JOC The Journal of Organic Chemistry

ARTICLE

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Imidazolidene Carboxylate Bound $MBPh_4$ Complexes (M = Li, Na) and Their Relevance in Transcarboxylation Reactions

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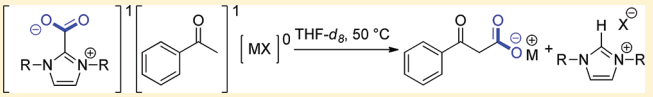
Supporting Information

ABSTRACT: Combination of 1,3-bis(2,6-diisopropylphenyl)-imidazolum-2-carboxylate ($IPrCO_2$) with the Lewis acids $MBPh_4$, where M = Li or Na, provided two separate complexes. The crystal structures of these complexes revealed that coordination to $NaBPh_4$ yielded a dimeric species, yet coordination of $IPrCO_2$ with $LiBPh_4$ yielded a monomeric species. Combination of 1,3-bis(2,4,6-trimethylphenyl)imidazolum-2-carboxylate ($IMesCO_2$) with $LiBPh_4$ also afforded a dimeric species that was similar in global structure to that of the $IPrCO_2$+$NaBPh_4$ dimer. In all three cases, the cation of the organic salt was coordinated to the oxyanion of the zwitterionic carboxylate. Thermogravimetric analysis of the crystals demonstrated that decarboxylation occurred at lower temperatures than the decarboxylation temperature of the parent NHC·CO_2 (NHC = *N*-heterocyclic carbene). Kinetic analysis of the transcarboxylation of $IPrCO_2$ to acetophenone with $NaBPh_4$ to yield sodium benzoylacetate was performed. First-order dependences were observed for $IPrCO_2$ and acetophenone, whereas zero -order dependence was observed for $NaBPh_4$. Direct dicarboxylation was observed when I^tBuCO_2 was added to MeCN in the absence of added $MBPh_4$.



INTRODUCTION

The ability to utilize carbon dioxide as a chemical feedstock has been a long desired goal in synthetic chemistry.[1−7] Every year, billions of tons of CO_2 are released into the atmosphere as waste.[8] The ability to harness CO_2 from the point of origin into high-yielding fine chemical processes would likely be a lucrative one as the souce of carbon could be collected from point-source waste streams. Yet, only a handful of solutions exist. For example, Darensbourg[9−11] and Coates[12−14] independently developed unique systems that copolymerize CO_2 with epoxides that afford biodegradable polycarbonate polymers that are adequate substitutes for bisphenol A based polymers. The synthesis of cyclic carbonates from the reaction of epoxides and CO_2 using various catalysts has also received a large amount of attention in recent years due to the industrial significance of cyclic carbonates.[15−20] The Kolbe-Schmitt and Grignard reactions are relevant reactions when discussing the topic of CO_2 incorporation into fine chemicals. However, both reactions are largely limited to phenolic and halogenated substrates, respectively.[21−23]

Transition metal catalysts have found a home in CO_2-incorportation chemistry.[24−28] A protocol utilizing a gold-carbene species to carboxylate heteroaromatic and activated nonphenolic aryl species has been developed.[29] Ni[30,31] catalysts mediate the cycloaddition of CO_2 with diynes[32−34] as well as the carboxylation of styrenes[35,36] and alkylzinc compounds.[37,38] Similarly, the combination of Cu and 1,10-phen catalyzes the carboxylation of alkylboranes.[39] In addition, a handful of non-metal mediated incorporation of CO_2 reactions that afford noncyclic carbonate products have been developed.[40−46]

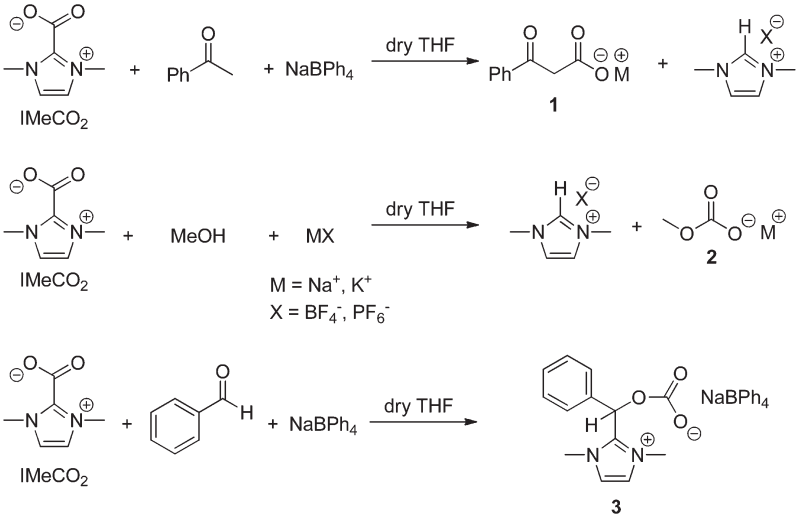
Tommasi et al. demonstrated the fixing of carbon dioxide onto acetophenone to form benzoyl acetate (**1**), methanol to form monomethyl carbonate (**2**), and benzaldehyde to form **3** by employing NHC·CO_2's as a trans-carboxylating reagent (NHC = *N*-heterocyclic carbene, Scheme 1).[40−42] The scope was further expanded as other compounds containing acidic α-protons, such as acetone, cyclohexanone, and benzylcyanide, could be carboxylated. Although DBU can be used to faciliate similar carboxylation reactions, the ambiguity by which DBU interacts with CO_2 has hampered the development of further carboxylation chemistry.[47,48] In contrast, the factors that influence binding of CO_2 to NHCs are better understood.[49−51] This, in conjunction with the facile tunability of both the sterics and electronics of NHCs,[52] led us to believe that more effective NHC·CO_2 mediated carboxylation reactions could be developed. As such, we embarked on an investigation of the mechanism of the transcarboxylation reaction.

RESULTS AND DISCUSSION

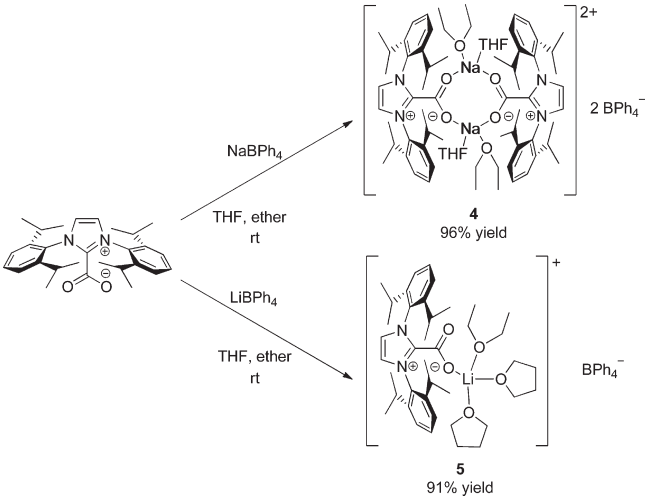
Syntheses and Characterization of (NHC·CO_2)·$MBPh_4$ Complexes. Carboxylation of acetophenone requires NHC·CO_2 as well as 1 equiv of $MBPh_4$ (where M = Li, Na, or K). Thus, precomplexation of the NHC·CO_2 with $MBPh_4$ could play an important role in carbon dioxide transfer. Although the original transcarboxylation reactions reported by Tomassi utilized 1,3-dimethylimidazolium-2-carboxylate ($IMeCO_2$), the insolubitily of $IMeCO_2$ led us to redirect our focus to more soluble NHC·CO_2 adducts such as $IPrCO_2$ and $IMesCO_2$ ($IPrCO_2$ = 1,3-bis(2,6-diisopropylphenyl)imidazolum-2-carboxylate; $IMesCO_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolium-2-carboxylate). Importantly, transcarboxylation reactions employing either $IPrCO_2$

Received: August 9, 2011
Published: September 12, 2011

Scheme 1. Transcarboxylation Reactions Performed by Tommasi with NHC·CO_2's

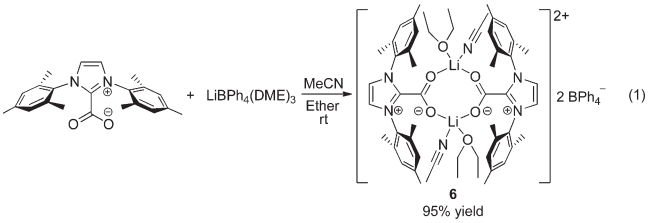


Scheme 2. Formation of $IPrCO_2$·$MBPh_4$ Complexes



or $IMesCO_2$ afford product **1** in comparable yields to those obtained with $IMeCO_2$ (vide infra). Addition of $NaBPh_4$ to a suspension of $IPrCO_2$ in THF[53] led to a homogeneous solution. A layer of ether was added and allowed slow diffusion into the solution ultimately giving compound **4** as a crystalline solid in 96% yield (Scheme 2). Interestingly, compound **4** is a dimer where the carboxylate acts as a bridging ligand between two Na atoms. A similar carboxylate complex (**5**) was formed when $IPrCO_2$ was added to $LiBPh_4$ in lieu of $NaBPh_4$. However, single crystal X-ray structural analysis showed that this complex was a monomer, rather than a dimer. Again, the main group metal (i.e., Li) binds, in this case, to only one oxygen of a single carboxylate group. Both complexes had distinctly different ^{1}H NMR shifts from noncomplexed $IPrCO_2$.

In an effort to determine whether the formation of monomeric or dimeric complexes was a general phenomenon for NHC·CO_2+$MBPh_4$ compounds, reactions with $IMesCO_2$ were also evaluated. When $IMesCO_2$ was added to $LiBPh_4$ in MeCN and then crystallized via slow diffusion with ether, complex **6** was obtained in 95% yield (eq 1). Structural analysis of **6** revealed that, in contrast to the reaction of $IPrCO_2$ with $LiBPh_4$, the reaction with $IMesCO_2$ with $LiBPh_4$ afforded a dimeric complex. Thus, although coordination of the NHC·CO_2 to the cation of $MBPh_4$ appears to be general, formation of either a monomer or a dimer can only be determined a posteriori.



A variety of salts were added to a series of carboxylates to examine possible trends in solubility (Table 1). All NHC·CO_2's alone were insoluble in THF (entries 1−4) and were either sparingly soluble in MeCN (entries 5, 6, 8) or reacted with MeCN (entry 7, vide infra). When MX (where M^+ = Li, Na, or K and X^- = BPh_4) was added to a suspension of $IMeCO_2$ in MeCN, no reaction occurred and only a suspended solid remained (entry 9). Addition of variety of salts to $IPrCO_2$ resulted in homogeneous solutions (entries 10−13, 15). As noted, addition of either $LiBPh_4$ or $NaBPh_4$ to $IPrCO_2$ led to the formation of isolable compounds (**4** and **5**, respectively) that were amenable to crystallographic analysis (vide supra). The addition of $LiBF_4$, LiI, or NaI to $IPrCO_2$ in MeCN also led to homogeneous solutions (entries 13 and 15). Unfortunately, all attempts in isolating compounds suitable for X-ray analysis were unsuccessful. Interestingly, soluble complexes were not obtained upon the addition of $NaBF_4$, KBF_4, or KI salts to $IPrCO_2$ (entries 14 and 16). Homogeneous solutions were observed upon the addition of $LiBPh_4$ and LiI salts to $IMesCO_2$ (entries 17 and 18). Similarly, addition of $LiBPh_4$ or $NaBPh_4$ to I^tBuCO_2 also led to homogeneous solutions (entry 19). However, a complex with limited solubility formed when $KBPh_4$ was added (entry 20).

Selected bond lengths and the NHC·CO_2 torsional angles for compounds **4**−**6** as well as the parent $IPrCO_2$ are listed in Table 2. No structural data exists for $IMesCO_2$. However, given

dx.doi.org/10.1021/jo201647b |J. Org. Chem. 2011, 76, 8413–8420

Table 1. Solubility of Salts and Carboxylates in Various Conditions

entry	NHC·CO_2	salt	solvent[a]	solubility
1	$IPrCO_2$	none	THF	insoluble[b]
2	$IMesCO_2$	none	THF	insoluble[b]
3	I^tBuCO_2	none	THF	insoluble[b]
4	$IMeCO_2$	none	THF	insoluble[b]
5	$IPrCO_2$	none	MeCN	limited[c]
6	$IMesCO_2$	none	MeCN	limited [c]
7	I^tBuCO_2	none	MeCN	reaction with MeCN
8	$IMeCO_2$	none	MeCN	limited[c]
9	$IMeCO_2$	$MBPh_4$ (M = Li, Na, K)	THF or MeCN	insoluble
10	$IPrCO_2$	$LiBPh_4$ (**4**)	THF or MeCN	homogeneous soln
11	$IPrCO_2$	$NaBPh_4$ (**5**)	THF or MeCN	homogeneous soln
12	$IPrCO_2$	$KBPh_4$	THF or MeCN	homogeneous soln[d]
13	$IPrCO_2$	$LiBF_4$	MeCN	homogeneous soln[d]
14	$IPrCO_2$	MBF_4 (M = Na, K)	MeCN	insoluble
15	$IPrCO_2$	MI (M = Li, Na)	MeCN	homogeneous soln[d]
16	$IPrCO_2$	KI	MeCN	insoluble
17	$IMesCO_2$	$LiBPh_4$ (**6**)	THF or MeCN	homogeneous soln
18	$IMesCO_2$	LiI	MeCN	homogeneous soln[d]
19	I^tBuCO_2	$MBPh_4$ (M = Li, Na)	THF	homogeneous soln[d]
20	I^tBuCO_2	$KBPh_4$	THF	limited[c]

[a] These solvents solvated either the $NHCCO_2$ or the salt. [b] No proton signals were observed in THF-d_8. [c] Proton signals were observed although the sample did dissolve completely. [d] All attempts to grow crystals provided crystals of unsuitable quality for single crystal analysis.

Table 2. Bond Lengths and Torsional Angles of $IPrCO_2$ and Compounds 4, 5, and 6

bond lengths (Å)	$IPrCO_2$	$IPrCO_2$+ $LiBPh_4$ (**5**)	$IPrCO_2$+ $NaBPh_4$ (**4**)	$IMesCO_2$+ $LiBPh_4$ (**6**)
C_2-C_6	1.510	1.511	1.525	1.515
C_6-O_2	1.222	1.221	1.239	1.232
C_6-O_1	1.225	1.254	1.233	1.235
O_1-M_1	NA	1.951	2.244	1.906
O_2-M_2	NA	NA	2.236	1.887
N_1-C_2	1.335	1.345	1.344	1.342
N_3-C_2	1.332	1.336	1.333	1.338
carboxylate torsional angle $N_1C_2-C_6-O_1$ (deg)	89.75	78.61	27.66	36.47

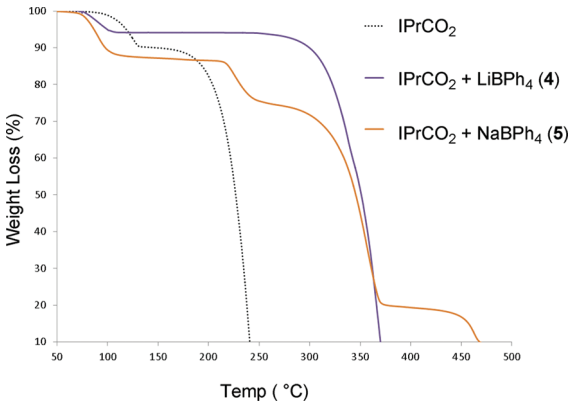


Figure 1. TGA curves of $IPrCO_2$, $IPrCO_2$+$LiBPh_4$ (**4**), and $IPrCO_2$+$NaBPh_4$ (**5**).

the electronic and overall steric similarities between $IMesCO_2$ and $IPrCO_2$, the structure of dimer **6** was compared to that of $IPrCO_2$. In all cases, complexation to either Li or Na affects the C_6-O bond length and, to a lesser extent, the C_2-C_6 bond length. In $IPrCO_2$, the C_6-O_1 and C_6-O_2 bond lengths are equivalent, which reflects the contributions of two equivalent resonance structures. For dimers **4** and **6**, the C_6-O_1 and C_6-O_2 bond lengths are again equivalent, as expected, yet are elongated with respect to uncomplexed $IPrCO_2$. In general, compounds **4**–**6** display both shortened C–O bond lengths (average =1.236 Å) as well as M–O bond lengths [average = 1.915 Å for Li (**5** and **6**) and average =2.240 Å for Na (**4**)] relative to known M-carboxylates.[54−56] For example, the C–O and Na–O bond lengths of a similar Na *meta*-iodobenzoate complex are 1.260/1.264 and 2.476 Å, respectively. Furthermore, anhydrous lithium and sodium formate crystals possess carboxylate C–O bond lengths of 1.242 and 1.246 Å, respectively, and the Li–O and Na–O bond lengths of 1.950 and 2.451 Å, respectively.

The most marked structural change from complexes with either Na or Li is in the different torsional angles. That is, binding markedly lowers the $N_1-C_2-C_6-O_1$ torsional angle. For monomer **5**, the carboxylate moiety moved approximately 11° toward planarity with the imidazolium ring (i.e., 89.75° in $IPrCO_2$ vs 78.61° in **5**). An even more striking move toward planarity was observed in dimers **4** and **6**. Specifically, the torsional angles decreased over 50° to 27.66° and 36.47°, respectively.

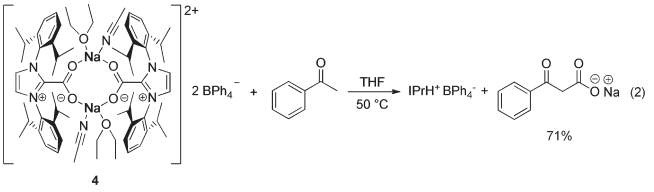
We recently evaluated a series of NHC·CO_2 complexes and found that decarboxylation correlated closely to torsional angles.[50] Carboxylates possessing a larger torsional angle underwent decarboxylation at a lower temperature. As a consequence, binding to Li or Na in compounds **4**–**6** could stabilize the

dx.doi.org/10.1021/jo201647b |J. Org. Chem. 2011, 76, 8413–8420

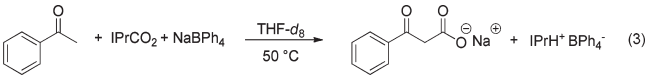
carboxylate, thereby inhibiting decarboxylation. Surprisingly, TGA analyses of the $IPrCO_2 \cdot MBPh_4$ and $IMesCO_2 \cdot LiBPh_4$ complexes revealed decarboxylation actually occurred at lower temperatures than for the parent $IPrCO_2$ or $IMesCO_2$ (Figures 1 and 2). Decarboxylation of $IPrCO_2$ occurs at 108 °C.[49] In contrast, both $IPrCO_2$+$LiBPh_4$ (**5**) and $IPrCO_2$+$NaBPh_4$ (**4**) complexes lose CO_2 at temperatures below 100 °C (76 and 81 °C, respectively, Figure 1). In conjunction with the loss of CO_2, loss of coordinated solvent molecules (THF and ether) was also observed at these temperatures. Thus, coordination to Li or Na significantly lowers the temperature required for decarboxylation.

The activation of $IMesCO_2$ was also displayed in the $IMesCO_2$+$LiBPh_4$ complex **6** (Figure 2). The $IMesCO_2$+$LiBPh_4$ complex had three stages of weight loss, the first one occurring at 71 °C where CO_2, ether, and THF were detected on the mass spectrometer. This first decomposition is 84 °C lower than that of $IMesCO_2$. The TGA analysis indicates that there is activation of the $NHC \cdot CO_2$ complexes where thermal decarboxylation is facilitated relative to that of the parent $NHC \cdot CO_2$. The temperature at which each decomposition stage and the % of mass lost at each stage of weight loss are listed in Table 3.

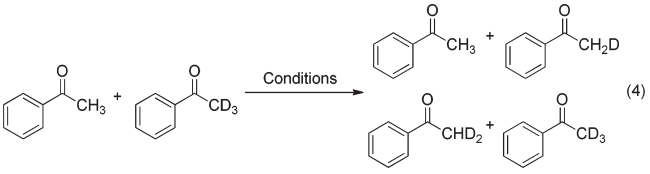
Carboxylation Reactions with $(NHC \cdot CO_2) \cdot MBPh_4$ Complexes. Complex **4** was evaluated as a potential "all-in-one" carboxylating agent. When stoichiometric amounts of **4** were added to acetophenone in THF at 50 °C for 4 h, sodium benzoylacetate was formed in 71% yield (eq 2).



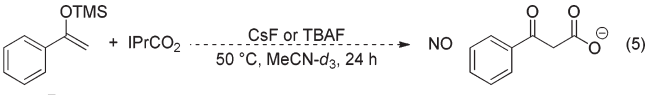
Kinetic Analysis. Kinetic analysis of the $IPrCO_2/NaBPh_4$-mediated carboxylation reaction of acetophenone at 50 °C in THF-d_8 was performed (eq 3, Table 4). Not surprisingly, carboxylation reactions were first-order in acetophenone (Figure 3). However, our investigations revealed that the reaction was first-order in $IPrCO_2$ yet independent of $NaBPh_4$ concentration (Figure 3). These results were particularly surprising given the dimer coordination mode we obtained from the individual reaction between $IPrCO_2$ and $NaBPh_4$ and the activation of the $NHC \cdot CO_2$ with salts observed via TGA. Interestingly, an equilibrium kinetic isotope effect of 1.57 ± 0.14 was observed when acetophenone was replaced with acetophenone-d_3 in a carboxylation reaction (entry 1 vs entry 9). In addition, a carboxylation reaction run under an atmosphere of CO_2 was an order of magnitude slower (entry 10).



Deuterium Exchange Reactions. A series of exchange reactions involving a 1:1 mixture of acetophenone and acetophenone-d_3 were evaluated (eq 4, Table 5). The control reaction of mixing acetophenone with acetophenone-d_3 showed no exchange of deuterium, even at prolonged reaction times of 1 week (entry 1). When 1 equiv of 1,3,4,5-tetramethylimidazolylidene (IMe_{Me}) was added to a C_6D_6 solution containing the control mixture of acetophenone and acetophenone-d_3, complete scrambling of the enol proton occurred within minutes (entry 2). When IMe_{Me} was substituted with the less basic IPr (calculated pK_a of 1,3-bis(2,6-dimethylphenyl)imidazolylidene = 17.0 ± 0.11 in DMSO vs 23.9 ± 0.28 of IMe_{Me}),[57] facile scrambling was still observed (entry 2), indicating that facile deprotonation/reprotonation occurs regardless of which NHC catalyst is added.



Reaction of $IPr \cdot CO_2$ and TMS Enol. Given the lack of $NaBPh_4$ dependence determined from kinetic analysis, carboxylation reactions between a preformed enolate and $IPrCO_2$ were evaluated. Specifically, $IPrCO_2$, TMS enol (**7**), and CsF were combined in MeCN-d_3 and heated to 50 °C (eq 5). After 24 h, no reaction of the $IPrCO_2$ was observed although complete consumption of the TMS enol occurred. Similar results were obtained when TBAF was used in lieu of CsF. In contrast, direct carboxylation of acetophenone was achieved through the reaction between the potassium enolate and dry ice at −78 °C to give benzoyl acetic acid in 85% after acidic workup.[58]



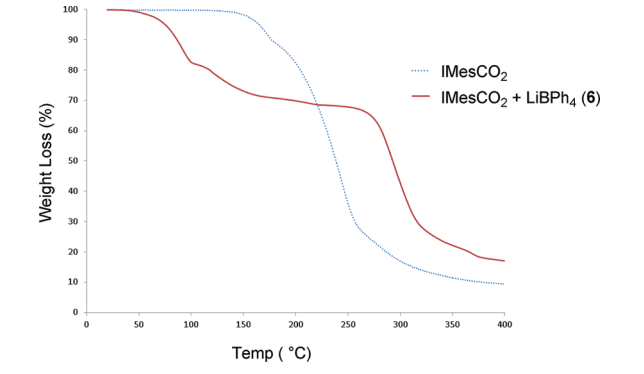


Figure 2. TGA plots of $IMesCO_2$ and $IMesCO_2$+$LiBPh_4$ (**6**).

Table 3. Mass Percent Lost and Temperatures at Each Stage of Decomposition

	mass lost (%), temperature (°C)				
decomposition stage	$IPrCO_2$	$IPrCO_2$+$LiBPh_4$ (**4**)	$IPrCO_2$+$NaBPh_4$ (**5**)	$IMesCO_2$+$LiBPh_4$ (**6**)	$IMesCO_2$
1	9.8, 108	6.2, 81	22.1, 76	17.9, 71	9.6, 155
2	90.9, 198	93.0, 339	10.3, 239	11.5, 115	78.0, 216
3	NA	NA	54.5, 329	52.1, 277	NA
4	NA	NA	13.9, 430	NA	NA

dx.doi.org/10.1021/jo201647b |J. Org. Chem. 2011, 76, 8413–8420

Table 4. Kinetic Analysis of the Carboxylation of Acetophenone[a]

entry	[acetophenone], equiv	[$NaBPh_4$], equiv	k_{obs} rate constant ($\times 10^{-3}$ M·s^{-1})[b]
1	0.22 M, 5	0.23 M, 5.3	−7.8 ± 0.5
2	0.22 M, 5	0.35 M, 7.9	−7.7 ± 0.8
3	0.22 M, 5	0.46 M, 10.5	−7.8 ± 0.01
4	0.22 M, 5	0.69 M, 15.7	−8.0 ± 0.1
5	0.22 M, 5	0.46 M, 10.5	−7.8 ± 0.5
6	0.33 M, 7.5	0.46 M, 10.5	−10.5 ± 0.6
7	0.44 M, 10	0.46 M, 10.5	−13.7 ± 1.3
8	0.66 M, 15	0.46 M, 10.5	−23.9 ± 0.3
9	0.22 M, 5[c]	0.23 M, 5.3	−4.9 ± 0.3
10	0.22 M, 5	0.23 M, 5.3	−0.43 ± 0.06[d]

[a] Reaction conditions: [$IPrCO_2$] = 0.043 M (1 equiv) in THF-d_8, 50 °C. [b] All runs were performed at least twice. [c] Acetophenone-d_3 was used. [d] The reaction solution was sparged with CO_2, and the reaction was ran with a CO_2 atmosphere.

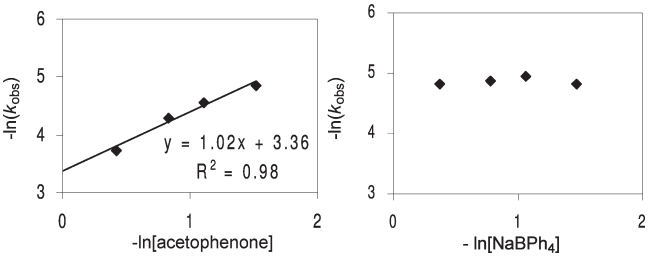
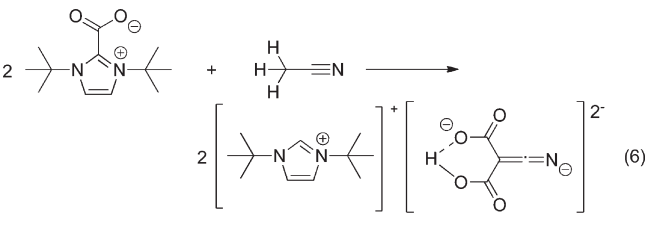


Figure 3. Plots of −ln[acetophenone] vs −ln[$NaBPh_4$] vs −ln(k_{obs}) for the carboxylation of acetophenone at 50 °C.

Reaction of I^tBuCO_2 with Acetonitrile. Although no carboxylation products were detected between the reaction of $IPrCO_2$ and TMS enol **7**, direct carboxylation of MeCN does occur *in the absence of NaBPh*$_4$. During our attempts to recrystallize I^tBuCO_2 in MeCN and ether, single crystals of a dianionic, dicarboxylated ketenimide product were obtained (eq 6). A proton from the acetonitrile is covalently bound to one oxygen (1.113 Å) and forms a strong hydrogen bond to the other oxyanion (1.323 Å) between the planar dicarboxylate moieties. A reaction mechanism for the formation of the ketenimide is proposed in Scheme 3. Carbon dioxide dissociation from I^tBuCO_2 affords the free carbene, I^tBu, which then deprotonates the α-proton of MeCN to afford a ketenimide. Nucleophilic attack of either free carbon dioxide (shown) or of I^tBuCO_2 gives rise to the initial carboxylation observed. The process is then repeated to ultimately afford dicarboxylated product **8**.



(6)

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Table 5. NHC-Catalyzed H/D Exchange Reaction

	conditions				
entry	catalyst	additives	solvent	temp	H/D scrambling ($t_{1/2}$)
1	none	none	C_6D_6	rt	not observed
2	IMe_{Me}	none	C_6D_6	rt	>5 min
3	IPr	none	C_6D_6	rt	3 h
4	$IPrCO_2$	none	CD_3CN	50 °C	50 min
5	$IPrCO_2$	$NaBPh_4$	CD_3CN	50 °C	NA[a]
6	$IPrCO_2$	CO_2 (g)	CD_3CN	50 °C	not observed
7	$IPrCO_2$	$NaBPh_4$, CO_2 (g)	CD_3CN	50 °C	not observed

[a] Scrambling occurred, but slowly. Integration was not possible due to overlap of the IPr septet in the acetophenone methyl region. The point at which scrambling was detected was at 3 h.

CONCLUSION

Despite the isolation of a variety of interesting NHC·CO_2+$MBPh_4$ complexes, our data suggest that the complexes do not remain aggregated during carboxylation. That is, carboxylation reactions rates were independent $NaBPh_4$ concentration. Our evidence also points away from a mechanism that involves a salt-assisted deprotonation of acetophenone (i.e., enhanced acidity of the α-proton through precoordination of the Na^+ to either the carbonyl or the arene).[59,60] In addition, facile carboxylation of MeCN occurred in the absence of added salt. Thus, the role of $NaBPh_4$ may be to help bring the NHC·CO_2 into solution such that it is available to react. Indeed, our investigations indicate that the addition of salts to otherwise insoluble NHC·CO_2 compounds led to homogeneous solutions. Given the propensity of the carboxylated product to undergo spontaneous decarboxylation, the role of the $NaBPh_4$ may also serve to stabilize the product through ion-pairing. A proposed mechanism that is analogous to carboxylation of MeCN is shown in Scheme 4.

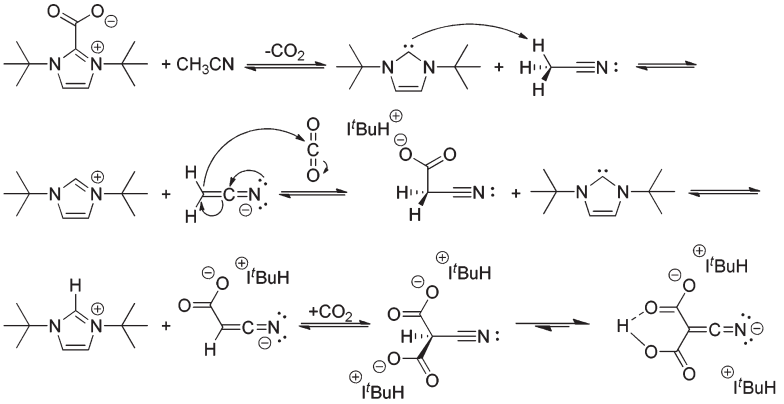
EXPERIMENTAL SECTION

General Procedures. All reactions and procedures were conducted under an atmosphere of N_2 using standard Schlenk techniques or in a N_2-filled glovebox unless otherwise noted. ^{1}H and ^{13}C nuclear magnetic resonance spectra of pure compounds were acquired at 500 and 125 MHz, respectively, unless otherwise noted. All spectra are referenced to residual solvent peaks. The abbreviations s, d, dd, dt, dq, t, q, quint, sept, m stand for singlet, doublet, doublet of doublets, doublet of triplets, doublet of quartets, triplet, quartet, quintet, septet, and multiplet, respectively. All coupling constants, *J*, are reported in Hz. All ^{13}C NMR spectra were proton decoupled. All TGA analyses were performed in a N_2 atmosphere at a heating rate of 5 °C/min.

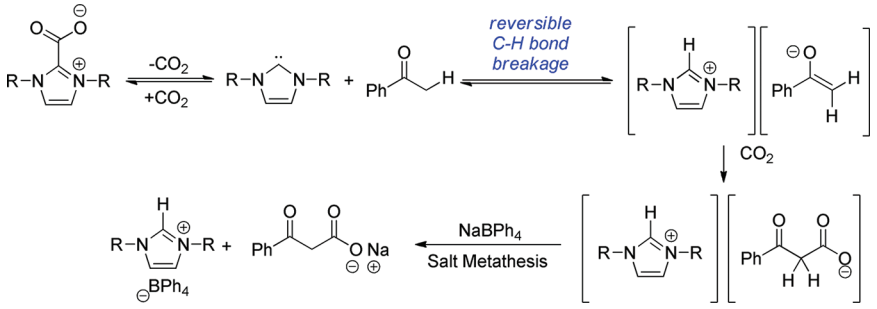
Nondeuterated solvents were purified and deoxygenated by passing through packed silica columns. All oil from NaH was removed by thorough washing with hexanes. $LiBPh_4(DME)_3$, $KBPh_4$, LiI, NaI, KI, $LiBF_4$, $NaBF_4$, and KBF_4 were dried by placing in a 130 °C oven for several days, further dried and cooled under a high vacuum over the solid for 30 min, and stored in a N_2-filled glovebox. $NaBPh_4$ was dried by dissolving in a minimal amount of THF and stirring with NaH for 30 min, filtering through Celite, and removing solvent in vacuo and stored under nitrogen. All other reagents were purchased from the chemical provider without further purification, unless specified. All NMR solvents were thoroughly dried using standard procedures prior to use. All NHC·CO_2's used were synthesized using previously reported procedures.[49] Carboxylation of acetophenone was performed using a modification of an existing procedure.[52] Deuterated solvents were

dx.doi.org/10.1021/jo201647b |J. Org. Chem. 2011, 76, 8413–8420

Scheme 3. Proposed Mechanism for the Formation of 8



Scheme 4. Proposed Reaction Mechanism for the Carboxylation of Acetophenone



purchased from Cambridge. CD_3CN was dried and distilled from CaH_2, and THF-d_8 was distilled from benzophenone-Na.

Syntheses of NHC·CO_2+MX complexes. *Preparation of* $[(IPrCO_2Na)_2]^{2+}2[BPh_4]^{2-}$ (***4***). In a 5 mL dram vial, $IPrCO_2$ (0.025 g, 57 μmol, 1 equiv) was weighed and dissolved in a minimal amount of dry THF (or MeCN). In another 5 mL dram vial, $NaBPh_4$ (0.020 g, 59 μmol, 1.03 equiv) was weighed and dissolved in a minimal amount of THF (or MeCN). The saturated solution of $IPrCO_2$ was added to the saturated solution of $NaBPh_4$, and the vial was placed into an empty 25 mL dram vial. Ether was added to the 25 mL vial, and the vial was capped. Within 12 h, slow diffusion of ether into the THF solution containing $IPrCO_2$ and $NaBPh_4$ afforded **4** (40 mg, 88% yield) as colorless crystals. ^{1}H NMR (THF-d_8, ppm) δ 7.43 (t, 2H, J = 7.8), 7.41 (s, 2H), 7.27 (d, 4H, J = 7.8), 7.23 (m, 8H), 6.77 (t, 8H, J = 7.5), 6.62 (t, 2H, J = 7.2), 3.36 (q, 3H, J = 7.0), 2.49 (sept, 4H, J = 6.9), 1.19 (d, 12H, J = 6.8), 1.16 (d, 12H, J = 7.0), 1.08 (t, 5H, J = 7.1). ^{13}C NMR (THF-d_8, ppm) δ 165.6, 165.2, 164.8, 164.4, 147.3, 146.2, 145.8, 137.4, 137.1, 136.9, 136.6, 132.5, 131.6, 130.97, 125.7, 125.2, 124.6, 124.1, 123.8, 122.2, 121.7, 121.4, 121.0, 68.0, 66.11, 30.1, 29.85, 26.1, 24.4, 24.3, 23.5, 23.41, 15.53, 15.44.

Preparation of $[IPrCO_2Li]^+[BPh_4]^-$ (***5***). In a 5 mL dram vial, $IPrCO_2$ (0.025 g, 57 μmol, 1 equiv) was weighed and dissolved in a minimal amount of dry THF (or MeCN). In another 5 mL dram vial, $LiBPh_4(DME)_3$ (0.036 g, 59 μmol, 1.03 equiv) was weighed and dissolved in a minimal amount of THF (or MeCN). The saturated solution of $IPrCO_2$ was added to the saturated solution of $LiBPh_4(DME)_3$, and the vial was placed into an empty 25 mL dram vial. Ether was added to the 25 mL vial, and the vial was capped. Within 12 h, slow diffusion of ether into the THF solution containing $IPrCO_2$ and $NaBPh_4$ afforded **5** (39 mg, 95% yield) as colorless crystals. ^{1}H NMR (THF-d_8, ppm) δ 7.46 (t, 2H, J = 7.8), 7.42 (s, 2H), 7.31 (d, 4H, J = 7.8), 7.23 (m, 8H), 6.79 (t, 8H, J = 7.3), 6.64 (t, 2H, J = 7.1), 3.57 (m, 3.4H), 3.35 (q, 0.6H, J = 7.0), 2.48 (sept., 4H, J = 6.9), 1.73 (m, 3.4H), 1.22 (d, 12H, J = 6.8), 1.17 (d, 12H, J = 7.0), 1.08 (t, 1.1H, J = 7.0) ^{13}C NMR (THF-d_8, ppm) δ 165.1, 164.8, 164.4, 155.8, 146.2, 145.8, 136.9, 132.7, 131.6, 124.5, 125.46, 125.44, 125.42, 125.40, 124.8, 124.7, 124.5, 68.0, 29.8, 26.1, 24.3, 23.3, 15.4.

Preparation of $[(IMesCO_2Li)_2]^{2+}2[BPh_4]^{2-}$ (***6***). In a 5 mL dram vial, $IMesCO_2$ (0.020 g, 57 μmol, 1 equiv) was weighed and dissolved in a minimal amount of dry THF (or MeCN). In another 5 mL dram vial, $LiBPh_4(DME)_3$ (0.036 g, 59 μmol, 1.03 equiv) was weighed and dissolved in a minimal amount of THF (or MeCN). The saturated solution of $IPrCO_2$ was added to the saturated solution of $LiBPh_4$-$(DME)_3$, and the vial was placed into an empty 25 mL dram vial. Ether was added to the 25 mL vial, and the vial was capped. Within 12 h, slow diffusion of ether into the THF solution containing $IPrCO_2$ and $NaBPh_4$ afforded **6** (33 mg, 85% yield) as colorless crystals. ^{1}H NMR (THF-d_8, ppm) δ 7.26 (m, 8H), 7.07 (s, 2H), 7.02 (s, 4H), 6.81 (t, 8H, J = 7.1), 6.67 (t, 4H, J = 7.1), 3.61 (m, 6H), 3.39 (q, 0.8H, J = 7.0), 2.32 (s, 6H), 2.09 (s, 12H), 1.77 (m, 6H), 1.18 (t, 1.2H, J = 7.0). ^{13}C NMR (THF-d_8, ppm) δ 165.5, 165.1, 164.7, 164.4, 156.2, 145.9, 142.1, 141.2, 136.9, 135.7, 134.9, 132.6, 131.6, 130.4, 129.7, 169.6, 125.5, 125.4, 126.04, 122.9, 121.7, 121.5, 68.0, 26.2, 20.9, 20.8, 17.4, 17.2.

Combination of $IPrCO_2$+$KBPh_4$. $IPrCO_2$ (0.020 g, 46 μmol, 1equiv) and $KBPh_4$ (0.018 g, 48 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry THF-d_8 until a homogeneous solution was obtained. ^{1}H NMR (THF-d_8, ppm) δ 7.46 (t, 2H, J = 7.8), 7.44 (s, 2H), 7.32 (d, 4H, J = 7.8), 7.28 (m, 8H), 6.81 (t, 8H, J = 7.5), 6.67 (t, 4H, J = 7.2), 2.54 (sept, 4H, J = 6.8), 1.25 (d, 12H, J = 6.8), 1.20 (d, 12H, J = 6.8). ^{13}C NMR (THF-d_8, ppm) δ 163.9, 163.5, 163.2, 162.8, 144.4, 135.3, 131.4, 129.8, 132.9, 123.8, 123.0, 122.5, 119.9, 28.2, 22.7, 21.9.

dx.doi.org/10.1021/jo201647b |*J. Org. Chem.* 2011, 76, 8413–8420

Combination of IPrCO$_2$+LiBF$_4$. IPrCO$_2$ (0.020 g, 46 μmol, 1 equiv) and LiBF$_4$ (0.005 g, 48 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry CD$_3$CN until a homogeneous solution was obtained. ^{1}H NMR (CD$_3$CN, ppm) δ 7.54 (s, 2H), 7.52 (t, 2H, *J* = 7.8), 7.34 (d, 4H, *J* = 7.8), 2.38 (sept, 4H, *J* = 6.8), 1.18 (d, 12H, *J* = 6.9), 1.20 (d, 12H, *J* = 6.7). ^{13}C NMR (THF-*d*$_8$, ppm) δ 155.0, 146.4, 145.6, 144.8, 133.3, 131.7, 131.5, 130.8, 125.6, 125.4, 125.1, 124.8, 30.1, 29.9, 24.5, 24.5, 23.6, 23.5.

Combination of IPrCO$_2$+LiI. IPrCO$_2$ (0.020 g, 46 μmol, 1 equiv) and LiI (0.007 g, 48 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry CD$_3$CN until a homogeneous solution was obtained. ^{1}H NMR (CD$_3$CN, ppm) δ 7.60 (s, 2H), 7.52 (t, 2H, *J* = 7.8), 7.34 (d, 4H, *J* = 7.8), 2.36 (sept, 4H, *J* = 6.8), 1.17 (d, 12H, *J* = 6.5), 1.13 (d, 12H, *J* = 6.7). ^{13}C NMR (THF-*d*$_8$, ppm) δ 155.5, 146.9, 146.1, 133.7, 132.2, 132.0, 131.3, 127.7, 127.5, 126.2, 126.0, 125.6, 125.3, 30.6, 30.4, 25.2, 25.1, 25.0, 24.4, 24.3, 24.1, 24.0.

Combination of IPrCO$_2$+NaI. IPrCO$_2$ (0.020 g, 46 μmol, 1 equiv) and NaI (0.008 g, 48 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry CD$_3$CN until a homogeneous solution was obtained. ^{1}H NMR (CD$_3$CN, ppm) δ 7.53 (s, 2H), 7.53 (t, 2H, *J* = 7.8), 7.37 (d, 4H, *J* = 7.8), 2.48 (sept, 4H, *J* = 6.9), 1.22 (d, 12H, *J* = 6.9), 1.20 (d, 12H, *J* = 6.9). ^{13}C NMR (THF-*d*$_8$, ppm) δ 155.5, 147.3, 146.9, 146.1, 133.9, 132.4, 132.2, 131.4, 125.0, 124.8, 30.8, 30.7, 30.6, 30.5, 30.2, 25, 0.9, 25.1, 25.0, 24.9, 25.2, 24.1, 23.2.

Combination of IMesCO$_2$+LiI. IMesCO$_2$ (0.030 g, 86 μmol, 1 equiv) and LiI (0.012 g, 90 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry CD$_3$CN until a homogeneous solution was obtained. ^{1}H NMR (CD$_3$CN, ppm) δ 7.51 (s, 2H), 7.08 (s, 4H), 7.37 (d, 4H, *J* = 7.8), 2.34 (sept, 6H), 2.05 (s, 12H). ^{13}C NMR (THF-*d*$_8$, ppm) δ 154.9, 143.2, 141.5, 140.6, 137.5, 134.8, 134.6, 131.8, 130.8, 130.0, 129.8, 129.6, 129.4, 129.1, 128.8, 128.6, 125.0, 124.8, 123.6, 123.4, 123.2, 122.9, 20.40, 20.32, 20.26, 16.9, 16.8, 16.6, 16.4.

Combination of I^{t}BuCO$_2$+LiBPh$_4$. I^{t}BuCO$_2$ (0.030 g, 130 μmol, 1 equiv) and LiBPh$_4$(DME)$_3$ (0.083 g, 140 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry THF-*d*$_8$ until a homogeneous solution was obtained. ^{1}H NMR (THF-*d*$_8$, ppm) δ 7.29 (m, 8H), 7.01 (s, 2H), 6.86 (s, 8H), 6.72 (t, 4H, *J* = 7.2), 3.42 (s, 4H), 3.26 (s, 6H), 1.58 (s, 18H). ^{13}C NMR (THF-*d*$_8$, ppm) δ 165.4, 164.2, 164.7, 164.5, 161.5, 144.5, 137.0, 136.9, 125.5, 121.7, 117.8, 117.6, 72.5, 62.4, 60.8, 58.7, 29.7, 29.6.

Combination of I^{t}BuCO$_2$+NaBPh$_4$. I^{t}BuCO$_2$ (0.030 g, 130 μmol, 1 equiv) and NaBPh$_4$ (0.048 g, 140 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry THF-*d*$_8$ until a homogeneous solution was obtained. ^{1}H NMR (THF-*d*$_8$, ppm) δ 7.25 (m, 8H), 7.08 (s, 2H), 6.81 (t, 8H, *J* = 7.4), 6.67 (t, 4H, *J* = 7.2), 1.63 (s, 18H). ^{13}C NMR (THF-*d*$_8$, ppm) δ 165.6, 165.2, 164.8, 164.4, 161.9, 145.6, 137.1, 136.9, 125.5, 121.7, 117.3, 117.2, 68.0, 62.2, 60.8, 29.7.

Combination of I^{t}BuCO$_2$+KBPh$_4$. I^{t}BuCO$_2$ (0.030 g, 130 μmol, 1 equiv) and KBPh$_4$ (0.050 g, 140 μmol, 1.05 equiv) were weighed out into separate 5 dram vials and then mixed using a minimal amount of dry THF-*d*$_8$ until a homogeneous solution was obtained. ^{1}H NMR (THF-*d*$_8$, ppm) δ 7.29 (m, 8H), 7.13 (s, 2H), 6.86 (t, 8H, *J* = 7.4), 6.71 (t, 4H, *J* = 7.2), 1.52 (s, 18H). ^{13}C NMR (THF-*d*$_8$, ppm) δ 165.7, 165.3, 164.9, 164.5, 161.6, 146.8, 137.1, 137.0, 125.7, 121.8, 63.1, 62.1, 60.9, 60.3, 29.7, 29.5.

*Preparation of 2[I^{t}BuH]$^{2+}$[dicarboxylatoketenimide]$^{2-}$ (**8**).* In a 5 mL dram vial, I^{t}BuCO$_2$ (0.050 g, 0.222 mmol, 1 equiv) was weighed and dissolved in a minimal amount of dry MeCN. The vial was placed into an empty 25 mL dram vial. Ether was added to the 25 mL vial, and the vial was capped. Within 12 h, slow diffusion of ether into the THF solution afforded **8** (40 mg, 37% yield) as colorless crystals. ^{1}H NMR (CD$_3$CN, ppm) δ 9.73 (s, 1H), 7.73 (s, 2H), 1.67 (s, 18H). ^{13}C NMR (MeCN-*d*$_3$, ppm) δ 164.5, 133.6, 120.9, 120.3, 61.1, 29.9, 27.7.

Pseudo-First -Order Kinetic Studies with IPrCO$_2$+NaBPh$_4$+Acetophenone in THF-*d*$_8$. *Order in IPrCO$_2$.* IPrCO$_2$ (0.020 g, 46 μmol, 1 equiv), NaBPh$_4$ (0.166 g, 485 μmol, 10.5 equiv), and trimethoxybenzene (0.035 g, 21 μmol, 5 equiv) were weighed into separate 5 dram vials. Dry THF-*d*$_8$ was then used to dissolve the all three solids. The solution was transferred to a NMR tube, and the vials were rinsed thoroughly to ensure complete transfer of the IPrCO$_2$, NaBPh$_4$, and TMB. The final volume of this solution was 1.00 mL. To the 1.0 mL of solution was added 54 μL of acetophenone to make a 1.054 mL solution. The solution was sealed with parafilm, mixed thoroughly, and placed into an ice bath. After heating the NMR spectrometer to 50.1 °C, the sample was inserted and initial rates of the reaction were measured.

Order in NaBPh$_4$. Three additional samples were prepared and evaluated in an analogous method as described above (i.e., Order in IPrCO$_2$). The concentration of IPrCO$_2$ (0.020 g, 46 μmol, 1 equiv), acetophenone (27 μL, 231 μmol, 5 equiv), and trimethoxybenzene (0.035 g, 21 μmol, 5 equiv) were kept constant for each sample. The concentration NaBPh$_4$ varied as follows: Sample 1 = 0.083 g, 243 μmol, 5.3 equiv; Sample 2 = 0.124 g, 364 μmol, 7.9 equiv; Sample 3 = 0.249 g, 728 μmol, 15.8 equiv. The following pseudo-first-order rate constants were obtained at different concentrations of acetophenone ($-k$, [NaBPh$_4$]), respectively: 7.8×10^{-3} M·s^{-1}, 0.23 M; 7.7×10^{-3} M·s^{-1}, 0.35 M; 8.1×10^{-3} M·s^{-1}, 0.69 M.

Order in Acetophenone. Three additional samples were prepared and evaluated in an analogous method as described above (i.e., Order in IPrCO$_2$). The concentration of IPrCO$_2$ (0.020 g, 46 μmol, 1 equiv), NaBPh$_4$ (0.166 g, 485 μmol, 10.5 equiv), and trimethoxybenzene (0.035 g, 21 μmol, 5 equiv) were kept constant for each sample. The concentration acetophenone varied as follows: Sample 1 = 40 μL, 346 μmol, 7.5 equiv; Sample 2 = 54 μL, 460 μmol, 10 equiv; Sample 3 = 81 μL, 693 μmol, 15 equiv. The following pseudo-first-order rate constants were obtained at different concentrations of acetophenone ($-k$, [acetophenone]), respectively: 7.8×10^{-3} M·s^{-1}, 0.22 M; 14.7×10^{-3} M·s^{-1}, 0.44 M; 24.1×10^{-3} M·s^{-1}, 0.66 M.

Effect of CO$_2$ (g) on Reaction. An NMR sample containing IPrCO$_2$ (0.020 g, 46 μmol, 1 equiv), NaBPh$_4$ (0.083 g, 243 μmol, 5.3 equiv), acetophenone (27 μL, 231 μmol, 5 equiv), and trimethoxybenzene (0.035 g, 21 μmol, 5 equiv) in 1 mL dry THF-*d*$_8$ (Total volume is 1.054 mL) was prepared analogously to the method described above. The solution was cooled and the N$_2$ atmosphere was removed and replaced with CO$_2$ three times. The sample was inserted into a preheated NMR spectrometer at 50.1 °C and the initial loss of IPrCO$_2$ was monitored to give the following pseudo-first-order rate constants were: 0.39×10^{-3} M·s^{-1} and 0.43×10^{-3} M·s^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray, ^{1}H NMR, and ^{13}C NMR data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We gratefully acknowledge the Department of Energy and the NSF for supporting this research.

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