C=O Scission and Reductive Coupling of Organic Carbonyls by a Redox-Active Diboraanthracene

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C=O Scission and Reductive Coupling of Organic Carbonyls by a Redox-Active Diboraanthracene

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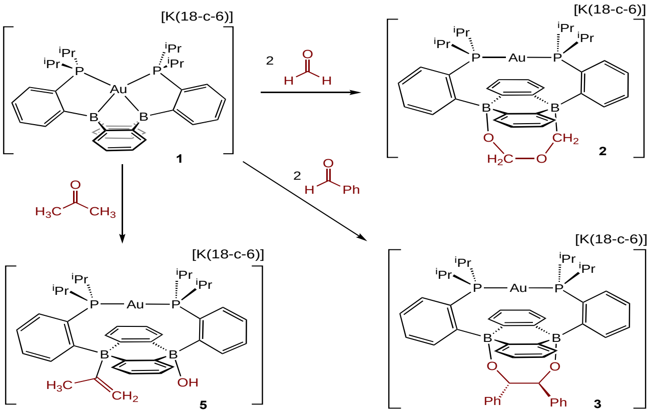
The boron-centered reactivity of the diboraanthracene-auride complex ([Au(B_2P_2)][K(18-c-6)]; (B_2P_2, 9,10-bis(2-(diisopropylphosphino)- phenyl)-9,10-dihydroboranthrene) with a series of organic carbonyls is reported. The reaction of [Au(B_2P_2)]$^-$ with formaldehyde or paraformaldehyde results in a head-to-tail dimerization of two formaldehyde units across the boron centers. In contrast, the reaction of [(B_2P_2)Au]$^-$ with two equivalents of benzaldehyde yields the pinacol coupling product via C–C bond formation. Careful stoichiometric addition of one equivalent of benzaldehyde to [Au(B_2P_2)]$^-$ enabled the isolation of an adduct corresponding to the formal [4+2] cycloaddition of the C=O bond of benzaldehyde across the boron centers. This adduct reacts with a second equivalent of benzaldehyde to produce the pinacol coupling product. Finally, the reaction of [Au(B_2P_2)]$^-$ with acetone results in a formal reductive deoxygenation with discrete hydroxo and 2-propenyl units bound to the boron centers. This reaction is proposed to proceed via an analogous [4+2] cycloadduct, highlighting the unique small molecule activation chemistry available to this platform.

Small molecule redox reactions such as H_2O splitting, N_2 fixation, and CO_2 reduction are central to many of the chemical challenges required for sustainable human growth.[1] These reactions require efficiently shuttling multiple redox equivalents between (often inert) chemical substrates. While this area has been dominated by transition metal chemistry, over the past 15 years, reactive main-group systems[2] have emerged that are capable of activating small molecules such as H_2,[3] CO_2,[4] and N_2.[5] Examples include Frustrated Lewis pairs (FLPs),[6] main-group multiple bonds[7] and low-valent main-group centers.[8] Despite these advances, the intrinsic redox chemistry associated with the partially filled d orbitals of transition metal complexes allows them to excel in the delivery or removal of multiple electrons to or from chemical substrates. By comparison, the more limited redox chemistry of the p-block elements represents an obstacle for achieving this reactivity at main group centers. By designing enhanced redox chemistry into main group reaction platforms, these challenges can be overcome, enabling new classes of molecules for exploration as electrocatalysts. The use of redox-active ligands on main group metals is one such strategy for addressing this challenge.[9]



Scheme 1. Reductive transformations of organic carbonyls mediated by [Au(B_2P_2)]$^-$ (**1**).

Conjugated boron-containing heterocycles are another strategy targeted for the development of redox-active p-block reaction platforms.[10] With the appropriate molecular design, such compounds can accept multiple electrons at relatively mild potentials and perform reactions with challenging substrates such as H_2, CO_2, and C_2H_4.[11] The 9,10-dihydro-9,10-diboraanthracene (DBA) platform has captured attention in this regard as it is capable of reversibly accepting two electrons to yield a reactive core capable of cleaving H_2[12] and other E–E bonds[13] as well as

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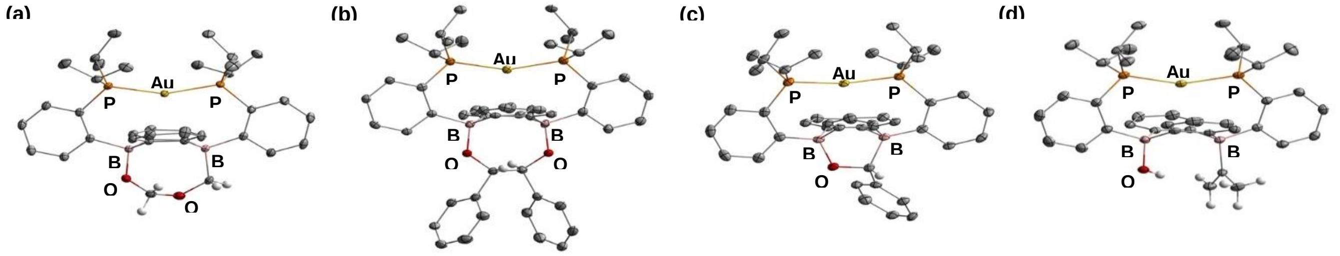


Figure 1. Thermal ellipsoid plots of **2** (50%, a), **3** (30%, b), **4** (30%, c) and **5** (50%, d). Unlabeled ellipsoids correspond to carbon. Most hydrogen atoms, all solvent molecules and K(18-c-6) units have been omitted for clarity.

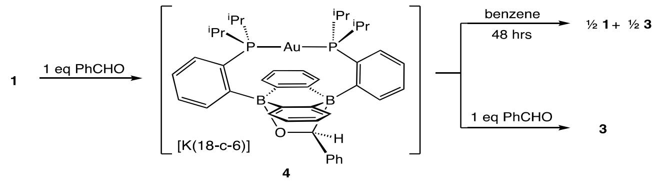
reducing CO_2.[14] As a ligand, DBA[15] and related 1,4-diboron containing heterocycles[16] have shown the ability to stabilize low-valent transition-metals. We recently reported the ligand B_2P_2 and its Cu, Ag,[17] Au[18] and Ni[19] complexes. In the case of Au, the fully reduced anion, $[Au(B_2P_2)][K(18\text{-}c\text{-}6)]$ (**1**), could be accessed at mild potentials (–2.05 V vs. Fc/Fc^+ in CH_3CN) and was identified as a donor-acceptor complex of anionic Au (auride). By comparison, dianion of 9,10-Mes_2DBA is formed at an $E_{1/2}$ of –2.48 V vs Fc/Fc^+ under the same conditions.[18] By utilizing the unusual Au–B interaction to modulate its DBA-centered reactivity, complex **1** undergoes protonation at the B atoms with weak acids to yield a borohydride that can then reduce CO_2 to formate.[21] Furthermore, direct reaction with CO_2 yields a CO_3 complex that was postulated to proceed through a cycloaddition intermediate, akin to a related species reported by Wagner.[14] Importantly, the DBA-bound reduction products can be released with strong acids or reductants, making these systems in principle catalytic. Inspired by this reactivity, we explored the chemistry of **1** with other compounds containing C=O functionalities. Herein we report that diverse reactivity, including examples of C–O and C–C bond formation in addition to an unusual example of acetone deoxygenation.

We first explored the reaction of **1** with formaldehyde, (Scheme 1, top). Exposure of **1** to paraformaldehyde in THF rapidly affords a colorless product that was identified by single crystal X-ray diffraction (XRD) as $[Au(B_2P_2)(OCH_2OCH_2)][K(18\text{-}c\text{-}6)]$ (**2**) (Figure 1a), resulting from the reductive head-to-tail dimerization of two equivalents of formaldehyde. The resulting $–OCH_2OCH_2–$ unit spans the two boron atoms on the DBA face opposite a roughly linear P-Au-P ($\angle$PAuP = 158.2°) complex. The C–O bonds of the formaldehyde range from 1.371(2) to 1.485(2) Å, consistent with single bonds, and the FT-IR spectrum of **2** contained no resonances indicative of C=O double bonds (see SI). The methylene resonances of the $–OCH_2OCH_2–$ moiety were detected as singlets at 4.80 and 4.21 ppm in the ^1H NMR spectrum, and the $^{11}B\{^1H\}$ NMR spectrum features resonances at –0.13 and –12.28 ppm corresponding to the O- and C-bound boron atoms, respectively. In order to confirm that the formation of **2** was the result of formaldehyde dimerization and not the excision of a dimeric unit from polymeric paraformaldehyde, we also synthesized **2** using monomeric formaldehyde generated via exposure of paraformaldehyde to acidic Amberlite resin (126⁺) in Et_2O suspension. Distillation of this Et_2O solution of CH_2O into a flask containing **1** gave **2** in good yield. A related boron-spanning O–C–O–C core is formed in the reaction of $[9,10\text{-}Me_2DBA]^{2-}$ sequentially with acetone followed by CO_2 as reported by Wagner.[14]

The formation of **2** prompted us to explore the analogous reaction with benzaldehyde (Scheme 1, diagonal). Reaction of **1** with two equivalents of benzaldehyde in toluene rapidly produced a colorless solution followed by the slow precipitation (30 mins) of a colorless crystalline solid, which was identified by single crystal XRD as $[Au(B_2P_2)(C_{14}H_{12}O_2)][K(18\text{-}c\text{-}6)]$ (**3**) (Figure 1b). Like compound **2**, compound **3** is the result of reductive dimerization of a carbonyl substrate, however, **3** contains a DBA-bound trans-1,2-diphenyl-1,2-ethanediolate moiety, the result of a C–C bond forming pinacol-coupling of two benzaldehyde units. Solution NMR spectroscopy of **3** is consistent with C_2 symmetry with the methine resonances of the 1,2-diphenyl-1,2-ethanediolate moiety appearing at 4.06 ppm in the ^1H NMR spectrum and 85.7 ppm in the ^{13}C NMR spectrum, as determined by a ^1H-^{13}C HSQC experiment.

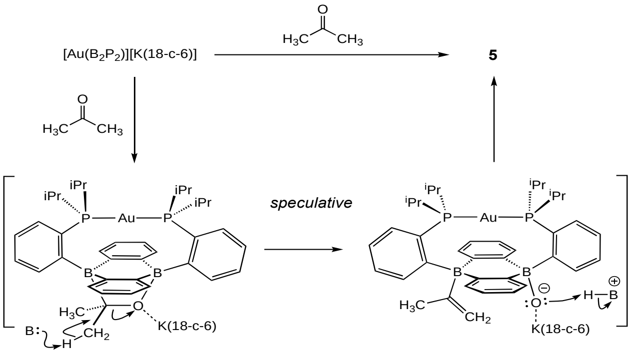
The presence of two equivalents of benzaldehyde in **3** prompted us to investigate potential intermediates in its formation from **1** (Scheme 2). Careful addition of one equivalent of benzaldehyde in toluene to a solution of **1** in the same solvent rapidly produced a nearly colorless solution with no observed precipitate. NMR analysis of this material revealed a set of coupled ^{31}P doublets at 49.57 (J_{PP} = 259.5 Hz) and 44.11 (J_{PP} = 259.0 Hz) ppm and $^{11}B\{^1H\}$ resonances at 0.03 and –7.96 ppm. These data are consistent with the formulation of this species as $[Au(B_2P_2)(PhCHO)][K(18\text{-}c\text{-}6)]$ (**4**). On standing, these solutions gradually become red with concomitant formation of a colorless precipitate. Spectroscopic analysis of the supernatant and precipitate identified them as **1** and **3**, respectively. Despite its eventual disproportionation into **1** and

3, a single-crystal of **4** suitable for single-crystal XRD (Figure 1c) confirmed the formal [4+2] cycloaddition of benzaldehyde across the B atoms of the DBA core. The benzaldehyde unit has an O–C bond of 1.471(7) Å, and FT-IR measurements of **3** confirm the absence of any C=O stretching bands (see SI). The observed disproportionation of **4** is consistent with the reversible addition of benzaldehyde to **1** and is evidence of the thermodynamic instability of **4** with respect to the pinacol product **3**. Subsequent addition of benzaldehyde to **4** results in the quantitative formation of the pinacol coupling product **3**. The cycloaddition of organic carbonyls with $[DBA]^{2-}$ systems has been observed in several cases, although in contrast to **4**, these products tend to be stable.[12b,14] Although conditions are known for the promotion of pinacol coupling reactions, they generally proceed through radical intermediates. While we cannot definitively exclude a radical-based mechanism for the formation of **3**, we note that **1** is insufficiently reducing to form the free benzaldehyde radical anion in solution and that the formation of **3** from the treatment of **4** with benzaldehyde is nearly instantaneous. These observations are consistent with a direct addition of benzaldehyde to **4**.



Scheme 2. Synthesis of **4** and its disproportionation into **1** and **3** over 48 hours in benzene solution at 22 °C.

Contrary to the reactions with formaldehyde and benzaldehyde, addition of acetone to **1** does not result in an immediate reaction (Scheme 1, left). These results contrast with Wagner's report of the rapid reaction of $[9,10\text{-}Me_2DBA]^{2-}$ with acetone at ambient temperature to form the corresponding cycloadduct.[14] Heating of a solution of **1** and one equivalent of acetone at 60 °C in C_6D_6 for 48 hours eventually led to the formation of a colorless solution, the major component of which featured two strongly coupled doublets at 48.6 and 45.0 (J_{PP} = 270 Hz) in the ^{31}P NMR spectrum. Following workup, single-crystal XRD revealed the product to be $[Au(B_2P_2)(C_3H_5)(OH)][K(18\text{-}c\text{-}6)]$ (**5**) (Figure 1d), which features hydroxide and 2-propenyl substituents at the two boron atoms. Although the structure of **5** suffers from modest disorder, the 2-propenyl unit is well-modelled over two positions. ^1H NMR spectroscopy of **5** in C_6D_6 shows the two olefinic propene C–Hs at 5.34 and 4.79 ppm with the former appearing as a broad singlet while the resonance at 4.79 ppm is resolved as a doublet (J = 6.6 Hz) consistent with geminal C-H coupling. The propene $-CH_3$ unit is detected as a singlet at 2.37 ppm. A ^1H-^{13}C HSQC experiment conducted in THF-d_8 located the C atoms of the propene unit at 177.8 (B-*C*), 115.8 ($CH_3C{=}CH_2$) and 26.3 ($CH_3C{=}CH_2$) ppm (See SI). $^{11}B\{^1H\}$ NMR spectroscopy of **5** in C_6D_6 displays two distinct B atoms, with signals at –0.77 and –7.93 ppm. Additionally, the O-*H* resonance was detected in the ^1H NMR spectrum as a singlet at 1.16 ppm and FT-IR spectroscopy produced a sharp band at 3572 cm^{-1}. No H_2 or B–H containing species were observed during the formation of **5**.



Scheme 3. Hypothetical base-promoted mechanism for the formation of **5**.

The formation of **5** was unexpected as examples of the direct C=O scission of a ketone to give an olefin and hydroxide are limited.[22] The direct oxidative addition of the C=O bond of ketones has been observed has for W complexes[23] as well as heterobimetallic Zr/Fe[24] and Zr/Co complexes.[25] These reactions, however, afford oxo/carbene species, not olefins. Given the prior observation of the benzaldehyde cycloadduct **4**, and Wagner's acetone cycloadduct,[14] we reasoned that a similar species may be an intermediate on the way to the formation of **5**. Such an intermediate could undergo a proton transfer from the α-carbon to the oxygen of the bound substrate with concomitant cleavage of the C–O bond (Scheme 3). Although we were unable to directly observe such an intermediate, the formation of **5** is modestly accelerated by the addition of catalytic base. To wit, when carried out in the presence of 10 mol% 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), the formation of **5** is complete within 36 hours, whereas in the absence of DBU, the corresponding reaction requires ca. 48 hours. The $[K(18\text{-}c\text{-}6)]^+$ unit may also be instrumental to this reactivity.[26] Ultimately, a more expeditious route to **5** was discovered that utilizes the triacetone adduct of NaI as an acetone source,[27] giving clean conversion to **5** in 1 hour at room temperature in THF. The origin of this rate enhancement is uncertain, but the presence of Na^+ may facilitate the elimination reaction via Lewis acid-base interaction with the oxygen atom.

Complex **1** has been shown to be a versatile reaction platform for reductive transformations of C=O containing small molecules. Unlike the metal-free DBA systems described by Wagner which generally form stable cycloadducts with carbonyl compounds,14 cycloadducts of **1** with carbonyls are unstable, leading either to dimerization reactions via C–C or C–O bond formation, or in the case of acetone, C–O scission. We attribute this to the geometric constraints imposed by the diphosphine-Au portion of the molecule on the diboron core. The Au center in **1** thus serves several roles, both geometrically constraining as well as taming the reducing power and charge of the diboron core. Along with related diboron heterocycles, these results highlight the increasing scope of redox small molecule activation that can be carried out by such systems. In this way, the conventional approach to reactive metal complex design, in which the ligands are used to tune the reactivity of the metal reaction center, is reversed. The reversal of roles for transition-metal and ligand in the $Au(B_2P_2)$ system are akin to the ligand centered reaction chemistry observed in other noninnocent ligands.[28] Using transition metal redox chemistry to enable multi-electron reactivity at main-group centers is an intriguing design principle for redox-active ligands and small molecule activation with main group elements. Efforts to extend this chemistry to catalytic applications are ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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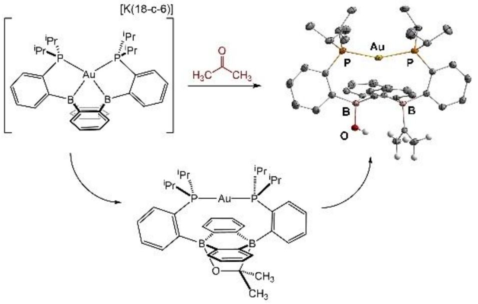

A gold-stabilized diboraanthracene mediates reductive transformations of carbonyls, including C–O and C–C bond formation, and deoxygenation of acetone to propene and hydroxide.