CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Ligand influence on the carbonyl hydroboration catalysis by alkali metal hydridotriphenylborates [(L)M][HBPh3] (M = Li, Na, K)

Authors: Jun Okuda, Thomas Spaniol, Hassan Osseili, and Debabrata Mukherjee

To be cited as: *Chem. Eur. J.* 10.1002/chem.201702818

Link to VoR: http://dx.doi.org/10.1002/chem.201702818

Supported by
ACES

WILEY-VCH

10.1002/chem.201702818

WILEY-VCH

FULL PAPER

Ligand influence on the carbonyl hydroboration catalysis by alkali metal hydridotriphenylborates [(L)M][HBPh$_3$] (M = Li, Na, K)

Hassan Osseili,[†] Debabrata Mukherjee,[†] Thomas P. Spaniol, and Jun Okuda*

Abstract: Alkali metal hydridotriphenylborates [(L^1)M][HBPh$_3$] (L^1 = Me$_6$TREN; M = Li, Na, K) chemoselectively catalyze the hydroboration of carbonyls and CO_2, with lithium being the most active system. A new series of complexes [(L^2)M][HBPh$_3$] [M = Li (**1**), Na (**2**), K (**3**)] with the cyclen-derived macrocyclic polyamine Me$_4$TACD (L^2) were synthesized in a 'one-pot' fashion and fully characterized including X-ray crystallography. In the crystal, **1**-**3** exhibit wide variation in metal coordination of the [HBPh$_3$]$^-$ anion from lithium to potassium. The structures differ from those in [(L^1)M][HBPh$_3$]. Effects of coordination of L^1, L^2, and other N- and O-donor multidentate ligands on [Li(HBPh$_3$)] were used to rationalize the catalytic activity in carbonyl hydroboration.

Introduction

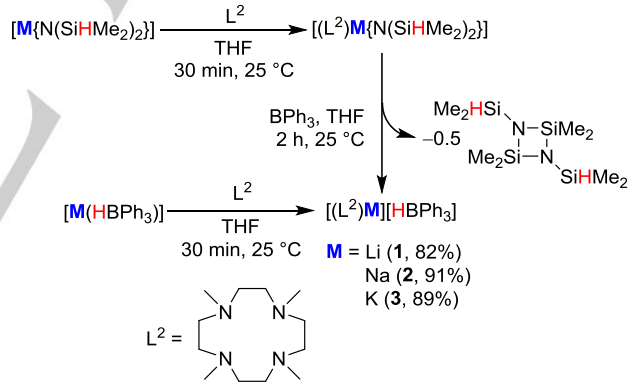
Molecular s-block metal compounds are historically important as stoichiometric reagents. Only recently does their use as catalysts attract increased attention.[1] Lighter alkali metal hydridoborates [M(H$_n$BR$_{4-n}$)] are routinely used as versatile reducing agents in organic synthesis (M = Li, Na, K; R = H, alkyl, aryl), offering fine-tuning of chemoselectivity.[2] Hydrido-triphenylborates [M(HBPh$_3$)] were introduced in the 1950's,[3] but remained mostly unnoticed despite their easy preparation[4] and significant hydridicity.[5] Only [K(HBPh$_3$)] was employed as a mild and selective reducing agent for carbonyl substrates.[4, 6] Structural data for [HBPh$_3$]$^-$ anion remained surprisingly limited as well,[7] especially compared to what is known of [BPh$_4$]$^-$.[8]

Our recent findings have resuscitated [M(HBPh$_3$)] since the well-characterized hydridotriphenylborates [(L^1)M][HBPh$_3$] (L^1 = Me$_6$TREN = tris{2-(dimethylamino)ethyl}amine; M = Li, Na, K) were recognized as active catalysts in the chemoselective hydroboration of carbonyls and CO_2 using pinacolborane (HBpin), with lithium showing the highest activity.[9] Stabilization of reactive organo-alkali metal species in monomeric form by this NNNN-type tripodal polyamine L^1 has already been recognized by Mulvey et al..[10]

The macrocyclic polyamine 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me$_4$TACD = L^2) has also been used as an NNNN-type neutral ligand to obtain stable complexes of s-,[11] d-,[12] and f-block[13] metals. The coordination pattern for open vs. closed chain multidentate ligands with the same donor set often exhibits significant difference, leading to different structures and reactivity.[14] Here we report the synthesis of complexes [(L^2)M][HBPh$_3$] (M = Li, Na, K) and compare their structures and catalytic hydroboration activity with those of [(L^1)M][HBPh$_3$]. Effects of the coordination of some other N- and O-type multidentate ligands were also examined. Benzophenone hydroboration with pinacolborane was chosen as the benchmark catalytic reaction.

Results and Discussion

[(L^1)M][HBPh$_3$] (M = Li, Na, K) were prepared in high yields by BPh$_3$-mediated β-hydride abstraction from the easily accessible tetramethyldisilazides [(L^1)M{N(SiHMe$_2$)$_2$}] in THF.[9] This route also worked well for other metals like magnesium[15] and zinc.[16] The same procedure was applied here and more conveniently in a 'one-pot' fashion. Tetramethyldisilazides [(L^2)M{N(SiHMe$_2$)$_2$}] were first generated in THF by mixing L^2 with [M{N(SiHMe$_2$)$_2$}] in 1:1 ratio. Treating them subsequently with BPh$_3$ readily provided [(L^2)M][HBPh$_3$] (M = Li (**1**), Na (**2**), K (**3**)] in high yields (Scheme 1). The same compounds were obtained by mixing L^2 with [M(HBPh$_3$)] in THF.[9]



Scheme 1. Synthesis of [(L^2)M][HBPh$_3$] (**1**-**3**).

Complexes **1**-**3** were isolated as colorless crystals and fully characterized. They are soluble in THF but insoluble in aromatic and aliphatic hydrocarbons, similar to the L^1 bonded derivatives. Their ^{1}H and ^{13}C{^{1}H} NMR spectra in THF-d_8 display the expected resonances of a coordinated L^2 and the [HBPh$_3$]$^-$ anion. A characteristic broad quartet at δ 3.50-2.94 ppm in the ^{1}H NMR spectrum and a sharp doublet at around δ –8.8 ppm ($^1J_{BH}$ = 76-79 Hz) in the ^{11}B NMR spectrum are attributed to the B–H moiety. All three compounds were authenticated by X-ray crystallography and the results show a major variation in coordination pattern for [HBPh$_3$]$^-$. Noticeable structural differences from the structures of [(L^1)M][HBPh$_3$] were also observed.

Complex **1** crystallized as a separate ion-pair with one THF molecule coordinated to the lithium (Fig. 1). The five-coordinate

[*] Hassan Osseili, Dr. Debabrata Mukherjee, Dr. Thomas P. Spaniol, Prof. Dr. Jun Okuda*
Institute of Inorganic Chemistry, RWTH Aachen University
Landoltweg 1, 52056, Aachen (Germany)
E-mail: jun.okuda@ac.rwth-aachen.de

[†] These authors have contributed equally.

Supporting information for this article is given via a link at the end of the document.

10.1002/chem.201702818

cationic lithium center thus adopts a distorted square-pyramidal geometry with the THF molecule occupying the axial position. In contrast, the sodium complex **2** is a contact ion pair (CPI) with non-covalent $Na^{+}\cdots C_{\pi}$ interactions ranging from 2.854(6)-3.448(7) Å (Fig. 2). One phenyl ring of the $[HBPh_3]^{-}$ anion is η^3-coordinated to the metal via the *ipso*- and two *ortho*- carbons. A 3-centered-2-electron Na···H–B [Na···H: 2.25(7) Å] bonding interaction is also evident that confers the sodium a formally eight-coordinate distorted square anti-prismatic geometry. The potassium complex **3** is also a contact ion pair with a 3-center-2-electron K···H–B (K···H: 2.73(7) Å] bonding interaction. Interestingly, the anion $[HBPh_3]^{-}$ in this case exhibits non-covalent $K^{+}\cdots C_{\pi}$ interactions [3.122(8)-3.280(7) Å] from two phenyl rings, both in η^2-fashion involving the *ipso* and one *ortho* phenyl carbons (Fig. 3). This increases the formal coordination number of potassium to nine with a distorted mono-capped square anti-prismatic geometry. None of these cation···C_{π} interactions resulted in distortion of the phenyl rings in both **2** and **3**, which is otherwise often the case.[9, 10g, 17] As expected, the metal-nitrogen distances increase going down the group, as Li [2.154(11)-2.301(12) Å] < Na [2.444(6)-2.574(6) Å] < K [2.791(7)-2.858(7) Å].

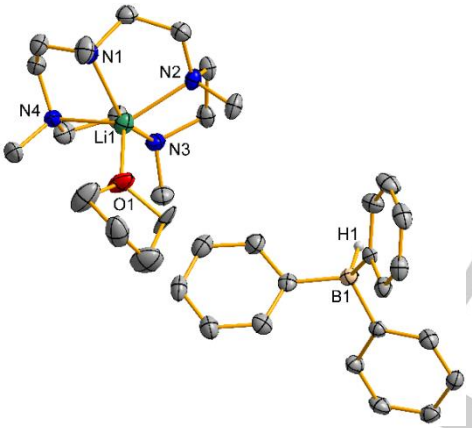


Figure 1. Molecular structure **1·THF**. Selected bond distances (Å): Li1–N1 2.301(12); Li1–N2 2.154(11); Li1–N3 2.256(11); Li1–N4 2.175(11); Li1–O1 1.921(10).

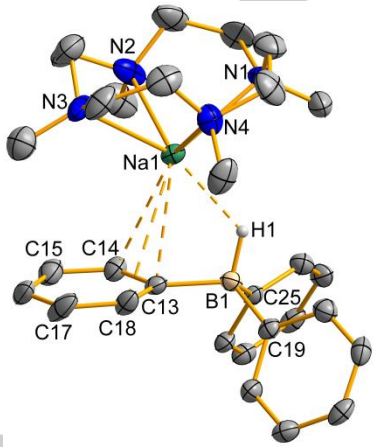


Figure 2. Molecular structure of **2**. Selected bond distances (Å): Na1–N1 2.574(6); Na1–N2 2.483(6); Na1–N3 2.552(6); Na1–N4 2.444(6); B1–C13 1.630(9); B1–C19 1.630(9); B1–C25 1.653(9); Na1···H1 2.25(7); Na1···C13 2.854(6); Na1···C14 3.075(7); Na1···C18 3.448(7). Selected torsion angles (°): ∠B1–C13–C14–C15 –179.9(6); ∠B1–C13–C18–C17 –178.6(7).

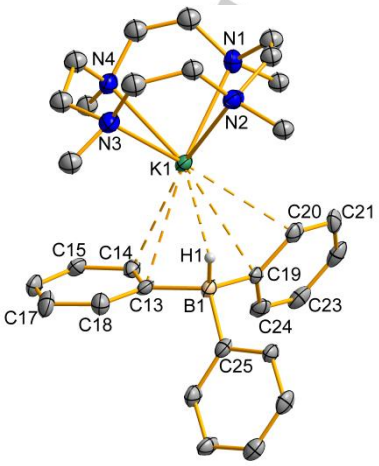


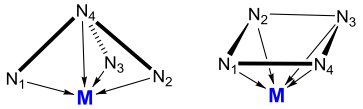
Figure 3. Molecular structure of **3**. Selected bond distances (Å): K1–N1 2.837(7); K1–N2 2.858(7); K1–N3 2.791(7); K1–N4 2.826(6): B1–C13 1.642(11); B1–C19 1.644(12); B1–C25 1.636(11); K1···H1 2.73(7); K1···C13 3.148(8); K1···C14 3.122(8); K1···C19 3.280(7); K1···C19 3.190(8). Selected torsion angles (°): ∠ B1–C13–C14–C15 –178.7(7); ∠ B1–C13–C18–C17 –179.5(7); ∠B1–C19–C20–C21 –179.9(6); ∠B1–C19–C24–C23 –179.8(6).

Non-covalent $M^{+}\cdots C_{\pi}$ interactions for the alkali metals, especially for the heavier congeners, are important for stabilization by coordinative saturation.[18] The Cambridge Structural Database (CSD) contains more than 300 crystal structures showing $K^{+}\cdots C_{\pi}$(arene) interactions. Such binding forces are important in biology for defining protein structures, ion transportation, molecular recognition, and enzyme catalysis.[19] Mulvey, Davidson *et al.* performed an elaborative study on alkali metal cation···C_{π}(arene) interactions using L^1 as the coligand. Complexes like $[(L^1)K][CH_2Ph]$,[10b] $[(L^1)K][CH_2C_6H_3\text{-}3,5\text{-}Me_2]$,[10d] $[(L^1)K][SiPh_3]$,[10g] and the heterobimetallic $[(L^1)K][Zn(t\text{Bu})_2(CH_2Ph)]$[10d] are all contact ion pairs in the solid state. Alkali metal cation to anion interaction in $[(L^1)M][A]$ (M = Li, Na, K; A = CH_2Ph, $CH_2C_6H_3$-3,5-Me_2] varies systematically.[10b, 10d] While the Li derivatives have Li–CH_2 σ-interactions, the potassium centers are exclusively π-arene bonded in η^6 fashion. The bonding situation for sodium is intermediate; the metal cation is slightly dislocated towards the π-arene while maintaining a partial Na–CH_2 σ-interaction. Earlier, R. v. Schleyer *et al.* and Stalke *et al.* performed similar studies with alkali metal triphenylmethyl and diphenylpyridylmethyl derivatives using PMDTA (*N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine) ligand.[20] R. v. Schleyer *et al.* later reviewed this topic comprehensively.[21]

In the case of L^1, both lithium and sodium derivatives crystallized as separate ion pairs $[(L^1)M(thf)][HBPh_3]$ (M = Li, Na) with one coordinated THF molecule.[9] Only $[(L^1)K][HBPh_3]$ is a contact ion pair, but the potassium ion is η^3-bonded [$K^{+}\cdots C_{\pi}$: 3.001(4)-3.118(4) Å] to a single phenyl ring and no K···H–B (K···H: 3.21 Å) bonding interaction is detected.[9]

As mentioned earlier, both L^1 and L^2 are NNNN-type Lewis donors that bind to $[M(HBPh_3)]$ in a κ^4-fashion in the solid state. But the spatial orientation of their donor sites varies. Nitrogen atoms of the three $CH_2CH_2NMe_2$ arms of the tripodal L^1 are coplanar forming a trigonal base during metal chelation, while the

apical nitrogen binds from the top (Fig. 4).[9] Metal-nitrogen distances as well as the distance from the trigonal base follow a trend of Li < Na < K. Whereas, the macrocyclic L^2 adopts a distorted boat-like conformation upon metal coordination with a square planar arrangement for its nitrogen atoms (Fig. 4). L^2→M distances also increases with size as Li (0.8368 Å) < Na (1.3362 Å) < K (1.8440 Å). This coordination diversity together with the *N*-substitution, that is two vs. one methyl groups, might well account for the observed structural differences between $[(L^1)M][HBPh_3]$ and $[(L^2)M][HBPh_3]$.



$Me_6TREN = L^1$ $Me_4TACD = L^2$

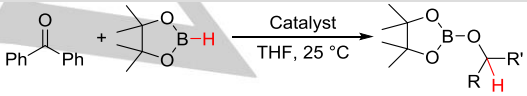
M = Li, Na, K

Figure 4. Binding patterns of L^1 and L^2 in $[(L^1)M][HBPh_3]$ and $[(L^2)M][HBPh_3]$, respectively.

The smallest and hardest lithium ion resides deepest inside the pocket of both L^1 and L^2 with an additional THF molecule bonded instead of the $[HBPh_3]^-$ anion. The largest and softer potassium ion opts for $K^+\cdots C_\pi$ interactions in both cases but to variable degrees. The sodium ion in between has no strong preference and exhibits both separate as well as contact ion pair structures. The counter anion can also influence. $[(L^2)Na(thf)][BAr^F]$ (BAr^F = tetrakis{3,5-bis(trifluoromethyl)-phenyl}borate) has a separate ion pair structure unlike **2**.[11a] The hydride-encapsulated heterobimetallic "inverse crowns" $[M_2Mg_2(NiPr_2)_4(\mu\text{-}H)_2(toluene)_2]$ (M = Na, K) have π-solvated toluene molecules for both sodium and potassium, but only weakly bonded in the case of sodium. Toluene can be removed under dynamic vacuum.[22]

The lithium catalyst $[(L^1)Li][HBPh_3]$ showed high activity in carbonyl hydroboration of benzophenone with a TOF of ≥ $60•10^3$ h^{-1};[9] the highest number so far among all the catalysts known to date, including the ones based on transition metals.[1f, 1g, 15, 23] Further studies have indicated that a dynamic coordination from L^1 in tandem with the THF solvent to the cationic lithium center was critical for this high activity.[24] Lewis acidity of the metal cation may contribute significantly.[15, 25] The activities of **1**-**3** were tested in benzophenone hydroboration using HBpin (Table 1). The lithium catalyst **1** was significantly less active than $[(L^1)Li][HBPh_3]$ and gave TOF values of $0.56•10^3$ h^{-1} and $2•10^3$ h^{-1} with 0.01 and 0.1 mol% of catalyst loading, respectively (entry 1 and 2). Compared to **1**, the sodium catalyst **2** (entry 3, TOF: $0.08•10^3$ h^{-1}) and the potassium catalyst **3** (entry 4, TOF: $0.04•10^3$ h^{-1}) were 25 and 50 times less active. Activities of $[(L^1)M][HBPh_3]$ followed a similar trend as Li >> Na ~ K, but the superiority of lithium was more pronounced (>300 times).[9] $[(L^1)M][HBPh_3]$ (M = Na, K; TOF: $0.5•10^3$ h^{-1}) were also more active catalysts than **2** and **3**.[9]

Table 1. Hydroboration of benzophenone catalyzed by **1**-**3**.[a]

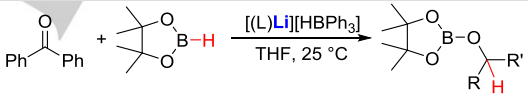


Entry	Catalyst	mol%	Time (h)[b]	TOF (10^3 h^{-1})
1	**1**	0.01	18	0.56
2	**1**	0.1	0.5	2
3	**2**	0.1	12	0.08
4	**3**	0.1	24	0.04

[a] n(HBpin) = 0.27 mmol, n(substrate) = 0.27 mmol, 0.5 mL of solvent. [b] Time for complete substrate consumption, detected by NMR spectroscopy.

Effect of ligand coordination was further extended towards some other neutral multidentate N- and O donors (Table 2). The ancillary ligand-free $[Li(HBPh_3)]$ itself showed high activity with a TOF of $13.33•10^3$ h^{-1} at 0.01 mol% of catalyst loading (entry 1).[9] Compared to that, L^1 (entry 2 and 3) showed a strong influence by reaching a TOF of above $60•10^3$ h^{-1}.[9] Open-chain polyamine tridentate PMDTA (entry 4) and bidentate TMEDA (N,N,N',N'-tetramethylethylenediamine, entry 5) had almost no to slightly negative effect of coordination since both gave a TOF of $10•10^3$ h^{-1}. The closed-chain tetradentate polyamine L^2 (entry 6 and 7) on the other hand reduced the activity by 25 times, compared to the ligand-free $[Li(HBPh_3)]$. Likewise, macrocyclic polyether 12-crown-4 (12-c-4) showed a negative impact with a TOF of $1.33•10^3$ h^{-1} (entry 8).

Table 2. Ligation effect on $[Li(HBPh_3)]$ in catalytic hydroboration of benzophenone.[a]



Entry	L	mol%	Time (h)[b]	TOF (10^3 h^{-1})
1	---	0.01	0.75	13.3
2	L^1	0.01	<0.17	≥60
3	L^1	0.001	1.5	66.6
4	PMDTA	0.01	1	10
5	TMEDA	0.01	1	10
6	L^2	0.01	18	0.6
7	L^2	0.1	0.5	2
8	12-c-4	0.1	0.75	1.3

[a] n(HBpin) = 0.27 mmol, n(substrate) = 0.27 mmol, 0.5 mL of solvent. [b] Time for complete substrate consumption, detected by NMR spectroscopy.

$[(PMDTA)Li][HBPh_3]$ (**4**) and $[(12\text{-}c\text{-}4)Li][HBPh_3]$ (**5**) were isolated by mixing the ligands with $[Li(HBPh_3)]$ in THF and were fully characterized including an X-ray crystal structure analysis for **5** (Fig. 5). It revealed a THF coordinated separate ion pair structure as **1** and $[(L^1)Li][HBPh_3]$. Crown ether complexes of alkali metal tetraphenylborates were crystallographically characterized.[26] **5** is isostructural with $[(12\text{-}c\text{-}4)Li(thf)][BPh_4]$.[26] The Li–O distances are within the expected range of 2.0187(2)-2.0665(1) Å.

10.1002/chem.201702818

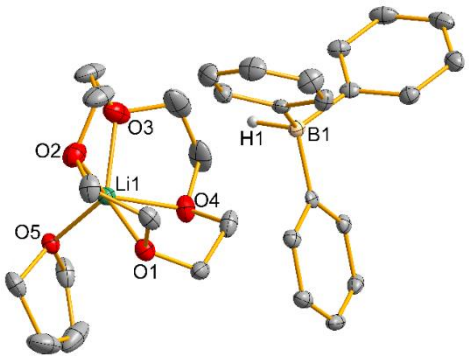


Figure 5. Molecular structure of **5·THF**. Selected bond distances (Å): Li1–O1 2.0665(1); Li1–O2 2.0463(2); Li1–O3 2.0187(2); Li1–O4 2.0428(2); Li1–O5 1.9008(1).

Thus, L^1 proved to be a better ligand support in carbonyl hydroboration catalysts based on alkali metals.[24] It apparently clings on to the lithium in solution and prevents oligomerization while retaining the Lewis acidity at the same time.[9, 27] Dynamic coordination further ensures accessibility of the metal center.[9, 24] PMDTA and TMEDA presumably fail to bind lithium tightly enough in THF and thus exhibit almost no influence. This is supported by the fact that a [(TMEDA)Li][$HBPh_3$] complex could not be isolated by reacting [Li($HBPh_3$)] with TMEDA in THF or even in neat TMEDA. Attempted crystallization from a reaction mixture at −30 °C invariably resulted in the precipitation of [Li($HBPh_3$)]. This is intriguing considering the innumerable examples of TMEDA bonded lithium complexes.[28] However, that may not reflect the magnitude of the chelate effect or the overall strength of the TMEDA→Li interaction. Competition between TMEDA and THF for the de-aggregation of lithium reagents can be puzzling.[27, 29] For example, [Li{$N(SiMe_3)_2$}] independently reacts with 5 equivalents of THF and TMEDA to give dimeric [[Li{$N(SiMe_3)_2$}(thf)]$_2$ and monomeric [(TMEDA)Li{$N(SiMe_3)_2$}], respectively.[27] Thus, TMEDA seems to coordinate stronger, but an equimolar mixture of THF and TMEDA provides [Li{$N(SiMe_3)_2$}(thf)]$_2$ exclusively.[27] Likewise, THF has a substantially greater affinity towards LDA than does TMEDA.[30] Single crystals for the THF-solvated derivatives [M(thf)$_n$($HBPh_3$)] (M = Li, Na, K) could not be obtained.

12-c-4 is known to be an ideal fit for the lithium ion[31] and L^2 can be considered as the aza-version of 12-c-4.[32] The coordinated THF molecules in recrystallized **1·THF** and **5·THF** are weakly bonded and can be removed under vacuum as in the case of [(L^1)Li(thf)][$HBPh_3$].[9] Unlike L^1,[24] no spectroscopic evidence for a labile binding of L^2 and 12-c-4 was found in **1** and **5** in the temperature range between 193 and 298K. L^2 and 12-c-4 thus apparently provide rigid chelations to Li^+ and saturate its coordination sphere. This may also significantly decrease the Lewis acidity/electrophilicity of lithium, which is ultimately manifested in their poorer performance in hydroboration catalysis.

Conclusion

Me_6TREN and Me_4TACD are both tetradentate but differ in their coordination topology. Both are suitable as ancillary ligands for mononuclear group 1 metal complexes. The present work has shown the differences in the structure and catalytic hydroboration activity of [(L)M($HBPh_3$)] (M = Li, Na, K). Some other chelating ligands were also studied, showing significant variation in catalytic activity with the ligand choice for lithium (Fig. 6). While the tripodal Me_6TREN offers a unique combination of flexible coordination and retention of Lewis acidity, the macrocyclic crown ether (12-c-4) and tetraaza crown (Me_4TACD) impart more rigidity and decreased Lewis acidity. TMEDA and PMDTA have only marginal effect compared to the ligand-free catalysis.

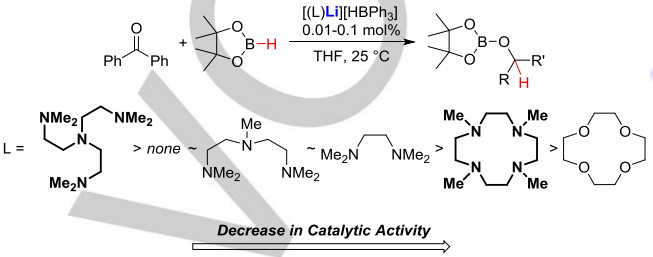


Figure 6. Influence of the donor L in [(L)Li][$HBPh_3$] on the catalytic hydroboration of benzophenone by pinacolborane.

Experimental Section

General considerations. All reactions were performed in a dry argon atmosphere using standard Schlenk techniques or under argon atmosphere of a glovebox, unless otherwise indicated. Prior to use, glassware was dried overnight at 130 °C and solvents were dried, distilled, and degassed using standard methods. [M($HBPh_3$)] and [(L^1)M][$HBPh_3$] (M = Li, Na, K),[4, 9] and [L^2][33] were synthesized according to the literature procedure. BPh_3 (95% pure) was purchased from abcr and purified by sublimation. ^{1}H, ^{13}C{^{1}H}, ^{11}B, and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker DRX400 spectrometer at ambient temperature unless otherwise mentioned. Chemical shifts (δ in ppm) in the ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual signals of the deuterated solvents. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet) br (broad). IR spectra were recorded on KBr pellets using an AVATAR 360 FT-IR spectrometer. Elemental analyses were performed on an elementar vario EL machine. X-ray diffraction data were collected on a Bruker APEX II diffractometer. Single crystal diffraction data is reported in crystallographic information files (cif) accompanying this document.

[(L^2)Li][$HBPh_3$] (1). A solution of Li{$N(SiHMe_2)_2$}] (0.100 g, 0.718 mmol) and L^2 (0.165 g, 0.722 mmol) in THF (2 mL) were stirred at room temperature. After 10 min, a solution of BPh_3 (0.177 g, 0.730 mmol) in 1 mL of THF was added dropwise and the resulting mixture was stirred for additional 2 h at room temperature. The solution was concentrated under reduced pressure. Addition of *n*-pentane (5 mL) precipitated a white solid, which was further washed with *n*-pentane (3 x 2 mL) and dried under vacuum to give analytically pure **1** (0.315 g, 0.658 mmol, 92% yield) as a white powder. X-ray diffraction quality single crystals were obtained from slow *n*-pentane diffusion into a concentrated THF solution of **1** at −35 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 7.26 (m, 6 H, *o*-Ph), 6.83 (m, 6 H, *m*-Ph), 6.66 (m, 3 H, *p*-Ph), 3.23 (br, q, 1 H, *H*B), 2.53 (m, 8 H, CH_2), 2.21 (s, 20 H, CH_2 and N*Me*). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 166.1 (*ipso*-Ph), 136.7 (*o*-Ph), 126.1 (*m*-Ph), 121.7 (*p*-Ph), 54.5 (CH_2), 44.3 (N*Me*). ^{11}B NMR (128 MHz, THF-d_8): δ −10.0 (d, $^1J_{BH}$ = 76 Hz). ^{7}Li{^{1}H} NMR (156 MHz, THF-d_8): δ −1.8. IR (KBr): ν = 2212-1800 cm^{-1} (multiple bands, ν_{BH}). Anal. Calcd. For $C_{30}H_{44}N_4BLi$: C, 75.31; H, 9.27; N, 11.71. Found: C, 75.02; H, 9.13; N, 11.53.

[(L^2)Na][HBPh$_3$] (2). A solution of L^2 (0.100 g, 0.438 mmol) in 2 mL of THF was added dropwise to a solution of [Na(HBPh$_3$)] (0.114 g, 0.428 mmol) in 1 mL of THF. The resulting mixture was stirred for 0.5 h at room temperature. All the volatiles were removed under reduced pressure to give a white solid. The solid was washed with *n*-pentane (3 x 2 mL) and dried under vacuum to give analytically pure **2** (0.196 g, 0.396 mmol, 91% yield) as a white powder. X-ray diffraction quality single crystals were obtained from slow *n*-pentane diffusion into a concentrated THF solution of **2** at –35 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 7.28 (m, 6 H, *o*-Ph), 6.91 (m, 6 H, *m*-Ph), 6.76 (m, 3 H, *p*-Ph), 3.23 (br, q, 1 H, *H*B), 2.51 (m, 8 H, C*H*$_2$), 2.17 (s, 20 H, C*H*$_2$ and N*Me*). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 164.0 (*ipso*-Ph), 136.4 (*o*-Ph), 126.7 (m-Ph), 122.6 (p-Ph), 54.5 (CH$_2$), 44.7 (NMe). ^{11}B NMR (128 MHz, THF-d_8): δ –8.4 (d, $^1J_{BH}$ = 76 Hz). IR (KBr): ν = 2158-1980 cm^{-1} (multiple bands, ν_{BH}). Anal. Calcd. for $C_{30}H_{44}N_4BNa$: C, 72.87; H, 8.97; N, 11.33. Found: C, 72.14; H, 8.95; N, 11.27.

[(L^2)K][HBPh$_3$] (3). A solution of L^2 (0.100 g, 0.438 mmol) in 2 mL of THF was added dropwise to a solution of [K(HBPh$_3$)] (0.118 g, 0.418 mmol) in 1 mL of THF. The resulting mixture was stirred for 0.5 h at room temperature. All the volatiles were removed under reduced pressure to give a white solid. The solid was washed with *n*-pentane (3 x 2 mL) and dried under vacuum to obtain analytically pure **3** (0.188 g, 0.369 mmol, 89% yield) as a white powder. X-ray diffraction quality single crystals were obtained from slow *n*-pentane diffusion into a concentrated THF solution of **3** at –35 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 7.30 (m, 6 H, *o*-Ph), 6.94 (m, 6 H, *m*-Ph), 6.78 (m, 3 H, *p*-Ph), 3.20 (br, q, 1 H, *H*B), 2.25 (m, 28 H, C*H*$_2$ and NMe$_2$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 163.6 (*ipso*-Ph), 136.3 (*o*-Ph), 126.9 (*m*-Ph), 122.8 (*p*-Ph), 54.9 (*C*H$_2$), 44.5 (N*Me*). ^{11}B NMR (128 MHz, THF-d_8): δ –7.9 (d, $^1J_{BH}$ = 78 Hz). IR (KBr, cm^{-1}): ν = 2168-1980 cm^{-1} (multiple bands, ν_{BH}). Anal. Calcd. for $C_{30}H_{44}N_4BK$: C, 70.57; H, 8.69; N, 10.97. Found: C, 70.23; H, 8.54; N, 11.28.

[(PMDTA)Li][HBPh$_3$] (4). A solution of PMDTA (0.100 g, 0.577 mmol) in 2 mL of THF was added dropwise to a solution of [Li(HBPh$_3$)] (0.143 g, 0.571 mmol) in 1 mL of THF. The resulting mixture was stirred for 0.5 h at room temperature. All the volatiles were removed under reduced pressure to give a white solid. The solid was washed with *n*-pentane (3 x 2 mL) and dried under vacuum to afford analytically pure **4** (0.221 g, 0.522 mmol, 91% yield) as a white powder. ^{1}H NMR (400 MHz, THF-d_8): δ 7.23 (m, 6 H, *o*-Ph), 6.83 (m, 6 H, *m*-Ph), 6.66 (m, 3 H, *p*-Ph), 3.44 (br, q, 1 H, *H*B), 2.42 (m, 4 H, C*H*$_2$), 2.32 (m, 4 H, C*H*$_2$), 2.30 (s, 3 H, N*Me*), 2.21 (s, 12 H, N*Me*$_2$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 165.9 (*ipso*-Ph), 136.7 (*o*-Ph), 126.1 (*m*-Ph), 121.8 (*p*-Ph), 59.0 (*C*H$_2$), 57.2 (*C*H$_2$), 46.3 (N*Me*$_2$), 43.6 (N*Me*). ^{11}B NMR (128 MHz, THF-d_8): δ –8.2 (d, $^1J_{BH}$ = 79 Hz). ^{7}Li{^{1}H} NMR (156 MHz, THF-d_8): δ –0.4. IR (KBr): ν = 2151-1900 (multiple bands, ν_{BH}). Anal. Calcd. for $C_{27}H_{39}N_3BLi$: C, 76.60; H, 9.29; N, 9.93. Found: C, 76.12; H, 8.95; N, 9.39.

[(12-c-4)Li][HBPh$_3$] (5). A solution of 12-crown-4 (0.100 g, 0.567 mmol) in 2 mL of THF was added dropwise to a solution of [Li(HBPh$_3$)] (0.140 g, 0.560 mmol) in 1 mL of THF. The resulting mixture was stirred for 0.5 h at room temperature. All the volatiles were removed under reduced pressure to give a white solid. The solid was washed with *n*-pentane (3 x 2 mL) and dried under vacuum to give analytically pure **5** (0.233 g, 0.546 mmol, 98% yield) as a white powder. X-ray diffraction quality single crystals were obtained from slow *n*-pentane diffusion into a concentrated THF solution of **5** at –35 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 7.29 (m, 6 H, *o*-Ph), 6.86 (m, 6 H, *m*-Ph), 6.69 (m, 3 H, *p*-Ph), 3.33 (br, q, 1 H, *H*B), 3.57 (s, 16 H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 164.7 (*ipso*-Ph), 136.7 (*o*-Ph), 126.3 (*m*-Ph), 122.0 (*p*-Ph), 70.1 (*C*H$_2$). ^{11}B NMR (128 MHz, THF-d_8): δ –8.0 (d, $^1J_{BH}$ = 78 Hz). ^{7}Li{^{1}H} NMR (156 MHz, THF-d_8): δ –0.4. IR (KBr): ν = 2212-1880 cm^{-1} (multiple bands, ν_{BH}). Anal. Calcd. for $C_{26}H_{32}O_4BLi$: C, 73.26; H, 7.57. Found: C, 72.59; H, 7.93.

Typical NMR-scale catalytic hydroboration. A J. Young-style NMR tube was charged with substrate (0.27 mmol), HBpin (0.27 mmol), and 0.5 mL of a 2:1 mixture of THF and THF-d_8. Desired catalyst loading was set by adding an appropriate volume of THF-d_8 stock solution of catalyst of known concentration using a microliter syringe. Reaction progress was monitored at room temperature using NMR spectroscopy. The products were characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy and compared with literature data.[9]

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft through the International Research Training Group "Selectivity in Chemo- and Biocatalysis" for financial support and the Alexander von Humboldt Foundation for a fellowship to D. M. We also thank M.Sc. K.-N. Truong and Prof. U. Englert for collecting X-ray data.

Keywords: Alkali metals • Catalysis • Hydroboration • Me$_6$TREN • Aza-crown

[1] a) S. Krieck, M. Westerhausen, *Inorganics* **2017**, *5*, 17; b) Y. Sarazin, J.-F. Carpentier, *Chem. Rec.* **2016**, *16*, 2482-2505; c) M. S. Hill, D. J. Liptrot C. Weetman, *Chem. Soc. Rev.* **2016**, *45*, 972-988; d) S. Harder, *Chem. Rev.* **2010**, *110*, 3852-3876; e) R. Rochat, M. J. Lopez, H. Tsurugi, K. Mashima, *ChemCatChem* **2016**, *8*, 10-20; f) K. Revunova, G. I. Nikonov, *Dalton Trans.* **2015**, *44*, 840-866; g) C. C. Chong, R. Kinjo, *ACS Catal.* **2015**, *5*, 3238-3259.

[2] a) C. B. Herbert, P. V. Ramachandran, in *Reductions in Organic Synthesis, Vol. 641*, American Chemical Society, **1996**, pp. 1-30; b) S. Krishnamurthy, H. C. Brown, *J. Org. Chem.* **1979**, *44*, 3678-3682; c) B. Singaram, T. E. Cole, H. C. Brown, *Organometallics* **1984**, *3*, 774-777; d) H. C. Brown, S. Narasimhan, *J. Org. Chem.* **1982**, *47*, 1604-1606; e) H. C. Brown, S. Krishnamurthy, J. L. Hubbard, R. A. Coleman, *J. Organomet. Chem.* **1979**, *166*, 281-291; f) H. C. Brown, S. Krishnamurthy, *J. Chem. Soc., Chem. Commun.* **1972**, 868-869; g) H. C. Brown, G. W. Kramer, J. L. Hubbard, S. Krishnamurthy, *J. Organomet. Chem.* **1980**, *188*, 1-10; h) C. A. Brown, S. Krishnamurthy, *J. Org. Chem.* **1986**, *51*, 238-240; i) C. A. Brown, J. L. Hubbard, *J. Am. Chem. Soc.* **1979**, *101*, 3964-3966; j) B. Singaram, T. C. Jackson, J. Harrison, *Synlett* **1996**, *1996*, 383-384; k) E. R. H. Walker, *Chem. Soc. Rev.* **1976**, *5*, 23-50.

[3] a) G. Wittig, G. Keicher, A. Rückert, P. Raff, *Justus Liebigs Ann. Chem.* **1949**, *563*, 110-126; b) G. Wittig, A. Rückert, *Justus Liebigs Ann. Chem.* **1950**, *566*, 101-113; c) G. Wittig, W. Stilz, *Justus Liebigs Ann. Chem.* **1956**, *598*, 85-92.

[4] N. M. Yoon, K. E. Kim, J. Kang, *J. Org. Chem.* **1986**, *51*, 226-229.

[5] Z. M. Heiden, A. P. Lathem, *Organometallics* **2015**, *34*, 1818-1827.

[6] a) N. M. Yoon, K. E. Kim, *J. Org. Chem.* **1987**, *52*, 5564-5570; b) K. E. Kim, S. B. Park, N. M. Yoon, *Synth. Commun.* **1988**, *18*, 89-96.

[7] a) V. K. Dioumaev, K. Plössl, P. J. Carroll, D. H. Berry, *Organometallics* **2000**, *19*, 3374-3378; b) E. L. Werkema, R. A. Andersen, A. Yahia, L. Maron, O. Eisenstein, *Organometallics* **2009**, *28*, 3173-3185; c) K. Yan, G. Schoendorff, B. M. Upton, A. Ellern, T. L. Windus, A. D. Sadow, *Organometallics* **2013**, *32*, 1300-1316; d) H. Li, A. J. A. Aquino, D. B. Cordes, F. Hung-Low, W. L. Hase, C. Krempner, *J. Am. Chem. Soc.* **2013**, *135*, 16066-16069.

[8] More than 4000 structures containing [BPh$_4$]$^-$ have been deposited in CSD.

[9] D. Mukherjee, H. Osseili, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2016**, *138*, 10790-10793.

[10] a) D. M. Cousins, M. G. Davidson, C. J. Frankis, D. Garcia-Vivo, M. F. Mahon, *Dalton Trans.* **2010**, *39*, 8278-8280; b) M. G. Davidson, D. Garcia-Vivo, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, *Chem. Eur. J.* **2011**, *17*, 3364-3369; c) A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, G. M. Robertson, S. D. Robertson, *Angew. Chem. Int. Ed.* **2011**, *50*, 8375-8378; *Angew. Chem.* **2011**, *123*, 8525-8528; d) D. R. Armstrong, M. G. Davidson, D. Garcia-Vivo, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, *Inorg. Chem.* **2013**, *52*, 12023-12032; e) A. R. Kennedy, R. E. Mulvey, R. I. Urquhart, S. D. Robertson, *Dalton Trans.* **2014**, *43*, 14265-14274; f) S. D. Robertson, A. R. Kennedy, J. J. Liggat, R. E.

Mulvey, *Chem. Commun.* **2015**, *51*, 5452-5455; g) V. Leich, T. P. Spaniol, J. Okuda, *Chem. Commun.* **2015**, *51*, 14772-14774; h) A. R. Kennedy, R. McLellan, G. J. McNeil, R. E. Mulvey, S. D. Robertson, *Polyhedron* **2016**, *103, Part A*, 94-99.

[11] a) J. Dyke, W. Levason, M. E. Light, D. Pugh, G. Reid, H. Bhakhoa, P. Ramasami, L. Rhyman, *Dalton Trans.* **2015**, *44*, 13853-13866; b) V. Leich, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2016**, *55*, 4794-4797; *Angew. Chem.* **2016**, *128*, 4872-4876.

[12] a) S. Arndt, M. U. Kramer, W. Fegler, Y. Nakajima, I. Del Rosal, R. Poteau, T. P. Spaniol, L. Maron, J. Okuda, *Organometallics* **2015**, *34*, 3739-3747; b) R. L. Webb, M. L. Mino, E. L. Blinn, A. A. Pinkerton, *Inorg. Chem.* **1993**, *32*, 1396-1402; c) J. Cho, R. Sarangi, J. Annaraj, S. Y. Kim, M. Kubo, T. Ogura, E. I. Solomon, W. Nam, *Nat. Chem.* **2009**, *1*, 568-572; d) J. Cho, R. Sarangi, H. Y. Kang, J. Y. Lee, M. Kubo, T. Ogura, E. I. Solomon, W. Nam, *J. Am. Chem. Soc.* **2010**, *132*, 16977-16986; e) H. Kang, J. Cho, K.-B. Cho, T. Nomura, T. Ogura, W. Nam, *Chem. Eur. J.* **2013**, *19*, 14119-14125; f) J. Wallick, C. G. Riordan, G. P. A. Yap, *J. Am. Chem. Soc.* **2013**, *135*, 14972-14974; g) S. Hong, Y.-M. Lee, K.-B. Cho, M. S. Seo, D. Song, J. Yoon, R. Garcia-Serres, M. Clemancey, T. Ogura, W. Shin, J.-M. Latour, W. Nam, *Chem. Sci.* **2014**, *5*, 156-162; h) P. Kumar, Y.-M. Lee, Y. J. Park, M. A. Siegler, K. D. Karlin, W. Nam, *J. Am. Chem. Soc.* **2015**, *137*, 4284-4287.

[13] W. Fegler, A. Venugopal, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2013**, *52*, 7976-7980; *Angew. Chem.* **2013**, *125*, 8134-8138.

[14] a) R. D. Hancock, M. P. Ngwenya, A. Evers, P. W. Wade, J. C. A. Boeyens, S. M. Dobson, *Inorg. Chem.* **1990**, *29*, 264-270; b) J. L. Down, J. Lewis, B. Moore, G. Wilkinson, *J. Chem. Soc.* **1959**, 3767-3773; c) J. S. Bradshaw, K. E. Krakowiak, R. M. Izatt, *The Chemistry of Heterocyclic Compounds, Aza-Crown Macrocycles*, Vol. 51, John Wiley & Sons, Inc., **1993**; d) *The Chemistry of Heterocyclic Compounds*, John Wiley & Sons, Inc., **2008**, pp. 1-29.

[15] D. Mukherjee, S. Shirase, T. P. Spaniol, K. Mashima, J. Okuda, *Chem. Commun.* **2016**, *52*, 13155-13158.

[16] D. Mukherjee, A. K. Wiegand, T. P. Spaniol, J. Okuda, *Dalton Trans.* **2017**, *46*, 6183-6186.

[17] a) C. Strohmann, C. Daschlein, *Chem. Commun.* **2008**, 2791-2793; b) V. Leich, K. Lamberts, T. P. Spaniol, J. Okuda, *Dalton Trans.* **2014**, *43*, 14315-14321.

[18] S.-C. Roşca, H. Roueindeji, V. Dorcet, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Inorganics* **2017**, *5*, 13.

[19] a) D. A. Dougherty, *Acc. Chem. Res.* **2013**, *46*, 885-893; b) S. L. De Wall, E. S. Meadows, L. J. Barbour, G. W. Gokel, *Proc. Natl. Acad. Sci.* **2000**, *97*, 6271-6276; c) D. A. Dougherty, *Science* **1996**, *271*, 163-168; d) J. C. Ma, D. A. Dougherty, *Chem. Rev.* **1997**, *97*, 1303-1324; e) L. M. Salonen, M. Ellermann, F. Diederich, *Angew. Chem. Int. Ed.* **2011**, *50*, 4808-4842; *Angew. Chem.* **2011**, *123*, 4908-4944; f) M. M. Watt, M. S. Collins, D. W. Johnson, *Acc. Chem. Res.* **2013**, *46*, 955-966; g) A. S. Mahadevi, G. N. Sastry, *Chem. Rev.* **2013**, *113*, 2100-2138; h) C. R. Kennedy, S. Lin, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2016**, *55*, 12596-12624; *Angew. Chem.* **2016**, *128*, 12784-12814.

[20] a) U. Pieper, D. Stalke, *Organometallics* **1993**, *12*, 1201-1206; b) D. Hoffmann, W. Bauer, P. v. R. Schleyer, U. Pieper, D. Stalke, *Organometallics* **1993**, *12*, 1193-1200.

[21] C. Lambert, P. R. v. Schleyer, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1129-1140.

[22] D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, *Chem. Commun.* **2002**, 376-377.

[23] a) M. Arrowsmith, T. J. Hadlington, M. S. Hill, G. Kociok-Kohn, *Chem. Commun.* **2012**, *48*, 4567-4569; b) C. C. Chong, H. Hirao, R. Kinjo, *Angew. Chem. Int. Ed.* **2015**, *54*, 190-194; *Angew. Chem.* **2015**, *127*, 192-196; c) T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2014**, *136*, 3028-3031; d) A. A. Oluyadi, S. Ma, C. N. Muhoro, *Organometallics* **2013**, *32*, 70-78; e) S. Yadav, S. Pahar, S. S. Sen, *Chem. Commun.* **2017**, *53*, 4562-4564; f) K. Manna, P. Ji, F. X. Greene, W. Lin, *J. Am. Chem. Soc.* **2016**, *138*, 7488-7491; g) N. Eedugurala, Z. Wang, U. Chaudhary, N. Nelson, K. Kandel, T. Kobayashi, I. I. Slowing, M. Pruski, A. D. Sadow, *ACS Catal.* **2015**, *5*, 7399-7414; h) L. Koren-Selfridge, H. N. Londino, J. K. Vellucci, B. J. Simmons, C. P. Casey, T. B. Clark, *Organometallics* **2009**, *28*, 2085-2090; i) A. Kaithal, B. Chatterjee, C. Gunanathan, *Org. Lett.* **2015**, *17*, 4790-4793; j) J. Guo, J. Chen, Z. Lu, *Chem. Commun.* **2015**, *51*, 5725-5727; k) S. Bagherzadeh, N. P. Mankad, *Chem. Commun.* **2016**, *52*, 3844-3846; l) G. Zhang, H. Zeng, J. Wu, Z. Yin, S. Zheng, J. C. Fettinger, *Angew. Chem. Int. Ed.* **2016**, *55*, 14369-14372; *Angew. Chem.* **2016**, *128*, 14581-14584; m) M. W. Drover, L. L. Schafer, J. A. Love, *Angew. Chem. Int. Ed.* **2016**, *55*, 3181-3186; *Angew. Chem.* **2016**, *128*, 3233-3238; n) I. P. Query, P. A. Squier, E. M. Larson, N. A. Isley, T. B. Clark, *J. Org. Chem.* **2011**, *76*, 6452-6456; o) V. K. Jakhar, M. K. Barman, S. Nembenna, *Org. Lett.* **2016** *18*, 4710-4713; p) A. Y. Khalimon, P. Farha, L. G. Kuzmina, G. I. Nikonov, *Chem. Commun.* **2012**, *48*, 455-457; q) P. A. Lummis, M. R. Momeni, M. W. Lui, R. McDonald, M. J. Ferguson, M. Miskolzie, A. Brown, E. Rivard, *Angew. Chem. Int. Ed.* **2014**, *53*, 9347-9351; *Angew. Chem.* **2014**, *125*, 9501-9505; r) A. E. King, S. C. E. Stieber, N. J. Henson, S. A. Kozimor, B. L. Scott, N. C. Smythe, A. D. Sutton, J. C. Gordon, *Eur. J. Inorg. Chem.* **2016**, *2016*, 1635-1640.

[24] H. Osseili, D. Mukherjee, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2017**, DOI: 10.1021/jacs.6b06319.

[25] D. Mukherjee, H. Osseili, K.-N. Truong, T. P. Spaniol, J. Okuda, *Chem. Commun.* **2017**, *53*, 3493-3496.

[26] B. Wilde, A. Jaenschke, F. Olbrich, *Z. Anorg. Allg. Chem.* **2008**, *634*, 166-172.

[27] a) D. B. Collum, *Acc. Chem. Res.* **1992**, *25*, 448-454; b) B. L. Lucht, M. P. Bernstein, J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc.* **1996**, *118*, 10707-10718.

[28] A CSD search gave nearly 800 hits.

[29] Neufeld, R. Michel, R. Herbst-Irmer, R. Schöne, D. Stalke, *Chem. Eur. J.* **2016**, *22*, 12340-12346.

[30] M. P. Bernstein, F. E. Romesberg, D. J. Fuller, A. T. Harrison, D. B. Collum, Q. Y. Liu, P. G. Williard, *J. Am. Chem. Soc.* **1992**, *114*, 5100-5110.

[31] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.

[32] D. Mukherjee, T. P. Spaniol, J. Okuda, *Dalton Trans.* **2017**, *46*, 651-655.

[33] J. Coates, D. Hadi, S. Lincoln, *Aust. J. Chem.* **1982**, *35*, 903-909.

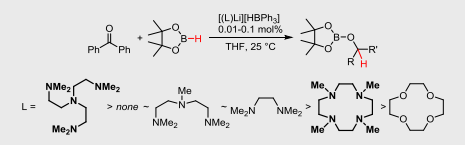
10.1002/chem.201702818

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Comparison of ligands L on the catalytic carbonyl hydroboration by [(L)M][$HBPh_3$] (M = Li, Na, K) confirms the unique combination of Me_6TREN and lithium for high activity.



*Hassan Osseili, Debabrata Mukherjee, Thomas P. Spaniol, Jun Okuda**

Page No. – Page No.

Ligand influence on the carbonyl hydroboration catalysis by alkali metal hydridotriphenylborates [(L)M][$HBPh_3$] (M = Li, Na, K)