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Alkali Metal Hydridotriphenylborates [(L)M][HBPh$_3$] (M = Li, Na, K): Chemoselective Catalysts for Carbonyl and CO_2 Hydroboration

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Supporting Information

ABSTRACT: Light alkali metal hydridotriphenylborates M[HBPh$_3$] (M = Li, Na, K), characterized as tris{2-(dimethylamino)ethyl}amine (L) complexes [(L)M][HBPh$_3$], act as efficient catalysts for the chemoselective hydroboration of a wide range of aldehydes and ketones using pinacolborane HBpin. The lithium derivative showed a remarkably high TOF of ≥17 s^{-1}. These compounds also catalyze the hydroborative reduction of CO_2 to give formoxyborane HCO$_2$Bpin without any over-reduction.

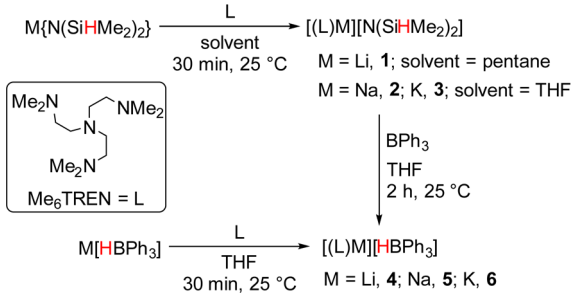
In contrast to saline light alkali metal hydrides MH (M = Li, Na, K), hydridoborates M[HBR$_3$] (R = alkyl, aryl, alkoxy, etc.) are widely used as stoichiometric reducing agents in organic synthesis.[1] The nature of the metal M and the boron substituents R influence the selectivity.[2] For instance, Li[HBEt$_3$] is strongly reducing and less selective,[3] while K[HBPh$_3$] is mild and chemoselective for carbonyl reduction.[4] Although hydridotriphenylborates M[HBPh$_3$] (M = Li, Na, K) could be synthesized from the reaction of saline MH with BPh$_3$,[4a,5] only a few compounds containing the [HBPh$_3$]$^-$ anion have been reported and they are rarely applied.[4,6] Recently, nucleophilic main group metal hydrides[7] and 1,3,2-diazaphospholene[8] received attention as catalysts for carbonyl and CO_2 hydrosilylation or hydroboration. Provided the hydridic B–*H* bond in [HBPh$_3$]$^-$[9] would allow insertion followed by σ-bond metathesis,[7] catalysis by [HBR$_3$]$^-$ would be conceivable.[10]

Herein, we report that a series of well-defined, soluble group 1 metal hydridotriphenylborates [(L)M][HBPh$_3$] (M = Li, **4**; Na, **5**; K, **6**) show *catalytic* activity toward the hydroboration of carbonyls and CO_2. Coordination by the tetradentate tris{2-(dimethylamino)ethyl}amine (Me$_6$TREN = L), known to induce deaggregation of alkali metal compounds, was crucial.[11]

Complexes **4**–**6** were prepared by treating M[HBPh$_3$] with Me$_6$TREN in THF, but can also be synthesized in high yields following a BPh$_3$ mediated β-Si*H* abstraction from the easily accessible tetramethyldisilazides **1**–**3** in THF (Scheme 1). Cyclodisilazane (Me$_2$HSiN–SiMe$_2$)$_2$, the head-to-tail dimer of silaimine Me$_2$HSiN=SiMe$_2$, was identified as the major byproduct. This synthetic route is clean, unlike Brown's earlier attempts from *t*BuLi and BPh$_3$, which gave Li[HBPh$_3$] contaminated with the BPh$_3^{-\bullet}$ radical anion.[12] Presumably, the ancillary Me$_6$TREN renders a stronger hydridic character onto the Si–H bonds in **1**–**3** to facilitate the process.

The borohydrides **4**–**6** are colorless crystalline solids and insoluble in aliphatic and aromatic hydrocarbons but highly soluble in THF. Their ^{1}H NMR spectra in THF-d_8 suggest a C_{3v} symmetric κ^4-coordination of Me$_6$TREN. Characteristic doublets at around δ −8.2 ppm ($^1J_{BH}$ = 78 Hz) in the ^{11}B NMR spectra are attributed to [HBPh$_3$]$^-$. Complexes **4** and **6** were also characterized by single crystal X-ray crystallography (Figure 1).[13]

Scheme 1. Synthesis of [(L)M][HBPh$_3$] (4–6) from [(L)M][N(SiHMe$_2$)$_2$] (1–3)



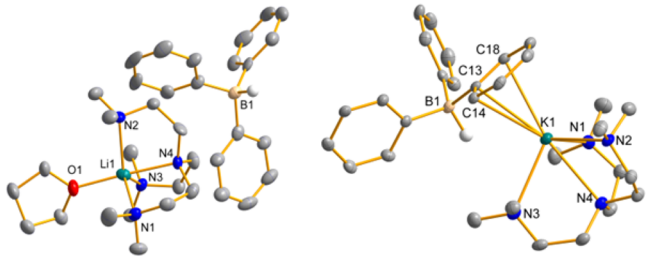


Figure 1. Molecular structures of **4** and **6**. Displacement parameters are shown at 50% probability. Hydrogen atoms except the B–H's are omitted for clarity.

While the lithium compound **4** is a separate ion pair, the potassium **6** is zwitterionic. The sodium analogue **5** is also a separate ion pair, but the poor quality of the X-ray data prevents further discussion. The THF molecule in **4** presumably binds during the crystallization process. For comparison, both [(L)Li][HBEt$_3$] and [(L)Li][BH$_4$] are neutral compounds with bridging hydrides and are soluble in benzene.[11a] Complex **6** is structurally related to that of [(L)KCH$_2$Ar] (Ar = C$_6$H$_5$, C$_6$H$_3$Me$_2$)[11c,d] and [(L)KSiPh$_3$].[11f] One phenyl ring of the [HBPh$_3$]$^-$ is η^3-coordinated to the potassium via the *ipso-*/*ortho-* carbons and is significantly

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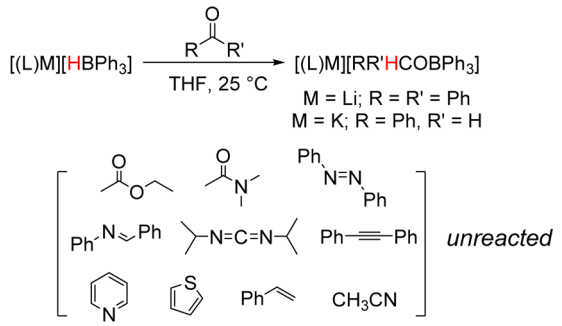
distorted. The K···H distance (3.21 Å) is too long to be a bonding interaction. The boron centers in both **4** and **6** have nearly perfect tetrahedral geometry.

Carbonyl compounds such as benzophenone Ph_2CO and benzaldehyde PhCHO are readily inserted into the B−H bonds of **4**–**6** (Scheme 2) to give alkoxyborates, which were characterized in situ by solution NMR spectroscopy. Several other unsaturated functional groups did not react.

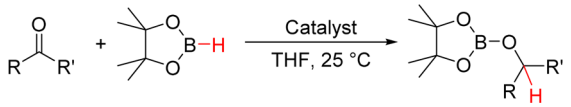
Scheme 2. Chemoselective Carbonyl Insertion in 4–6



Selective reduction of carbonyls in the presence of other reducible functional groups is challenging. Catalytic processes such as hydrosilylation,[14] hydroboration,[7b,c,8,15] hydrogenation,[16] and transfer hydrogenation[17] have been investigated to achieve this chemoselective transformation, including enantioselective reduction.[18] As summarized in Table 1, complexes **4**–**6** were found to catalyze carbonyl hydroboration with pinacolborane (HBpin) under mild conditions.

Benzophenone was chosen as the model substrate to compare the catalysts. Lithium complex **4** exhibited supreme efficiency, and a catalyst loading as low as 0.001 mol % led to complete reduction within 1.5 h, providing a remarkably high TOF of 66.6 × 10^3 h^{-1} or 17 s^{-1} (Table 1, entry 2). Complexes **5** and **6** are similar in activity but much poorer compared to **4** (entries 3 and 4). Ligand-free $Li[HBPh_3]$ was also active but not as much as **4** (entry 5). Thus, the coordination of Me_6TREN is critical for high activity. The activity of commercially available $Li[HBEt_3]$ was almost the same as that of $Li[HBPh_3]$ (entry 6), but unlike **4**, $[(L)LiHBEt_3]$ was much less active (entry 7). The TOF of the metal-free alkylammonium salt $[^nBu_4N][HBPh_3]$[19] was close to that of **5** and **6** (entry 8). BPh_3 was only marginally active compared to the other investigated catalysts (entry 9), which emphasizes the importance of the Ph_3B−H bond for faster catalysis. The high activity of the Li catalyst is probably due to its higher degree of polarization in the $[RR'CHOBPh_3]^-$ intermediate as compared with Na and K.[20] The reduction of other aromatic and aliphatic ketones and aldehydes was accomplished by using 0.01 mol % of **4** (entries 7–11), showing the applicability to a wide range of functional groups. In comparison, a copper carbene catalyst had the previously highest TOF of 1 × 10^3 h^{-1} for Ph_2CO hydroboration.[15f] For aldehydes, a TOF of >13.3 × 10^3 h^{-1} was reported for a molecular tin(II) hydride catalyst.[7c] Among the main group catalysts, the most active molecular magnesium catalyst recorded a TOF of 0.5 × 10^3 h^{-1} for Ph_2CO and 8 × 10^3 h^{-1} for PhCHO.[15a] Reduction of α,β-unsaturated cinnamaldehyde took place exclusively at the 1,2-position, but at a much slower rate (entry 14). The reaction time of 48 h showed the longevity of the catalyst, though. Catalyst **4** was again a better choice than the parent $Li[HBPh_3]$ (entry 15). 2-

Table 1. Carbonyl Hydroboration Catalyzed by Hydridotriphenylborates[a]



entry	R	R′	catalyst (mol %)	time (h)[b]	TOF (10^3 h^{-1})
1	Ph	Ph	**4** (0.01)	<0.17	≥60
2	Ph	Ph	**4** (0.001)	1.5	66.6
3	Ph	Ph	**5** (0.1)	5	0.2
4	Ph	Ph	**6** (0.1)	5	0.2
5	Ph	Ph	$Li[HBPh_3]$ (0.01)	0.75	13.3
6	Ph	Ph	$LiHBEt_3$ (0.01)	1	10
7	Ph	Ph	$[(L)LiHBEt_3]$ (0.01)	6	1.67
8	Ph	Ph	$[^nBu_4N][HBPh_3]$ (0.1)	6	0.16
9	Ph	Ph	BPh_3 (0.1)	5[c]	n.c.[d]
10	Ph	Me	**4** (0.01)	<0.17	≥60
11[e]	*p*-X-C_6H_4	H	**4** (0.01)	<0.17	≥60
12	$CH_3CH_2CH_2$	H	**4** (0.01)	<0.17	≥60
13	cyclohexyl	H	**4** (0.01)	<0.17	≥60
14[f]	PhCH=CH	H	**4** (0.01)	48	0.21
15[f]	PhCH=CH	H	$Li[HBPh_3]$ (0.01)	48[g]	n.c.[d]
16[f]	2-cyclohexen-1-one		**4** (1)	<0.17	n.c.[d]

[a]HBpin = 0.27 mmol, substrate = 0.27 mmol, 0.5 mL of solvent. [b]Time for complete substrate consumption, detected by NMR spectroscopy. [c]23% conversion. [d]n.c. = not calculated. [e]X = H, Me, OMe, NO_2, CN, Br, and F. [f]Regioselective 1,2-reduction. [g]64% conversion.

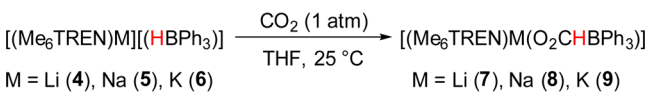
Cyclohexen-1-one was also rapidly reduced in 1,2-fashion with a higher catalyst loading (entry 16). Benzophenone was reduced on a mmol scale to show practical applicability. Notably, substrates such as esters, amides, and pyridine were not reduced, even at a higher loading of **4** and under forcing conditions.

To verify the chemoselectivity, a series of competitive hydroboration experiments were carried out by subjecting stoichiometric mixtures of benzophenone with all the other noncarbonyl substrates listed in Scheme 2 in the presence of 0.1 mol % of **4**. In all cases, the benzophenone was selectively reduced immediately. This also proves that the competing groups do not inhibit the catalysis.[21] Furthermore, catalyst **4** exhibited "living" behavior: once the first loading was consumed, the same reaction mixture successfully completed two more runs with equal activity. Additionally, catalyst **4** reacts with air or moisture very slowly, leading to only partial decomposition at ambient temperature after 24 h.

Selective reduction of aldehyde over ketone is another synthetically important transformation.[15g,22] Quite remarkably, 0.1 mol % of **4** preferentially reduced benzaldehyde over benzophenone with 95% selectivity.

Rapid CO_2 (1 atm) insertion took place into the B−H of $[HBPh_3]^-$ in **4**–**6** under ambient conditions (Scheme 3) to afford the formoxytriphenylborate complexes $[(L)M\{(HCO_2)$-

Scheme 3. CO_2 Insertion into the B−H Bonds of 4–6



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BPh_3}] (M = Li, **7**; Na, **8**; K, **9**), which were fully characterized. This has been previously reported only on a single occasion in a Pd/Pt system, and that too without structural characterization.[23] In contrast, CO_2 insertion in $[HB(C_6F_5)_3]^-$ is better studied, but requires harsher conditions ($t \geq 100$ °C or $P_{CO_2} \geq 1$ atm) and longer reaction times.[24]

X-ray analysis showed that the formoxy moieties are bridging between the metal and the boron with a varying coordination pattern (Figure 2).[25] The M···O1 distance systematically

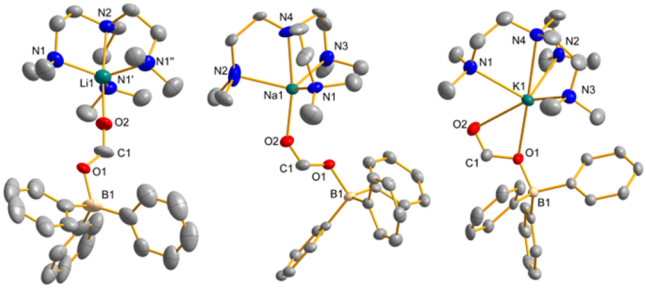
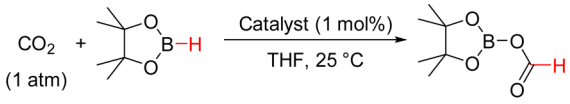


Figure 2. Molecular structures of **7**–**9**. Displacement parameters are shown at 50% probability. Hydrogen atoms are omitted for clarity.

changes following the trend Li > Na > K. In **7** and **9**, the formate has η^1 and η^2 coordination to Li and K, respectively, while **8** has an intermediate situation. Variation in anion coordination was also observed in their benzyl and mesityl complexes.[11c,d]

The hydridotriphenylborates **4**–**6** catalyzed the hydroboration of CO_2 as shown in Table 2. Boron-mediated CO_2

Table 2. Hydroboration of CO_2 with HBpin Catalyzed by Hydridotriphenylborates[a]



entry	catalyst	time (h)	TOF (h^{-1})
1	**4**	10	10
2	**5**	16	6.25
3	**6**	16	6.25
4	$[(nBu_4)N][HBPh_3]$	50	2

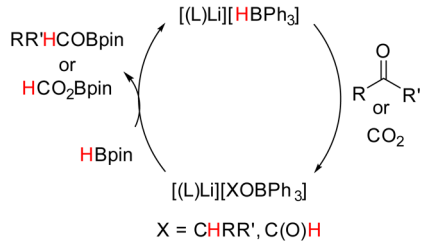
[a]HBpin = 0.14 mmol, 0.5 mL of solvent.

sequestration operates under mild conditions.[7b,24] CO_2 reduction by B–H bonds can be traced back to as early as the 1950s, when the reaction of CO_2 with $NaBH_4$ was reported.[26] Commercial BH_3(THF) solution also reacts with CO_2 (1 atm) at room temperature, with the reaction actually promoted by 0.5 mol % of $NaBH_4$ present as a stabilizer.[27] Some metal and organic catalysts have emerged for CO_2 hydroboration that use catecholborane (HBcat) or HBpin to produce formate, acetal, and methoxide derivatives.[24] A few hydroborates were shown to catalyze this process.[28]

Noticeably, the present system selectively provided the primarily reduced formoxyborane (HCO_2Bpin). Adding an extra equivalent of HBpin after completion did not result in further reduction. This also explains the inactivity of this system toward esters. A Cu[29] and a Pd[30] catalyst are the only two other examples known for this selectivity. The lithium catalyst was again better than the others (Table 2, entries 1–4). Overall, the activities are much lower compared to the carbonyl hydroboration, but superior to the Cu[29] and Ru[31] catalysts, and also the two other main group metals.[32]

Currently we propose a simplified mechanistic scheme[7] that takes into account the experimental finding that stoichiometric reactions of **4** with Ph_2CO as well as the intermediate with HBpin are complete instantaneously (Scheme 4). Although

Scheme 4. Proposed Catalytic Cycle for the Carbonyl and CO_2 Hydroboration Mediated by 4



rapid hydride exchange between $[BH_4]^-$ and BR_3 (R = alkyl) was postulated before,[10] we failed to observe an exchange between $[HBPh_3]^-$ and HBpin, as ^1H and ^{11}B NMR spectra of a 1:3.5 mixture of **4** and HBpin in THF-d_8 are identical to the individual spectra (see Supporting Information). The actual mechanism could be more complex since sodium alkoxides[15h] were reported to catalyze the addition of HBpin to carbonyls.[33] Further mechanistic and computational studies are currently underway.

The perfluorinated analogues $[(L)M][HB(C_6F_5)_3]$ (M = Li, **10**; Na, **11**; K, **12**) were synthesized by treating **1**–**3** with $B(C_6F_5)_3$. Their physical and spectroscopic properties are similar to those of **4**–**6**, but they were totally inert toward PhCHO or CO_2 (1 atm). This can be explained by the decreased hydridicity of the $[HB(C_6F_5)_3]$ anion.[9,24]

In conclusion, we have described the exceptional performance of compounds **4**–**6** as chemoselective hydroboration catalysts for carbonyl and CO_2 that outcompetes many other metal catalysts. Apparently the combination of the Lewis acidic alkali metal and the hydridic borate results in efficient catalysis. We are currently focusing on the elucidation of mechanistic details.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06319.

Experimental procedures; spectroscopic and X-ray data (PDF)

Crystallographic data for the new compounds (CIF)

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Notes

The authors declare no competing financial interest.

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(33) One reviewer suggested that the actual catalyst could be M[(RO)HBpin] rather than M[$HBPh_3$] that acts as an initiator after the initial addition of the substrate followed by the transfer of the RO group to HBpin and release of BPh_3. Further addition would give M[$(RO)_2$Bpin] that undergoes reaction with HBpin to form the product (RO)Bpin and M[(RO)HBpin]. So far we could not find any conclusive NMR spectroscopic evidence for these species or any effect by free BPh_3.

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