. | | |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| M | B | C | M–B | M–C | B–C |
| A | –0.15 | –0.32 | – | – | 1.64 |
| 3a | +0.62 | –0.47 | –0.14 | 0.25 | 0.15 | 1.47 |
| 3b | +0.51 | –0.44 | –0.10 | 0.29 | 0.18 | 1.41 |
| 3c | +0.34 | –0.53 | +0.04 | 0.43 | 0.17 | 1.27 |
| 4 | +1.12 | –0.68 | +0.07 | 0.40[a] | 0.08[a] | 1.27 |

[a] data are identical across both ligand systems. Calculated with v 6.0 of NBO.

**Figure 5.** a) Simplified bonding model for 3a–c and 4. Data on 3a including b) QTAIM, c) ETS-NOCV and d) NBO calculations.
bond reverses on coordination to the metal, with charge localising on the boron atom and being depleted from the carbon atom in all cases (Table 2). Deviation toward \( \eta^1 \) coordination (Cu → Ag → Au) is also accompanied by an increased polarisation of the B–C bond toward an ionic B–C\(^+\) structure as would be expected as the M–B interaction begins to become more important and the M–C interaction (and electron transfer from M to C) is disrupted. At the same time the C–N bond of the cAAC ligand shortens to compensate for the electron deficiency at carbon. The C–N bond length of the cAAC ligand takes values of 1.406(6), 1.413(5), 1.39(1), and 1.350(2) Å for 3a, 3b, 3c and 4 respectively.

Inspection of the key orbitals involved in bonding in 3a–c reveals this interaction conforms to the Dewar–Chatt–Duncanson model (Figure 5c). Qualitatively the \( \sigma \)-donation and \( \pi \)-backdonation components bonding can be inspected by second-order perturbation analysis. This analysis shows that donation from the \( \pi(B=C) \) bonding orbital to the vacant \( s(M) \) metal acceptor orbital is far larger than back-donation from filled metal \( d \)-orbitals to the \( \pi^+(B=C) \). Consistent with this finding, the calculated occupancy of the B–C \( \pi \)-orbital for 3a–3c is lower than A due to electron transfer occurring from the borataalkene to the metal (supplementary information, Table S3). Although the data are coherent across two different versions of NBO (v 6.0 and 3.1), the quantitative analysis of the donor-acceptor interactions by second order perturbation analysis is complicated by the very large and unrealistic energies (100–400 kcal mol\(^{-1}\)).

We turned to ETS-NOCV calculations to further support the bonding model and quantify the bonding interactions. Inspection of the \( \Delta E_{\text{orb}} \) energies reveals that the orbital (covalent) interaction increases in magnitude across the series 3c (118.9 kcal mol\(^{-1}\)) > 3b (71.1 kcal mol\(^{-1}\)) > 3a (58.9 kcal mol\(^{-1}\)) suggestive of a stronger binding of the [B=C]\(^-\) moiety to Au over Ag and Cu. The key contributors to \( \Delta E_{\text{orb}} \), \( \Delta \rho_1 \) and \( \Delta \rho_2 \) involve \( \sigma \)-donation from the \( \pi \) B–C orbital to the metal \( n \)-orbital (Cu, 4\( s \); Ag, 5\( s \); Au, 6\( s \)) and \( \pi \)-backdonation from the metal \( n \)-1d orbital to the \( \pi^+ \) B–C orbital. For example, for 3a, these \( \sigma \)-donation and \( \pi \)-back-donation components are quantified as contributing 28.4 and 5.3 kcal mol\(^{-1}\) to the total \( \Delta E_{\text{orb}} \) interaction (Figure 5d).

To gain a deeper understanding of the potential energy surface that connects \( \eta^1 \) and \( \eta^2 \) coordination in 3a–e, scans of the M–C bond between 1.5–3.4 Å were undertaken with DFT methods. These calculations revealed a flat potential energy surface about the equilibrium bond length. Only one energy minimum was located for each structure. Comparison of the series revealed that this minimum was displaced to longer M–C bond lengths for Cu (2.44 Å), Ag (2.62 Å) and Au (2.76 Å) respectively. The extent of displacement is beyond that expected for solely the difference in covalent radii of the group 11 metals. The calculations support the solid-state data and suggest that while deformation toward the \( \eta^2 \) coordination mode of the ligand is energetically accessible for the whole series, it occurs more readily for the heavier analogues.

To assess the strength of bonding of A to the coinage metal fragments and rationalize the ease of formation of 3a–c and 4 relative to their alkene analogues, an isodesmic equilibrium was considered (Scheme 2). There is a clear energetic driving force for the formation of the borataalkene complex over the alkene complex (\( \Delta G^{\text{rxn}} = -42\text{–}52 \) kcal mol\(^{-1}\)).

In summary, we report the preparation and analysis of a complete series borataalkene complexes (3a–c) of the coinage metals involving side-on coordination of a [B=C]\(^-\) ligand along with an analogous Zn complex (4). Calculations confirm that the bonding in these compounds is best described by the Dewar–Chatt–Duncanson model. The structural data and calculations also show the propensity of the ligand to adopt a variety of coordination modes defined by a spectrum in between \( \eta^2 \) and \( \eta^1 \) coordination. Deformation toward \( \eta^1 \) coordination is a phenomenon that is expected to be accompanied by the polarisation of the \( \pi \)-system of the coordinated ligand and is greatest for Au > Ag > Cu. Due to the isoelectronic relation between [B=C]\(^-\) and [C=C] moieties, 3a–c serve as isoelectronic models for catalytically relevant alkene complexes of group 11. Hence, our findings not only demonstrate new coordination chemistry of [B=C]\(^-\) units they provide unique insight into catalytically relevant isoelectronic alkene analogues.

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**Conflict of interest**

The authors declare no conflict of interest.
Stichwörter: borataalkene · boron · coinalge metal · gold catalysis · metal boryl complexes
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