Heavy Metal-Free Fischer-Tropsch Type Reaction: Sequential Homologation of Alkylborane Using a Combination of CO and Hydrides as Methylene Source

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ABSTRACT: Carbon homologation reactions occur within the well-known Fischer-Tropsch process, usually mediated by transition metal catalysts at high temperature. Here we report the low-temperature, heavy metal-free homologation of a carbon chain using CO as a C₁-source showing for the first time that transition-metal catalysts are not required for Fischer-Tropsch-type reactivity. Reaction of an alkylborane in the presence of either LiHBEt₃ or LiAlH₄ resulted in multiple CO insertion/reduction events to afford elongated chains by more than two methylene (-CH₂-) units, affording aldehyde products upon oxidative aqueous work-up. Theoretical and experimental mechanistic studies indicate that the boron-terminus is responsible for CO incorporation as well as sequential hydride delivery leading to reduction of acylborane intermediates to alkylboranes.

The Fischer-Tropsch (FT) process is a fundamental industrial reaction with significant societal and economic implications that involves the controlled homologation and hydrogenation of carbon monoxide (CO) to afford higher hydrocarbons with predominantly straight-chains in the range of C₄ to C₁₀.¹ The process involves the reductive coupling of CO units into methylene chains, and is a practical way of converting coal to gasoline, diesel oil, wax and smaller amounts of oxygenated compounds (e.g. alcohols, acids and ketones). For the FT process, iron- and cobalt-based heterogeneous catalysts have been widely used industrially under two different operating modes: (i) the high-temperature FT process with iron catalysts at 573–623 K, and (ii) the low-temperature FT process with either iron or cobalt catalysts at 473–513 K.²

The reductive coupling of CO mediated by heavy metals has been studied in order to gain insight into possible mechanisms by which FT processes occur,^{3–6} but analogous processes in the absence of heavy metals remain rather unexplored.^{7–9} Despite a dearth of reports, the non-transition metal mediated conversion of CO into methylene moieties has been previously been reported, namely *via* the reactions of organoboranes with CO in the presence of hydride species. In 1980, Brown *et al.* reported the three-step homologation of a linear alkylborane, involving the carbonylation of 9-octyl-BBN (BBN = 9-borabicyclo[2.2.1]nonane) with CO in the presence of LiAlH(OMe)₃, subsequent reduction using LiAlH₄, and finally hydrolysis with CH₃SO₃H to afford the C₁ elongated product, 9-nonyl-BBN (Scheme 1A).¹⁰ As the only example of two carbon homologation, in 1992, Yalpani and Köster reported the reaction of (Et₂BH)₂ with CO at 80 °C to detect butanol after alkaline hydroperoxide oxidation (Scheme 1B).¹¹ In this report, the authors proposed that CO inserted into the ethyl–boron bond to form a three-membered cyclic intermediate, and then further addition of hydride gives a homologue of alkylborane. Unfortunately, however, no mechanistic support was provided in these studies.

Scheme 1. Formation of methylene linkers from CO in the absence of heavy metals

More recently, in 2013, Stephan *et al.* reported that the reaction of B(C₆F₅)₃ with CO in the presence of *t*-Bu₃P and H₂ resulted in the formal methylene insertion into a C–B bond (Scheme 1C).¹² In this study, formation of a formylborate species is proposed as the intermediate, which undergoes C₆F₅ migration from the boron atom to the formyl carbon. Also in 2013, Braunschweig *et al.* reported the reactivity of CO across a stabilized B–B triple bond in which each of the boron atoms was stabilized by IDip (IDip = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene).¹³ In addition to carbon monoxide, other divalent carbon species or their analogs are known to undergo insertion to a C–

The key for multiple methylene elongation is the regeneration of alkyl borane species **A'** from intermediate **F**. Here, the B-center plays a critical role: once the B-center in **F** accepts a hydride from LiHBEt₃, the anionic borate species **G** undergoes a subsequent barrier-less C-O bond cleavage (deoxygenation) to regenerate the alkylborane **A'**. This species can then be involved in further homologation (in a manner identical to that described for **A**) to form **F'**, which is homologous with **F**.

Scheme 2. Mechanism for the boron-mediated homologation of alkenes using CO and LiHBEt₃ as the methylene source

Oxidative work-up of **F'** leads to the formation of aldehyde **2-2** (Table 1, entries 3-4). The highly exergonic nature (driving force) for the overall reaction from **A** to **F'** is attributed to the formation of strong B-O (or Al-O) and C-C bonds. As a side path from intermediate **F**, a competitive CO-coordination to form **H** is also feasible. The existence of **H** would retard the reaction from **F** to **G**, especially under high CO pressure. This is consistent with the observation that higher CO pressure of 5.0 MPa completely shut down the multiple CO insertion leading to the isolation of **2-1** in 48% yield as the sole aldehyde product (entry 5 in Table 1).

To support the mechanism proposed above, several high-pressure *in situ* NMR experiments were performed including isotopic labelling studies. Mixing 9-(2-phenethyl)-BBN (**A**) with 1 equiv. LiHBEt₃ and either ¹²CO or ¹³CO demonstrated that CO uptake into the product is reversible with a rate comparable to the NMR time-scale by a series of broad peaks between δ_C = 70-90 ppm (Figure S1). When lithium triethylborodeuteride (LiDBEt₃)³⁰ was used as a deuteride source, a low-field shift in the ²H NMR signal from δ_D = -1.79 ppm (free LiDBEt₃ δ_D = -1.74 ppm) to a series of peaks between δ_D = 2.11-3.84 was observed upon the addition of CO, indicating that the deuteride is indeed acting as a reducing agent to form -CD₂- or -CD(OH)-moieties (Figure S2). Additionally, when a combination of LiDBEt₃ and ¹³CO was used, the ²H signals change from broad singlets to give more complex splitting patterns, indicating that the deuterium is bound to the labelled carbonyl moiety.

High-resolution mass spectrometry analysis further revealed that the elongated carbon chain originates from the hydride in LiHBEt₃ and the CO in the isotope labeling experiments (Figure S3). The major mass-envelope for the reaction using LiHBEt₃ and ¹²CO corresponded to a molecular ion peak of 279.2127, which we propose to be the structure **I** depicted in Chart 1 (*M*_r = 279.18907 for ¹¹B). Similar insertion of O-atom into the B-C bond of the 9-BBN fragment³¹ has been reported.³² By isotope labeling of the reagents, the peak accordingly changes its mass number with enough precision to differentiate between the exchange of ¹²C to ¹³C and ¹H to ²H. When LiDBEt₃ was used, the mass peak increased to 280.2188 (**I-d₁**; expected mass = 280.1953, Δ*M*_r = 84 ppm), while using ¹³CO instead of ¹²CO a mass peak of 280.2151 was observed (**I***, expected mass = 280.1924, Δ*M*_r = 81 ppm). Finally, using both LiDBEt₃ and ¹³CO gave a mass peak of 281.1804 (**I*-d₁**, expected mass

281.1987, Δ*M*_r = 65 ppm). This further supports the reduction of the carbonyl moiety by the borohydride/deuteride reagents. Moreover, other peak clusters follow a similar pattern and can be analogously assigned (see Charts S1-2).

Chart 1. Comparison of masses of isotopically labelled intermediates observed in ESI-MS analyses^a of reactions of **A with either LiHBEt₃ or LiDBEt₃ and either ¹²CO or ¹³CO.**

^a See Figures S3, S4 in the Supporting Information for mass spectra

When phenylsilane (PhSiH₃) was further added to the reaction of alkyl-BBN, CO and LiHBEt₃, homologated alkenes and alkanes were generated, although the yields were very low (see Figure S5). In contrast, when silane was the sole hydride source (in the absence of LiHBEt₃), only 2-phenylethanol was detected after oxidative work-up, implying no CO insertion took place. Coexistence of both PhSiH₃ and LiHBEt₃ under CO pressure was essential for the alkene and alkane generation; addition of PhSiH₃ after release of the CO pressure afforded only aldehydes in the same way as without PhSiH₃ (see Supporting Information for details).

In conclusion, we found multiple methylene elongations mediated by boron are accessible, representing the first heavy metal-free FT type reaction. The operational temperature of 298 K is also remarkably low compared to the standard FT processes,

even including low-temperature processes (473 K).^{33, 34} Although the performance of this system still warrants improvement in terms of yield and selectivity, we believe, our mechanistic studies shed light on new direction of organoboron chemistry as a possible substitute for organo-transition metal chemistry.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details and additional NMR and GC charts, mass spectra (pdf).

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Notes

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