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Article

Manganese-Mediated C−C Bond Formation: Alkoxycarbonylation of Organoboranes

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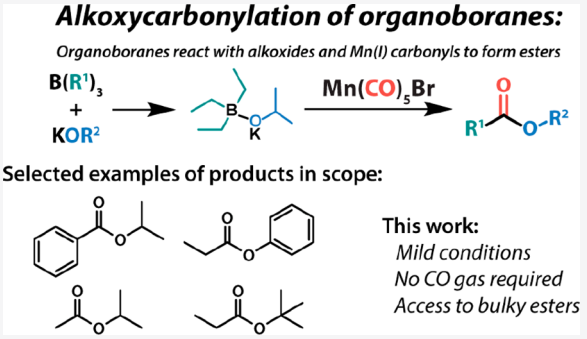
ABSTRACT: Alkoxycarbonylations are important and versatile reactions that result in the formation of a new C−C bond. Herein, we report on a new and halide-free alkoxycarbonylation reaction that does not require the application of an external carbon monoxide atmosphere. Instead, manganese carbonyl complexes and organo(alkoxy)borate salts react to form an ester product containing the target C−C bond. The required organo(alkoxy)borate salts are conveniently generated from the stoichiometric reaction of an organoborane and an alkoxide salt and can be telescoped without purification. The protocol leads to the formation of both aromatic and aliphatic esters and gives complete control over the ester's substitution (e.g., OMe, O^{t}Bu, OPh). A reaction mechanism was proposed on the basis of stoichiometric reactivity studies, spectroscopy, and DFT calculations. The new chemistry is particularly relevant for the field of Mn(I) catalysis and clearly points to a potential pathway toward irreversible catalyst deactivation.



INTRODUCTION

The alkoxycarbonylation reaction is an important and diverse synthetic method for the preparation of esters and related carbonyl compounds.[1,2] It finds widespread industrial application in the production of methyl formate, where methanol, carbon monoxide, and a methoxide salt are reacted at elevated temperature and pressure.[3,4] Subsequent hydrolysis releases the target methyl formate (Figure 1a). Several alternative applications of alkoxycarbonylations have been developed, differing in the nature of the substrate, the metal catalyst, as well as the CO source (selected examples in Figure 1b,c).

The first carbonylations were developed at BASF in the 1930s.[5] These transformations—now known as the Reppe (carbonylation) reaction—involve the reaction of alkenes and alkynes with CO and a nucleophile (water, alcohols, or acids) and produce carboxylic acids, esters, and anhydrides (Figure 1b).[6,7] The original reaction was catalyzed by the highly toxic $Ni(CO)_4$. The derived reactions have since been performed with a wide range of transition metals (Mn, Fe, Co, Ni, Mo, Ru, Rh, Pd, Ir, Pt).[1,5,7,8] Ever since its initial discovery, the substrate scope of alkoxycarbonylations has rapidly expanded to include aryl and alkyl halides,[9−12] alternative leaving groups,[13−16] as well as epoxides,[17] allyl phosphates and acetates,[18] and amines[19] (Figure 1c). Further improvements to the methodology have come from metal-free strategies,[14,20] and efforts to eliminate the need for an external CO pressure. Although CO is relatively cheap and abundant in industry, it can be difficult or undesirable to work with at smaller scale because many laboratories are not set up for handling hazardous gases. In these situations, it can be more attractive to generate the required CO *in situ*, e.g., from (solid) metal carbonyls under thermal or irradiative conditions,[21−25] from formates or formic acid,[26−28] or from CO_2.[29,30] (This is similar to the use of solid triphosgene to substitute gaseous phosgene.)

Here, we report on the reactivity of organoboranes in alkoxycarbonylations (Figure 1d). Organo(alkoxy)borates, formed from the reaction of an organoborane with an alkoxide, react with manganese carbonyl complexes to form a new C−C bond. The required organo(alkoxy)borate salt is generated from the stoichiometric reaction of an organoborane and an alkoxide and can be telescoped without purification. The alkoxycarbonylation reaction is significantly hampered without preformation of the organo(alkoxy)borate salt. This is rationalized by the finding that the manganese carbonyls, viz., $Mn(CO)_5Br$ and $Mn_2(CO)_{10}$, are highly reactive toward alkoxides and probably react before C-C coupling can occur. Without organoboranes, the reaction of manganese carbonyls with KO^{i}Pr leads to the formation of manganese acyl complexes, as well as an alkoxide-bridging manganese dimer complex. These experimental observations are rationalized in a complementary mechanistic study, where we combined

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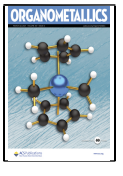

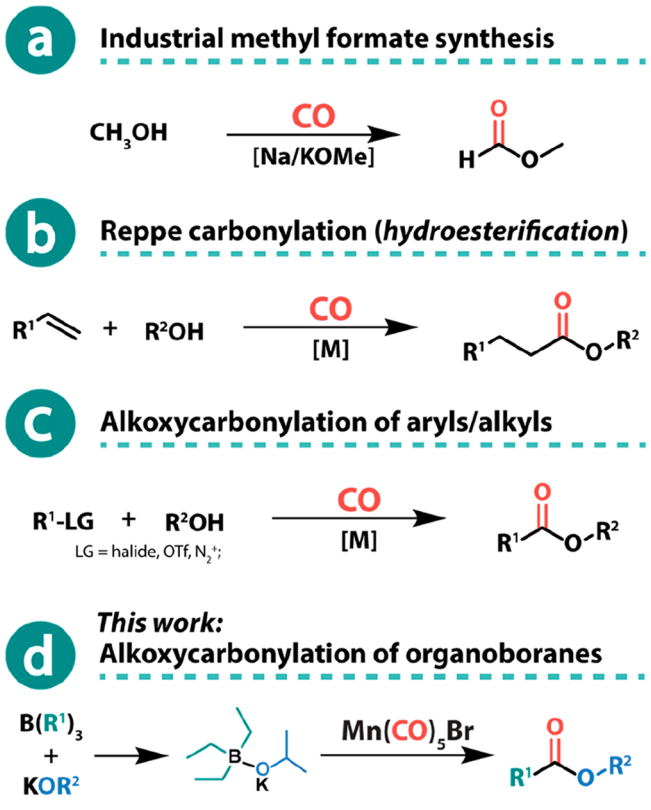

Figure 1. Selection of alkoxycarbonylation reactions described in the literature. (a) Industrial carbonylation of methanol to methyl formate. (b) Reppe carbonylation (also called *hydroesterification*) of olefins. (c) Alkoxycarbonylation of aryls and alkyls. The carbonylation reaction requires the presence of a leaving group. (d) Alkoxycarbonylation of organoboranes, described in this work.

stoichiometric reactivity tests, spectroscopic investigations, and DFT calculations.

RESULTS

Our investigation into the reactivity of $Mn(CO)_5Br$ was preceded by DFT calculations from our group.[31] These calculations suggested that nucleophiles (e.g., hydrides and alkoxides) could react with a Mn(I)-bound carbonyl ligand, thereby resulting in the formation of Mn formyl or acyl complexes (Figure 2a). This finding was supported by results from a literature study.[32−37] Experiments were performed to substantiate the computational results.

In a typical setting, the reaction of $Mn(CO)_5Br$ with 5 equiv of KO^iPr in an ^{i}PrOH/THF mixture resulted in a fast reaction, as indicated by a pronounced color change from yellow to golden orange, effervescence of CO, and the formation of a white precipitate. ^{1}H NMR and GC-MS analysis of the crude reaction mixture indicated the formation of the predicted isopropyl formate product (Figure 2b and SI). A follow-up experiment with KO^iPr-d_7 in ^{i}PrOD-d_8 confirmed that the observed C*H*O hydrogen atom in the observed isopropyl formate product originated from isopropanol (and not, e.g., from THF).

When the $KO^iPr/^i$PrOH solution was more conveniently generated from $KHBEt_3$ and ^{i}PrOH, the expected isopropyl formate could no longer be observed. Instead, a new product formed, which was identified as isopropyl propionate (Figure 2b). Performing the reaction with BBu_3 resulted in formation of isopropyl pentanoate, thereby confirming that the alkyl chain connected to the acyl carbon originated from the trialkylborane. Ester formation was significantly diminished if the trialkylborane and alkoxide were not precontacted prior to the reaction with the manganese complex (yields were not precisely measured for the initial exploratory experiments). This suggests the involvement of the trialkyl(isopropoxy)-borate anion instead of the free trialkylborane (Figure 2c). These anions are formed practically instantaneously at room temperature from the stoichiometric reaction of an organo-borane and an alkoxide salt and are readily characterized by ^{11}B NMR (−0.02 ppm for $K[Et_3B(O^iPr)]$ versus +75.4 ppm for free—unassociated—BEt_3).

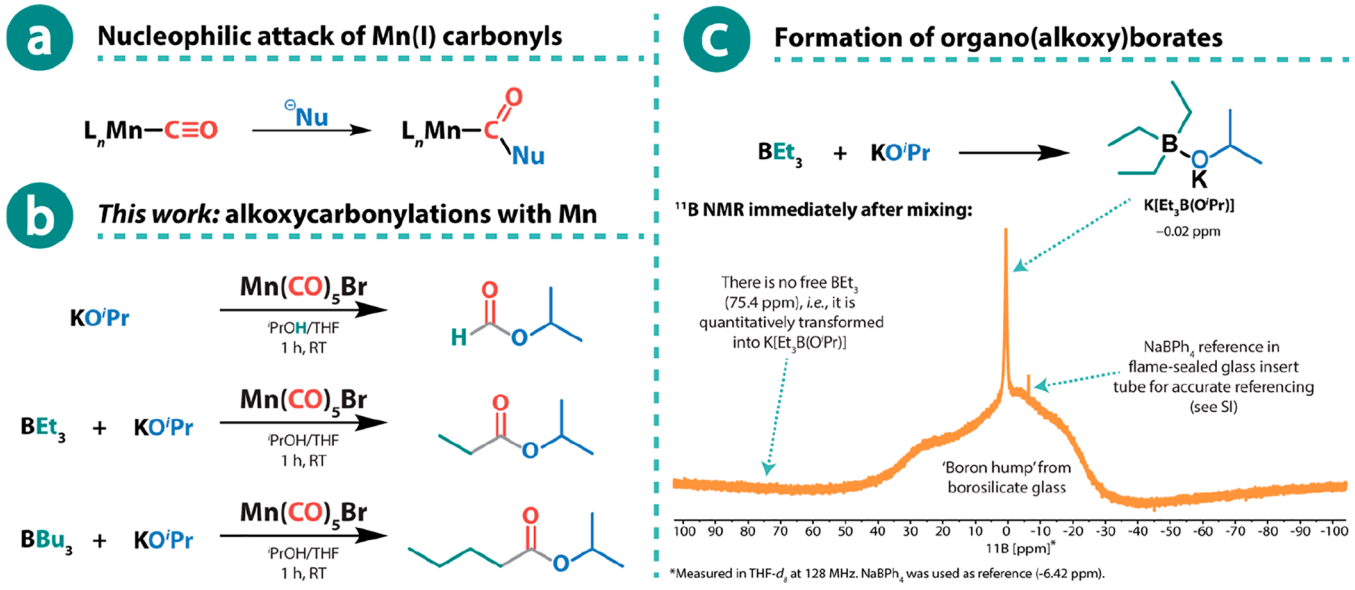

Figure 2. (a) Nucleophilic attack of Mn(I) carbonyl complexes, leading to Mn formyl and Mn acyl complexes. (b) Observed reactivity described in this work; formation of isopropyl formate and aliphatic esters. (c) Formation of $K[Et_3B(O^iPr)]$ and corresponding ^{11}B NMR spectrum.

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Organometallics 2021, 40, 674−681

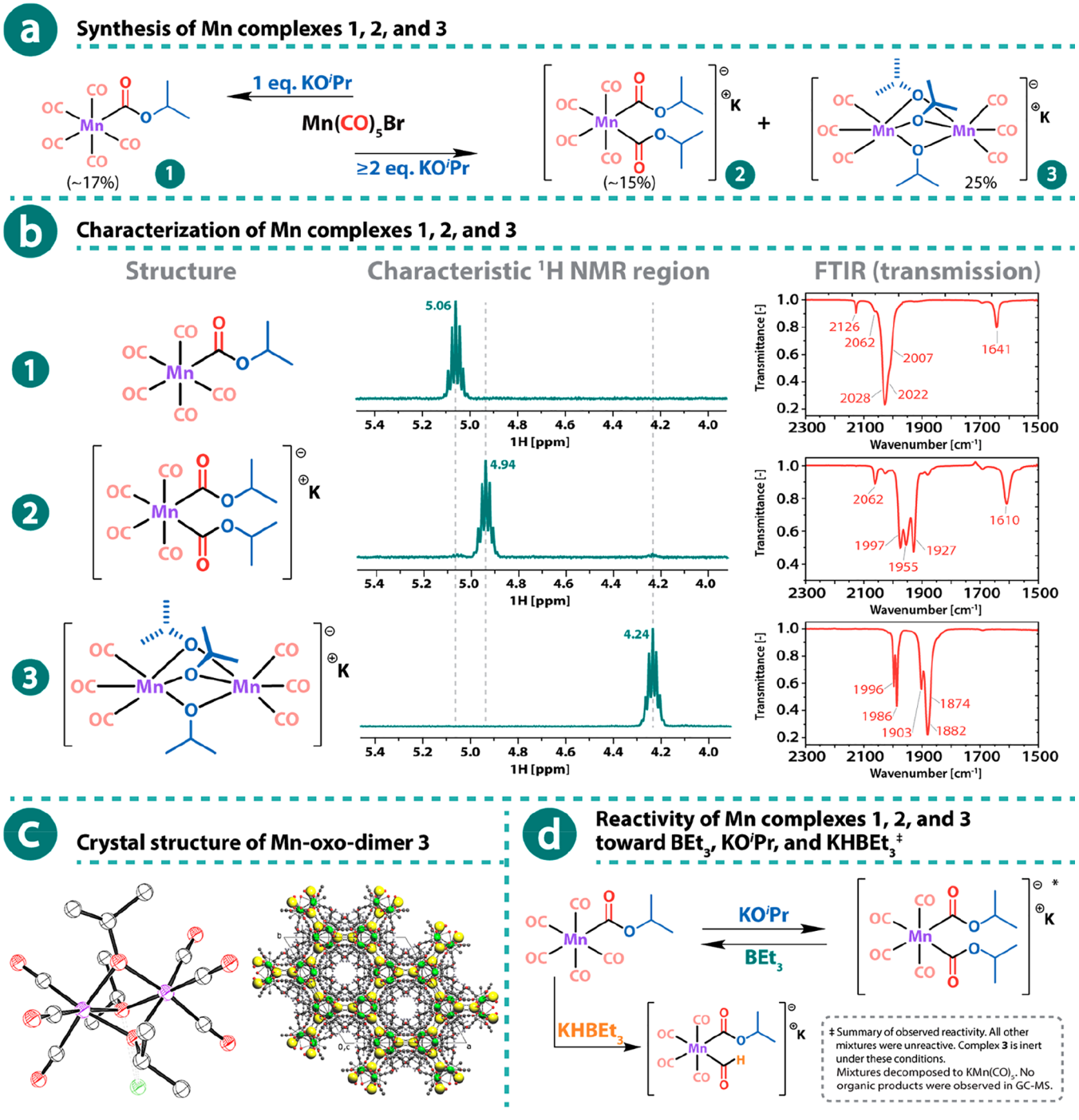

Figure 3. (a) Synthesis of Mn carbonyl complexes **1**, **2**, and **3**. Species **1** and **2** were not isolated. Indicated yields were approximated with ^{1}H NMR. (b) Characterization of **1**, **2**, and **3**: representative ^{1}H NMR region and transmission FTIR spectra. (c) Left: simplified ORTEP diagram of **3**. Hydrogen atoms were omitted for clarity. Key: Mn (purple), K (green), C (black and white), O (red). Right: rendering of 3D-coordination network of structure **3** in the solid state. Key: Mn (green), K (yellow), C (black), H (white), O (red). (d) Reactivity summary of **1** and **2** toward BEt_3, KO^{i}Pr, and $KHBEt_3$. Complex **3** was inert under these conditions. Reaction mixtures were unstable and decomposed over time to $KMn(CO)_5$. Yields were therefore not determined.

Encouraged by these results, we sought to understand the observed reactivity and to characterize potential intermediates formed in the reaction. The outcome of the reaction between $Mn(CO)_5Br$ and KO^{i}Pr (i.e., without the organoborane) was found to strongly depend on the exact reaction stoichiometry. Equimolar reaction of $Mn(CO)_5Br$ and KO^{i}Pr in THF at RT fully consumed the starting materials and predominantly led to Mn acyl complex **1**, as well as $Mn_2(CO)_{10}$, CO, and KBr (Figure 3a, details in SI). Compound **1** was characterized spectroscopically with ^{1}H NMR and FTIR (Figure 3b). ^{1}H NMR and FTIR indicate that **1** is a manganese alkoxycarbonyl complex with a characteristic septet in the ^{1}H NMR spectrum at 5.06 ppm, as well as a ν(C═O) band at 1642 cm^{-1}. These values are in good agreement with those reported for similar Mn acyl complexes.[38−40] The additional CO ligand in **1**

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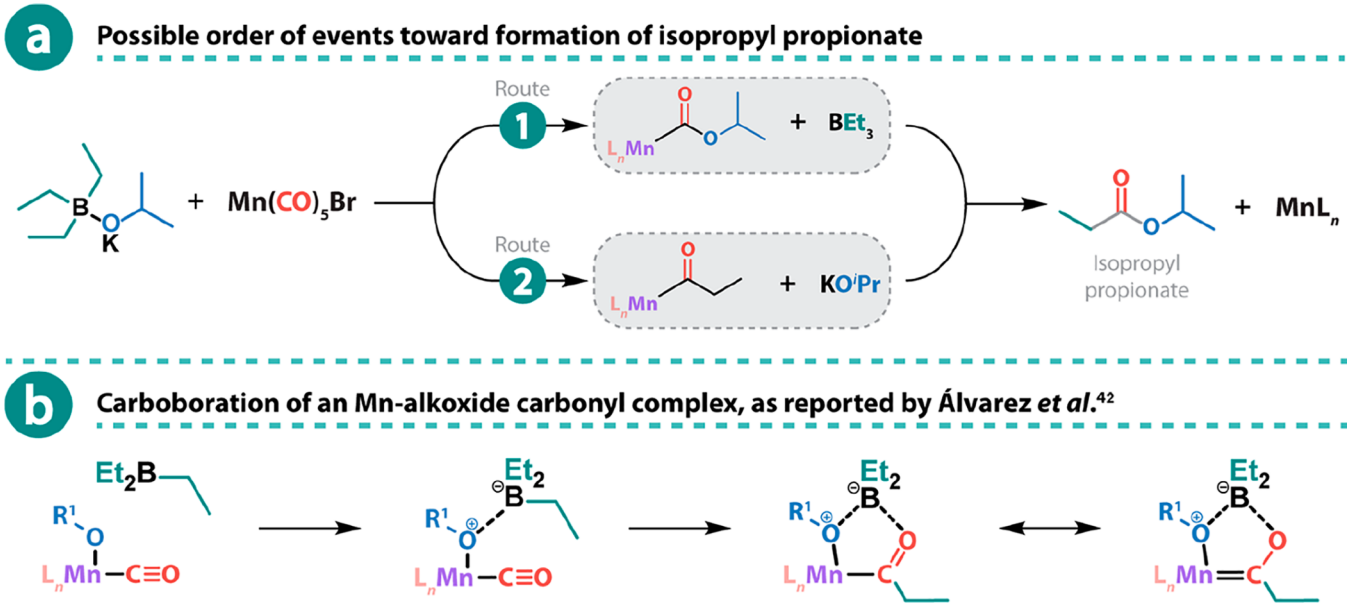

Figure 4. (a) Possible sequence of events toward formation of isopropyl propionate. Route 1: reaction of L_nMn with $^{-}O^{i}Pr$ and subsequent alkyl transfer. Route 2: reaction of L_nMn with Et and subsequent nucleophilic alkoxide attack. (b) Intramolecular carboboration of a Mn(alkoxy)carbonyl, as reported by Álvarez et al.[42]

presumably originates from CO available in the solution, which is liberated upon mixing of the reagents.

Under identical conditions, the reaction of $Mn(CO)_5Br$ with ≥2 equiv of $KO^{i}Pr$ results in a mixture of potassium salts of Mn dialkoxycarbonyl **2**, and alkoxide-bridging Mn-μ_2-isopropoxo-dimer **3** (Figure 3a, details in SI). Compounds **2** and **3** were characterized by $^{1}H/^{13}C$ NMR, FTIR, and ESI-MS (Figure 3b). Compound **2** was unstable in solution and fully degraded over the course of several days. This decomposition has been observed before for similar Mn/Re complexes[35,41] and is presumably induced by both heat and light (although attempted crystallization at −80 °C in the dark did not appreciably stop the decomposition). Gratifyingly, crystals suitable for XRD could be obtained for Mn-isopropoxo-dimer **3**.

Complex **2** features one $C\underline{\boldsymbol{H}}(CH_3)_2$ septet in the ^{1}H NMR spectrum at 4.94 ppm, suggesting that the isopropoxycarbonyl groups are chemically equivalent (Figure 3b). This is supported by the single C═O stretching band in the FTIR spectrum at 1610 cm^{-1}. The FTIR spectrum further contains a medium intensity band at 2062 cm^{-1}, and three strong bands at 1977, 1955, and 1927 cm^{-1}.[35] Similarly to complex **2**, the isopropoxy moieties in **3** are chemically equivalent in solution and appear as one septet at 4.24 ppm in the ^{1}H NMR spectrum. The FTIR spectrum features five sharp and intense bands at 1996, 1986, 1903, 1882, and 1874 cm^{-1}. Single crystal X-ray structure determination indicated that, in the solid state, **3** exists as a three-dimensional coordination network (Figure 3c). In this arrangement, the Mn and K atoms are 6-coordinated, and two isopropoxy fragments act as bridging ligands. The third bridging ligand between the symmetry-related Mn(I) tricarbonyl centers is provided by $KO^{i}Pr$.

Having identified a number of potentially important intermediates that provided context for further spectroscopic investigations, we shifted our focus to stoichiometric reactivity studies to better understand the observed alkoxycarbonylation chemistry (Figure 3d). Complexes **1**−**3** were reacted with 1 equiv of BEt_3, $KO^{i}Pr$, and $KHBEt_3$, and the resulting $^{1}H/^{11}B$ NMR and FTIR spectra were recorded (see SI). Addition of BEt_3 to solutions of **1** or **3** in THF did not lead to observable reactions. Interestingly, Mn diacyl **2** transformed into monoacyl **1** upon treatment with BEt_3 and ultimately formed $KMn(CO)_5$. This is similar to what was observed by Gladysz and co-workers, although no organic products were observed with GC-MS after decomposition to the manganate salt (i.e., we did not observe the expected isopropyl propionate ester).[37] The combination of potassium isopropoxide with **1** resulted in formation of dialkoxycarbonyl **2** and Mn-isopropoxo-dimer **3**. Thus, complex **2** appears to originate from the sequential addition of $KO^{i}Pr$ to $Mn(CO)_5Br$, and then to **1**. Complexes **2** and **3** did not show any reactivity toward $KO^{i}Pr$. Finally, $KHBEt_3$ was added to the three complexes to see if they could sustain formation of Mn formyls. Treatment of **1** with $KHBEt_3$ indeed led to the formation of a new anionic Mn(acyl)(formyl) complex, which decomposed to $KMn(CO)_5$ over the course of approximately a day.[37] Compounds **2** and **3** did not show reactivity toward the hydride reagent, thereby indicating that the remaining three/four Mn-carbonyl ligands of these complexes are significantly less reactive. In summary, Mn(I) carbonyls generally can undergo two sequential nucleophilic attacks on a carbon monoxide ligand, ultimately leading to anionic diacyl (or formyl) species. These compounds frequently are unstable and undergo thermal- or light-induced decomposition to $KMn(CO)_5$. This decomposition process is accelerated by the addition of trialkylboranes, although the underlying mechanism is not completely understood.[37]

We deduced that the observed isopropyl propionate ester can be formed via one of the two pathways illustrated in Figure 4a. In route 1, the alkoxide fragment is transferred to the Mn center first, resulting in the formation of a Mn-(isopropoxycarbonyl) compound similar to **1** or **2**. Isopropyl propionate is liberated upon alkyl transfer from BEt_3 to the Mn complex. Route 2 starts with the alkylation of a carbonyl with BEt_3 and forms a transient propionyl manganese carbonyl complex. This alkylation is followed by a nucleophilic attack on the acyl carbon by the alkoxide, ultimately resulting in

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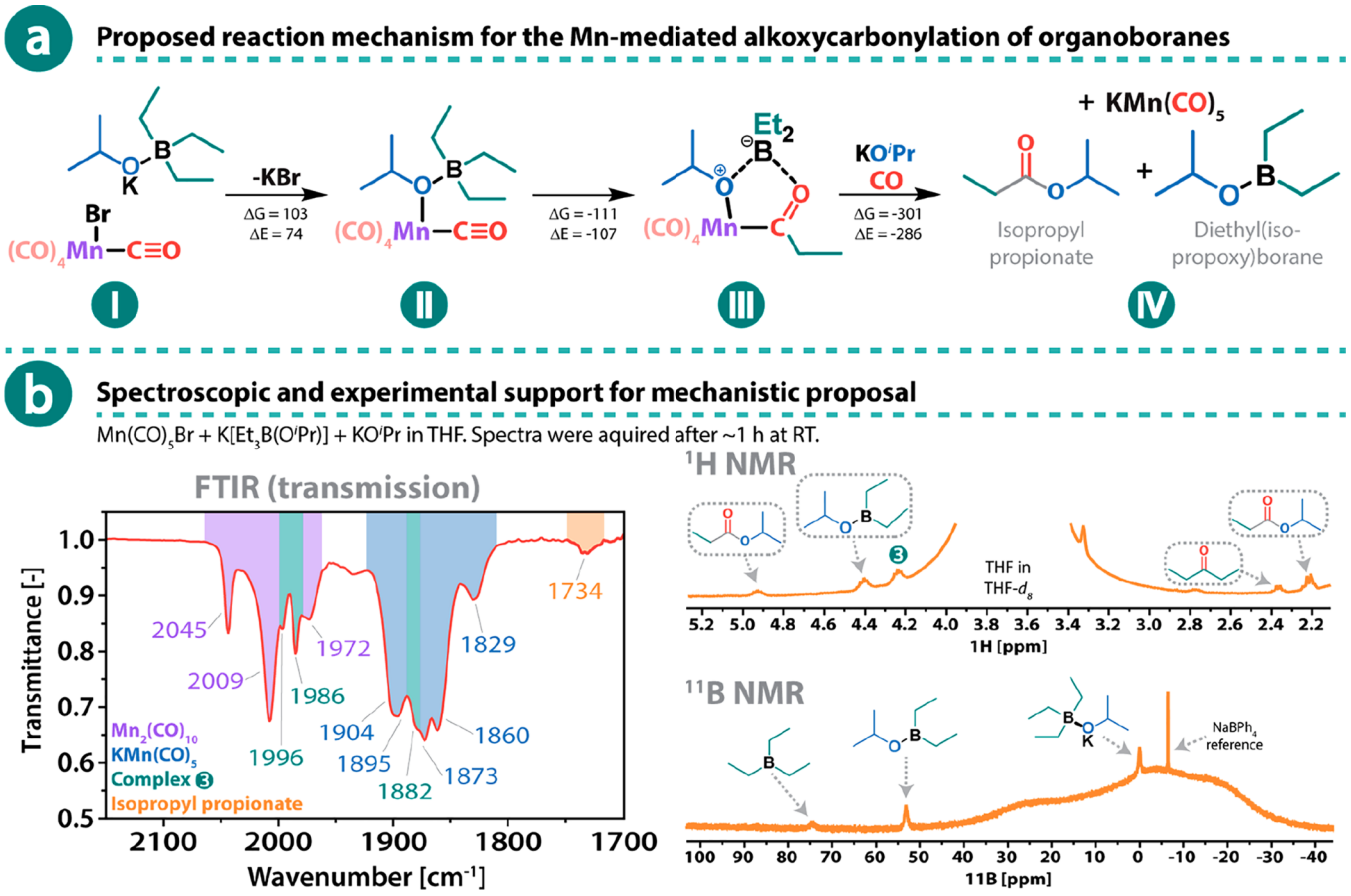

Figure 5. (a) Proposed reaction mechanism for the Mn-mediated alkoxycarbonylation of organoboranes. DFT calculations were performed at the PBE0/6-311+g(d,p) level of theory at 298.15 K in THF. ΔG and ΔE represent the Gibbs free energy changes and reaction energies in kJ mol^{-1}. (b) Spectroscopic and experimental support for the mechanistic proposal. FTIR shows the presence of $KMn(CO)_5$, whereas diethyl(isopropoxy)-borane is observed in ^{1}H and ^{11}B NMR.

liberation of the ester. On the basis of the observed reactivity, we propose that the first mechanism is unlikely; reaction of compounds **1** and **2** with BEt_3 did not produce any detectible organic products. However, our study did not produce definitive evidence against this pathway. (It is, for example, possible that the reaction proceeds via an unstable intermediate that could not be observed.) The second pathway has both literature precedent and experimental support. In their work on the intramolecular carboboration of Mn carbonyls, Miguel and co-workers reported the formation of a Mn boroxycarbene following the intramolecular migration of a precoordinated trialkylborane to a nearby Mn carbonyl.[42] They found that this migration was induced by coordination of BEt_3 to the nearby Mn-alkoxide and carbonyl, and subsequent formation of a tetrasubstituted borate anion (Figure 4b). This borate anion is very similar to the organo(alkoxy)borate substrate described herein.

The proposed reaction mechanism for the Mn-mediated alkoxycarbonylation of organoboranes is described in Figure 5a. We performed DFT calculations at the PBE0/6-311+g-(d,p) level of theory to better understand the proposed mechanism. First, $Mn(CO)_5Br$ (species **I**) reacts with triethyl(isopropoxy)borate to form Mn-alkoxy adduct **II** and KBr. This association is mildly endergonic at 103 kJ mol^{-1}. The intramolecular reaction then takes place, in which an alkyl group is transferred from BEt_3 to the nearby Mn-carbonyl (leading to **III**, ΔG = −111 kJ mol^{-1}). Finally, the target isopropyl propionate ester is liberated from **III** following the nucleophilic alkoxide attack on the acyl carbon. In this step, the original Mn(I) center is reduced to the manganate, i.e., Mn(−I). We propose that the coordinatively unsaturated Mn center then rapidly abstracts CO from the reaction mixture and liberates diethyl(isopropoxy)borane. Overall, the reaction is strongly exergonic with an overall computed Gibbs free energy change of −309 kJ mol^{-1}. The proposed mechanism in part rationalizes why ester formation was not observed when the organoborane and alkoxide were not precontacted; the reaction of Mn carbonyls with alkoxides is so fast that the alkyl group should be precoordinated to the alkoxide if it is to be transferred to the nearby carbonyl.

The proposed mechanism is supported by spectroscopic and experimental investigations (Figure 5b, details in SI). Post-reaction FTIR analysis revealed the presence of $KMn(CO)_5$, as well as $Mn_2(CO)_{10}$, Mn-isopropoxo-dimer **3**, and isopropyl propionate. These products were also detected with ^{1}H NMR. ^{11}B NMR further clearly indicated the formation of the anticipated diethyl(isopropoxy)borane product (^{11}B: δ 53.4 ppm). 3-Pentanone was detected as a side product in ^{1}H NMR and with GC-MS (the origin of this product is unclear at this time; see SI). Lastly, we investigated the feasibility of product liberation following the proposed nucleophilic alkoxide attack. The reaction of an independently prepared sample of propionyl manganese pentacarbonyl with KO^{i}Pr indeed

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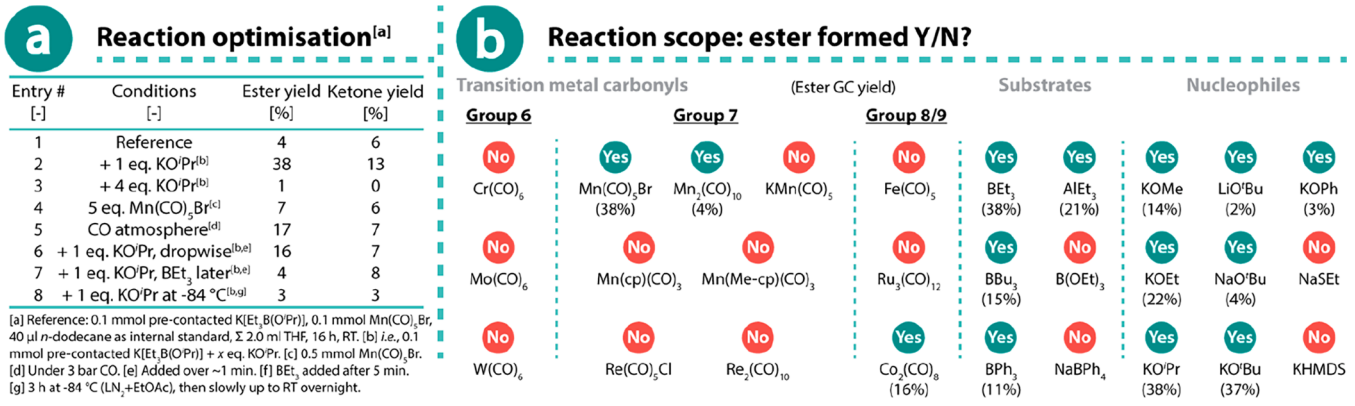

Figure 6. (a) Summarized results of reaction optimization experiments. (b) Results from reaction scope exploration: various transition metal carbonyls, boron substrates, and nucleophile salts were screened and evaluated for their capacity to form the anticipated (ester) product.

produced the anticipated isopropyl propionate ester, as well as the reduced $KMn(CO)_5$ (Figure S74).[33]

After having obtained mechanistic insight, we sought to improve the ester yield and explore the scope of the novel alkoxycarbonylation reaction (further details in Tables S4–S6). Under the standard conditions, the reaction gave an isopropyl propionate yield of 4%, while 3-pentanone was formed in 6% yield (Figure 6a). Addition of a second equivalent of KO^{i}Pr—as suggested by the proposed mechanism—resulted in a significantly higher yield of 38%. Further addition of KO^{i}Pr and $Mn(CO)_5Br$, reaction under CO atmosphere, alternative solvents, reduced reaction temperature, or altered addition procedures did not lead to further yield improvements.

The reaction scope was explored by performing a series of experiments with varied transition metal carbonyls, alternative boron substrates, and nucleophile salts (Figure 6b). Besides $Mn(CO)_5Br$, we found that only $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were capable of forming isopropyl propionate. Mn piano stool complexes $Mn(cp)(CO)_3$ and $Mn(Me\text{-}cp)(CO)_3$ were inactive under these conditions. $KMn(CO)_5$—which was observed as a product from the reaction—did not support formation of organic products. Reaction with alternative boron substrates was successful for BBu_3 and BPh_3 and led to the anticipated aliphatic and aromatic isopropyl esters in 15% and 11% yield. Substitution of BEt_3 for $AlEt_3$ resulted in a 21% yield of isopropyl propionate (compared to 38% for BEt_3). Boric esters and borates did not lead to ester formation. Finally, reaction with alternative alkoxide salts (KOMe, KOEt, KO^{t}Bu, KOPh) afforded the corresponding methyl, ethyl, *tert*-butyl, and phenyl esters. The observed yield of these compounds approximately increased with nucleophile size. Use of lithium- and sodium *tert*-butoxide did result in ester formation, albeit in much lower yield than when the potassium salt was used. The reaction with sodium thiolates or KHMDS did not produce the corresponding products.

CONCLUSION

In conclusion, we have developed a new alkoxycarbonylation reaction that is based on the reactivity of Mn carbonyl complexes and organo(alkoxy)borate salts. These salts could be conveniently prepared from the stoichiometric reaction of organoboranes and alkoxides and did not need to be purified or isolated before use. The described procedure enabled the formation of a variety of aliphatic and aromatic esters of diverse substitution and includes difficult to synthesize phenyl and *tert*-butyl esters. Finally, a reaction mechanism was proposed on the basis of stoichiometric reactivity studies, spectroscopy, and DFT calculations. The new chemistry that is described in this work suggested that Mn(I) complexes could undergo sequential nucleophilic attacks. These reactions in principle could lead to irreversible catalyst deactivation. Thus, we expect that understanding of the herein presented chemistry will lead to improvements of Mn(I) catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00781.

Detailed experimental and computational procedures, characterization, and screening results (DOI: https://doi.org/10.4121/14101928.v1) (PDF)

Coordinates of optimized structures (XYZ)

Accession Codes

CCDC 2039376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Organometallics 2021, 40, 674−681