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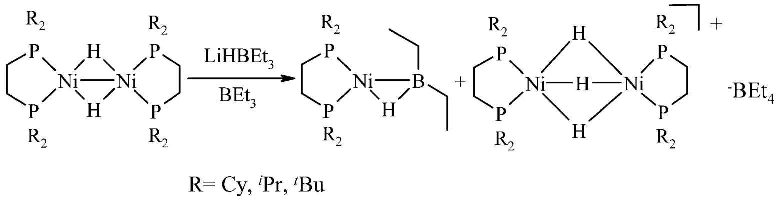

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σ-Borane Coordinated to Nickel(0) and Some Related Nickel(II) Trihydride Complexes

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Abstract: The reactions of the complexes [(dcype)NiH]$_2$, **1**, [(dippe)NiH]$_2$, **2**, and [(dtbpe)NiH]$_2$, **3**, with a mixture of BEt$_3$ and Super-Hydride (LiHBEt$_3$) afforded σ-borane nickel(0) compounds of the type [(dcype)Ni(σ-HBEt$_2$)], **4**, [(dippe)Ni(σ-HBEt$_2$)], **5**, [(dtbpe)Ni(σ-HBEt$_2$)], **6**, respectively, with the concomitant formation in each case of [(dcype)$_2$Ni$_2$(H)$_3$][BEt$_4$], **7**, [(dippe)$_2$Ni$_2$(H)$_3$][BEt$_4$], **8** and [(dtbpe)$_2$Ni$_2$(H)$_3$][BEt$_4$], **9**, respectively. X-ray crystal structures are reported for **4** and **8**.The reaction of BEt$_3$ and LiHBEt$_3$ was also reviewed in detail.

Introduction

The activation of unreactive bonds is currently a very active area in organometallic chemistry, although a relatively limited number of successful systems able to accomplish such cleavage have been reported thus far.[1] We have found the use of low-valent late-transition metal complexes to be practical in the C−C bond activation of aryl and hetero-aryl cyanides, that we have recently extended to a variety of alkylnitriles using [(dippe)NiH]$_2$. In all the cases, this leads to the formation of an η^2-nitrile complex of nickel (0) that in the case of aryl and hetero-aryl cyanides undergoes oxidative addition, with mild warming, to form the corresponding nickel(II) complexes. With the alkyl nitriles, such oxidative addition is strongly dependent on the chain length, and eventually it can be inhibited.[2] Both types of compounds were isolated and were fully characterized structurally. As part of our ongoing studies in the field, we decided to extend the chemistry of some of the nickel complexes to investigate the reactivity of other interesting substrates such as alkyl boranes and the closely related borohydrides, with the aim of stabilizing boron-containing moieties, among them σ-boranes coordinated to a low-valent late-transition metal such as nickel (0).

The area of borane and boryl reactivity has been actively studied,[3] particularly for transition metal complexes using a variety of early-[4] and late-transition metals,[5] the isolation of σ-borane complexes being of great interest due to their participation in a number of catalytic systems with steps involving B−H activation and release. Some relevant examples in that field have been published by Hartwig[6] with the use of early transition metals and by Sabo-Etienne[7] with the use of

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(1) For a recent review of these topics, see: *Topics in Organometallic Chemistry. Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer-Verlag: Berlin, 1999.

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polyhydride ruthenium (II) complexes. However, to the best of our knowledge, there are no examples of the use of a late transition metal with a d^{10} configuration to stabilize a coordinated σ−borane.

We report here our findings on the reactivity of nickel (I) hydride dimeric compounds to yield σ-borane nickel(0) complexes of the type [(diphosphine)Ni(σ-$HBEt_2$)], along with the co-formation of [(diphosphine)$_2Ni_2(H)_3$][BEt_4].

Results and Discussion

Stoichiometric Reaction of BEt_3 with $LiHBEt_3$: Concomitant Formation of $(HBEt_2)_2$ and $LiBEt_4$. The stoichiometric reaction of BEt_3 with Super-Hydride ($LiHBEt_3$-THF), at room temperature under argon, affords the concomitant formation of $(HBEt_2)_2$ and $LiBEt_4$; the reaction occurs immediately, after the reactants have been mixed. The ^1H NMR spectrum of this mixture, shows two overlapping, broad resonance signals centered at δ 0.86 and δ 0.84, that we have assigned as the methylene and methyl protons of $(HBEt_2)_2$. The appearance of the latter is consistent with the presence of a second pair of multiplets centered at δ 0.6 (*t* of 1:1:1:1 *q*, $^3J(^1H,^{11}B) = 3$ Hz) and δ −0.2 (*q* of 1:1:1:1 *q*, $^2J(^1H,^{11}B) = 4.2$ Hz) that correspond to the methyl and methylene protons of $[BEt_4]^-$.[8] A third small, broad resonance that overlaps with the $(HBEt_2)_2$ proton signals on the left-hand side (δ 1.02 to δ 0.95) was also observed in the ^1H NMR spectrum and was assigned to unreacted BEt_3 by direct comparison with an authentic sample of BEt_3, also in THF-d_8.[8a] Unreacted $LiHBEt_3$ was barely detectable, except for a very small, broad signal centered at δ 0.002, presumably associated to the $[HBEt_3]^-$ hydride. The fact that the proton resonances of both BEt_3 and $LiHBEt_3$ have practically disappeared, at least in the ^1H NMR time scale, is consistent with a thermodynamically favored reaction. Our interpretation of the reaction that occurs is as follows:

$$2\,BEt_3 + 2\,LiHBEt_3 \rightarrow (HBEt_2)_2 + 2\,LiBEt_4 \qquad (1)$$

The inspection of the ^{11}B and the $^{11}B\{^1H\}$ NMR spectra of the same reaction mixture, also shows that $LiHBEt_3$ and BEt_3 are consumed in a reaction where $(HBEt_2)_2$ and $LiBEt_4$ are formed. Both ^{11}B and $^{11}B\{^1H\}$ NMR spectra feature the presence of residual BEt_3, δ 70.75 (br), besides of $(HBEt_2)_2$, δ 37.72 (br) and $LiBEt_4$, δ −17.5, the latter appears as a narrow singlet that sharpens further upon proton decoupling and thus evidences the presence of a scalar coupling between the boron and the hydrogen atoms. The resonance for $LiBEt_4$ is also much sharper in the $^{11}B\{^1H\}$ NMR spectrum than the corresponding BEt_3 peak, indicating a lessening of quadrupolar interaction because of tetrahedral symmetry.[9] No remaining $LiHBEt_3$ was observed in either the ^{11}B or the $^{11}B\{^1H\}$ NMR spectra. This can be rationalized in terms of the reaction that occurs, although an exchange equilibrium between $LiHBEt_3$ and BEt_3 has also been reported previously.[10] The residual BEt_3 could nevertheless be exchanging with the $(HBEt_2)_2$ formed in the reaction, as the chemical shifts of both species are seemingly displaced from their ordinary values in THF (δ 78.3 for BEt_3 and δ 27.8 for $(HBEt_2)_2$) and appear at slightly closer proximity. In fact, this situation has been reported to occur by Wrackmeyer when $(HBEt_2)_2$ is independently prepared from BEt_3 and BH_3·THF.[11]

As part of the present work, once the stoichiometric reaction $LiHBEt_3$ with BEt_3 had been properly established, its role in the integrity and performance of the commercial stocks of Super-Hydride was investigated. At first glance, the reaction acts as a disproportionation of the Super-Hydride solution into $(HBEt_2)_2$ and $LiBEt_4$. Similarly, Brown has reported the disproportionation of $LiHB(OMe)_3$ into both $LiBH_2(OMe)_2$ and $LiB(OMe)_4$ during a series of studies performed during the 1950s.[12] This result is in agreement with Cole-Hamilton's observation, using ^{11}B NMR, for the formation of a significant amount of $[BH_2Et_2]^-$ (δ −16.54, *t*, $^1J(^{11}B,^1H) = 69$ Hz) besides $[BEt_4]^-$ (δ −16.02, *s*), in a batch of Super-Hydride.[8c] The existence of the closely related lithium dialkylboron-dihydrides, $Li[BH_2R_2]$, of 9-borabicyclo[3.3.1]nonane, 9-BBN, (δ −17.3), dicyclohexylborane (δ −12.5), and disiamylborane (δ −14.9), has also been confirmed by ^{11}B NMR.[13] The resonances of the latter were reported to appear in the tetrahedral boron region of the ^{11}B NMR spectra, at slightly lower field than the corresponding lithium tetraalkylborate analogues, which were concomitantly formed when the precursor boranes were reacted with alkyllithium sources such as *n*-BuLi. The lithium dialkylboron-dihydride signals appeared as triplets with $^1J(^{11}B,^1H)$ of 70 Hz as expected for one boron bound to two hydrogen atoms, whereas the tetraalkylborates appeared as singlets.

Furthermore, in that work, the reaction of equimolar amounts of the tetraalkylborate, lithium dialkyl-9-BBN, with 9-BBN was examined. On standing, 9-BBN reacted slowly with the tetraalkylborate to form lithium dihydride-9-BBN and B-alkyl-9-BBN. The process was thought to occur through the formation of the corresponding lithium trialkylborohydride, as an intermediate, which would rapidly lose the elements of lithium hydride to the stronger Lewis acid, 9-BBN, forming the final dialkylboron-dihydride and trialkylborane observed by ^{11}B NMR, as illustrated in Scheme 1. No traces of such intermediate (lithium trialkylborohydride) could be obtained from the reaction follow-up at the time.

The reaction of 9-BBN with lithium dialkyl-9-BBN, as pictured, is similar to the results reported by Cole-Hamilton with Super-Hydride,[8c] as much as there is an excess of $LiHBEt_3$ in the bulk solution that is likely to react with the $(HBEt_2)_2$ formed in situ to promote the equimolar formation of $Li[BH_2Et_2]$ and $Li[BEt_4]$. Moreover, since the reaction between $LiHBEt_3$ and BEt_3 as depicted in eq 1 is likely to be a simple reaction, the presence of BEt_3 in a batch of Super-Hydride should be enough

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[8] For a description of the chemical shifts of the CH_2 and CH_3 protons in the $[BEt_4]^-$ anion, see: (a) Noth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *12*, 23. (b) Thaler, E.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 374. For a complete description of the chemical shift, multiplicity, and coupling constants for CH_2 and CH_3 to ^{11}B in the $[BEt_4]^-$ anion in CD_3NO_2, see: (c) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2501.

[9] The ^{11}B chemical shift of BEt_3 is reported to be δ 86.6 while the chemical shift of $LiBEt_4$ is reported to be δ −17.48, relative to external BF_3·Et_2O; the chemical shift signs are updated according to present convention, denoting the resonances downfield from this standard as positive: Thompson, R. J.; Davis, J. C., Jr. *Inorg. Chem.* **1965**, *4*(10), 1464.

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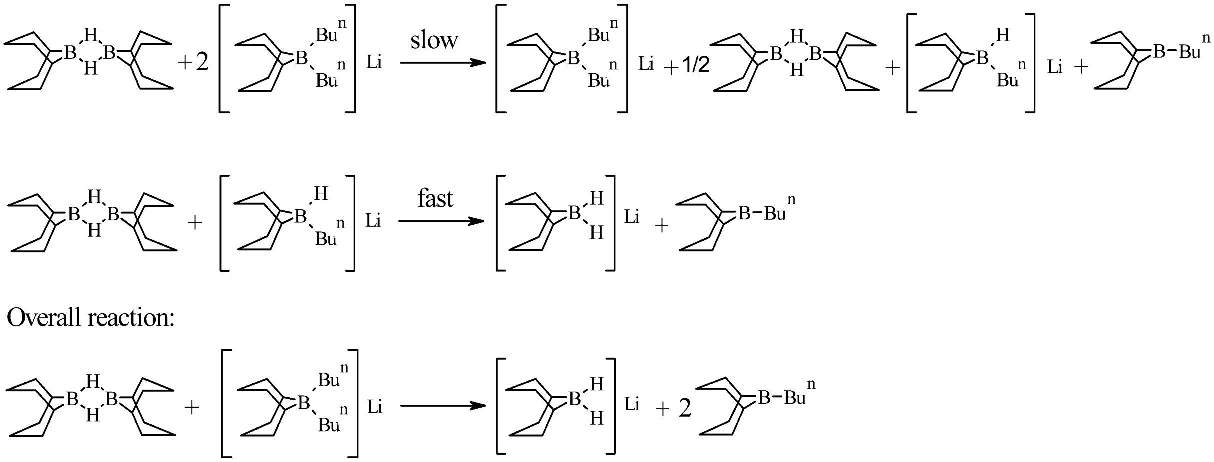
[13] Hubbard, J. L.; Kramer, G. W. *J. Organomet. Chem.* **1978**, *156*, 81.

Scheme 1. Reaction of 9-BBN with Lithium Dialkyl-9-BBN[13]



to engage in the disproportionation of the reagent. In our case, a rationale for the fact that the we detect $(HBEt_2)_2$ instead of the lithium dialkylborohydride, $Li[BH_2Et_2]$, may be given in terms of the spontaneity of the reaction and the stoichiometry used for it, that prevents further reactivity between $(HBEt_2)_2$ and $LiHBEt_3$, $(HBEt_2)_2$ being the stronger Lewis acid by analogy to 9-BBN. In a Super-Hydride batch, however, there is always an excess of $LiHBEt_3$, with respect to the amount of $(HBEt_2)_2$ presumably formed from a former reaction with BEt_3 as in eq 1, but $(HBEt_2)_2$ can react further with Super-Hydride to yield $Li[BH_2Et_2]$. Consequently, the presence of $Li[BH_2Et_2]$ and lithium tetraalkylborate, may be expected, particularly in old batches. An examination of the literature regarding examples of in situ formation of $LiBEt_4$ from Super-Hydride, in which $LiBEt_4$ happened to be reactive,[8b,c,14] proved that although Super-Hydride can be kept stable for quite long periods of time under inert conditions (Brown, has reported a 1 year stability of $LiHBEt_3$ in THF solution under dry nitrogen[15]), decomposition of the Super-Hydride solution into $LiBEt_4$ does occur. The degree of decomposition is very variable, ranging from a mere impurity to a very large extent, such that the quantitative formation of complexes with $[BEt_4]^-$ in 30−80% yield have been reported.[8c,14]

In light of such results, a rational explanation for the source of BEt_3 in the commercial Super-Hydride batches, leading to the decomposition of Super-Hydride is also necessary. Assuming that the Super-Hydride solution is provided without excess BEt_3 and properly kept in absence of moisture and air and the handling is done properly, it is likely that BEt_3 can originate from quenching of a small amount of $LiHBEt_3$ by adventitious water, giving free BEt_3 and LiOH. Relevant to the discussion at hand, Brown reported the preparation of $LiHBEt_3$ from LiH and BEt_3, under ∼50% excess of the given metal hydride over that required by the stoichiometry, *so as to maintain the final concentration of the reaction mixture at 1.0 M in trialkylborane.* The reaction was interpreted as irreversible in the presence of excess LiH as follows:[15]

$$\mathrm{LiH} + \mathrm{Et_3B} \xrightarrow[24\ \mathrm{h}]{\mathrm{THF},\ 25\ ^\circ\mathrm{C}} \underset{(100\%)}{\mathrm{LiHBEt_3}} \tag{2}$$

It is unclear if the stability tests performed as part of that publication were carried out using the same mixture employing excess alkali metal hydride, but if that had been the case, it is likely that the reversible formation of BEt_3 from $LiHBEt_3$ would have been blocked. Commercial Super-Hydride solution, however, is not reported to be provided with excess LiH,[16] which in turn would explain the fact that $LiHBEt_3$ can be decomposed gradually into $LiBEt_4$ and $(HBEt_2)_2$ or further, to $Li[BH_2Et_2]$.[8c]

Reactions of the Nickel (I) Hydrides with the $(HBEt_2)_2$/$LiBEt_4$ Mixture: Concomitant Formation of the Ni(0) σ-Alkylborane and Ni(II) Trihydride Complexes. Two equivalents of the corresponding nickel (I) hydride **1**, **2**, or **3** were added, at room temperature, to a mixture of Super-Hydride and BEt_3, and the concomitant formation of the Ni(0) σ-alkylboranes **4**, **5**, and **6** and the Ni(II) trihydride complexes **7**, **8**, and **9** was verified spectroscopically in each case for every pair of complexes: **4** and **7**, **5** and **8**, and **6** and **9**. The stoichiometries of the transformations that occur are depicted in Scheme 2.

The ^{11}B NMR chemical shifts of **4**, **5**, and **6**, 43.32 ppm for **4**, 45.38 ppm for **5**, and 48 ppm for **6**, all appear downfield of the free dialkylborane $(HBEt_2)_2$, indicative of the presence of metal−boron bonding in these complexes,[6d] while the chemical shifts of the $[BEt_4]^-$ complexes **7**, **8**, and **9**, all appear respectively as high-field narrow singlets centered at δ −17.5, that sharpen further upon ^{1}H decoupling. The fact that complexes **7**, **8**, and **9**, give rise to singlets in the $^{11}B\{^1H\}$ NMR spectrum is consistent with uncoordinated boron atoms as is expected for a tetraalkyl counterion such as $[BEt_4]^-$.

The ^{1}H NMR spectrum shows high field signals at −7, −6.96, and −7.5 ppm, for **4**, **5**, and **6** respectively, implying direct M−H bonding of the hydrogen atoms of the σ-coordinated alkylboranes in these complexes.[6d] This set of signals can be described as composed by featureless broad resonances; consequently, the magnitude of the scalar coupling could not be

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[14] (a) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 387. (b) Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1554. (c) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 4332. (d) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 3804. (e) Cameron, T. S.; Peach, M. E. *J. Chem. Crystallogr.* **1998**, *28*(12), 919.

[15] Brown, H. C.; Krishnamurty, S.; Hubbard, J. L. *J. Am. Chem. Soc.* **1978**, *100*(11), 3343.

[16] The presence of excess LiH, added to the commercial Super-Hydride (Aldrich) is not indicated on the label of the bottle or in the MSDS available for it.

Scheme 2. Stoichiometries for the Concomitant Formation of the Ni(0) σ-Alkylborane Complexes and the Ni(II) Trihydride Complexes

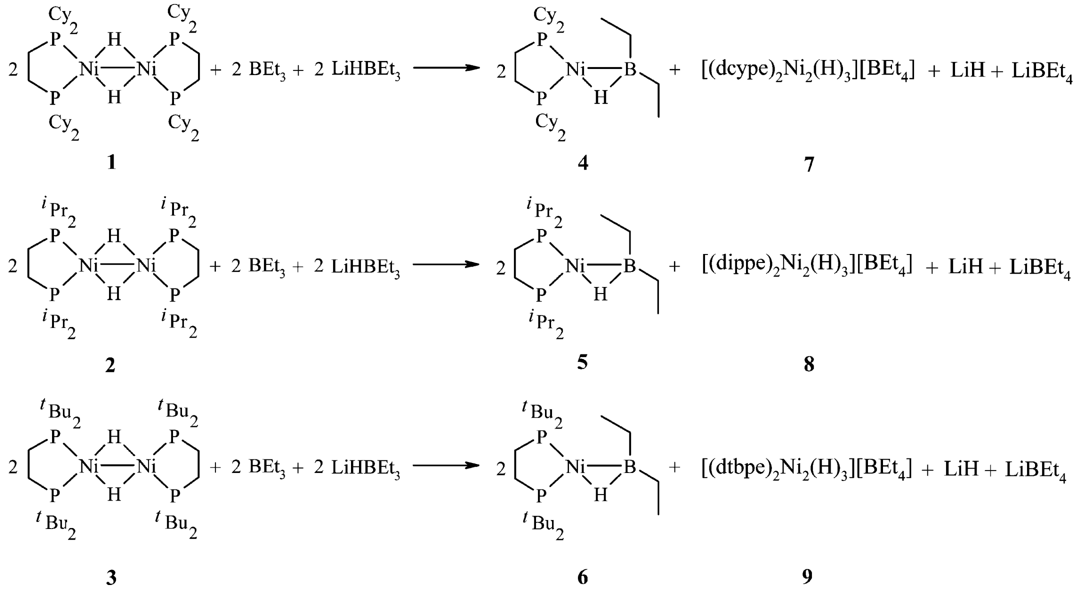

Table 1. $^{31}P\{^1H\}$ NMR Chemical Shifts (ppm) of the Asymmetric Doublets in Complexes **4**, **5**, and **6** and the $^2J_{P-P}$ Coupling Constants (Hz)

complex	δ_1	δ_2	$^2J_{P-P}$
4	72.16	58.27	77.8
5	77.52	66.43	67.8
6	95.90	84.12	63.9

determined. The Ni(II) trihydride complexes **7**, **8**, and **9** all show resonances at higher fields: −13.42 ppm for **7**, −13.31 ppm for **8** and, −15.5 ppm for **9**. These sets of signals are well-defined quintets with scalar coupling constants $^2J_{H-P}$ of 26 Hz that integrate for three hydrides in every case; the multiplicity exhibited by the three equivalent hydrides in **7**, **8**, and **9**, is indicative of the hydride coupling to the four equivalent phosphorus atoms in the dimeric structures. A similar feature is also present in the three starting hydrides **1**, **2**, and **3**.[17]

Further characterization of the Ni(0) σ-alkylboranes **4**, **5**, and **6** and Ni(II) trihydride complexes **7**, **8**, and **9**, was achieved from the $^{31}P\{^1H\}$ NMR spectrum of the corresponding mixtures. All the σ-alkylborane complexes exhibited two slightly broadened asymmetric doublets, characteristic of two types of phosphorus environments, with scalar coupling constants $^2J_{P-P}$ typical of Ni(0) compounds (see Table 1).[2] The fact that the $^{31}P\{^1H\}$ NMR resonances of compounds **4**, **5**, and **6** are characteristic of a Ni(0) system is important as the three center B−H−Ni connectivity is established for the σ-coordinated $HBEt_2$, allowing confirmation of the proposed structures, discarding any oxidative addition.[18]

The Ni(II) trihydride complexes **7**, **8**, and **9**, all exhibit a very sharp singlet at low field in the $^{31}P\{^1H\}$ NMR spectrum: δ 88.5 for **7**, δ 98.92 for **8**, and δ 110.1 for **9**. The latter resonances are observed as quartets upon partial ^1H coupling and become broad and featureless when total coupling to ^1H is permitted. The fact that the ^{31}P NMR signals of **7**, **8**, and **9** appear as quartets upon partial ^1H coupling is consistent with the existence of three equivalent hydrides in solution for all of these complexes, as deduced also from the integration of the respective high-field bridging hydride signals in the ^1H NMR spectra.

Complexes **4** and **8** were also characterized by X-ray crystallography (Figures 1 and 2, respectively). The acquisition parameters for **4** and **8** are given in Table 2 and selected bond distances and angles for each are given in Tables 3 and 4, respectively.

Molecular Structure Analysis of Complex 4. The structure of complex **4** was confirmed by single-crystal X-ray diffraction. The Ni−B bond distance of 2.172(6) Å coincides with the metal−boron bond distance in $(MeCp)Mn(CO)_2(\eta^2\text{-}HBCy_2)$ (2.187(3) Å) which, to the best our knowledge, constitutes the only example of a σ-alkylborane complex previously characterized by X-ray diffraction.[6d] The B−H (1.23(5) Å) and M−H (1.47(5) Å) bond lengths of complex **4** are also comparable to those of $(MeCp)Mn(CO)_2(\eta^2\text{-}HBCy_2)$ (1.24(2) Å and 1.49(2)

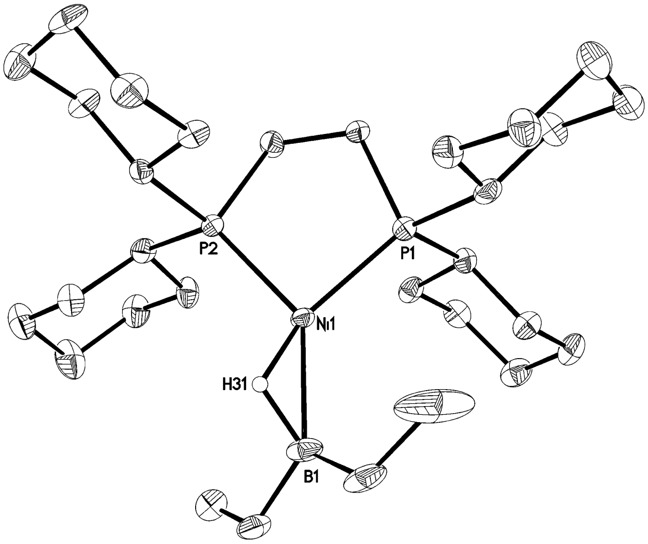

Figure 1. Molecular structure of complex **4** with thermal ellipsoids at the 50% probability level.

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(17) (a) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855. (b) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606.

(18) An oxidative addition to the B−H bond to produce a hydride−metal boryl complex would likely result in a significant lowering of the $^2J_{P-P}$ coupling constant value, expected to be on the order of 20 Hz for a Ni(II) system of this type, on the basis of prior observations with [(dippe)Ni(R)(CN)] and [(dippe)Ni(Ar)(CN)] complexes (see ref 2).

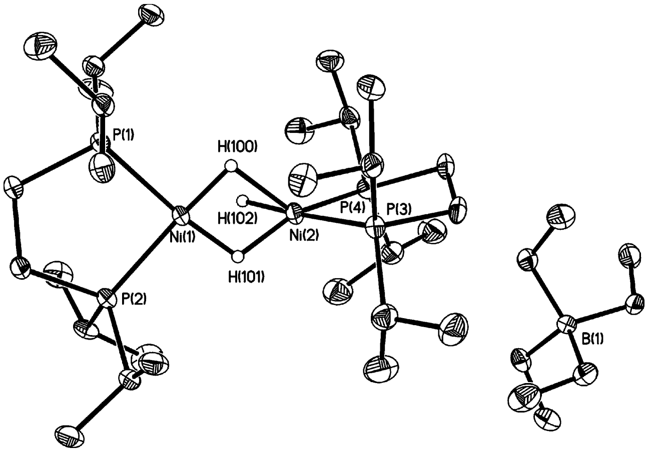

Figure 2. Molecular structure of complex **8** with thermal ellipsoids at the 30% probability level.

Table 2. Acquisition Parameters for **4** and **8**

	4	**8**
empirical formula	$C_{30}H_{59}BNiP_2$	$C_{36}H_{87}BNi_2P_4$
formula weight	551.23	772.17
crystal size/mm^3	0.23 × 0.14 × 0.12	0.32 × 0.26 × 0.17
color of crystal, shape	brown, rectangular	red, block
temperature (K)	100	100
d(calcd)/Mg m^{-3}	1.191	1.153
crystal system	monoclinic	triclinic
space group	Cc	$P\bar{1}$
a/Å	16.697(4)	9.704(2)
b/Å	11.156(2)	15.282(4)
c/Å	17.320(4)	15.492(4)
α/deg	90	102.588(5)
β/deg	107.592(4)	96.823(5)
γ/deg	90	90.702(5)
V/Å^3	3075.0(11)	2224.7(10)
Z value	4	2
μ/mm^{-1}	0.752	1.012
θ range/deg	2.23 to 25.04	1.36 to 28.32
completeness to theta/%	95.9	89.9
no. of rflns collected	5403	16089
no. of indep rflns (R_{int}/%)	3350 (3.33)	9949 (4.45)
abs cor	none	none
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/parameters	3350/2/313	9949/0/420
goodness-of-fit on F^2	1.054	0.895
final R indices ($I > 2\sigma(I)$)/%	$R = 4.25$, $R_w = 9.33$	$R = 4.99$, $R_w = 9.37$
R indices (all data)/%	$R = 4.70$, $R_w = 9.55$	$R = 8.70$, $R_w = 10.16$
largest diff peak and hole/e Å^{-3}	0.546 and −0.300	0.799 and −0.515

Table 3. Selected Bond Distances (Å) and Angles (deg) in Complex **4**

bond	Å	angle	deg
Ni(1)−B(1)	2.172(6)	H(31)−Ni(1)−B(1)	32.77
Ni(1)−H(31)	1.47(5)	B(1)−H(31)−Ni(1)	106.54
B(1)−H(31)	1.23(5)	Ni(1)−B(1)−H(31)	40.69
Ni(1)−P(1)	2.2061(14)	P(1)−Ni(1)−P(2)	89.62(5)
Ni(1)−P(2)	2.2101(14)	B(1)−Ni(1)−P(1)	131.12(18)
		B(1)−Ni(1)−P(2)	139.26(18)
		C(27)−B(1)−C(29)	114.8(4)

Table 4. Selected Bond Distances (Å) and Angles (deg) in Complex **8**

Bond Distances			
Ni(1)−Ni(2)	2.33	Ni(1)−H(101)	1.37(3)
Ni(1)−P(1)	2.1421(10)	Ni(1)−H(102)	2.02(3)
Ni(1)−P(2)	2.1384(10)	Ni(2)−H(100)	1.73(3)
Ni(2)−P(3)	2.1536(10)	Ni(2)−H(101)	1.50(3)
Ni(2)−P(4)	2.1281(10)	Ni(2)−H(102)	1.40(3)
Ni(1)−H(100)	1.37(3)		
Bond Angles			
P(2)−Ni(1)−P(1)	91.01(4)	H(100)−Ni(2)−H(102)	69.4(16)
P(4)−Ni(2)−P(3)	89.75(4)	H(101)−Ni(2)−H(102)	77.5(17)
H(100)−Ni(1)−H(101)	81.3(17)	P(3)−Ni(2)−H(101)	101.4(11)
H(100)−Ni(2)−H(101)	66.6(15)	P(4)−Ni(2)−H(101)	155.0(11)

Å, respectively), confirming the presence of diethylborane σ-coordinated to the Ni(0) moiety [(dippe)Ni], consistent with the spectroscopic data. The analysis of the angles in complex **4** shows further similarities with the σ-alkylborane complex (MeCp)Mn(CO)$_2$(η^2-HBCy$_2$); the angle described by the H−Ni−B system in complex **4** is 32.7°, cf. H−Mn−B (33.2(7)°). The angle described by Ni(1)−B(1)−H(31) (40.69°) is also very close to the Mn−B−H (41.1(9)°) angle in (MeCp)Mn(CO)$_2$(η^2-HBCy$_2$).

On comparing the M−B distance exhibited in **4** (2.172(6) Å) with the M−H distance in the same compound (1.47(5) Å), the difference between them may be explained by the presence of σ-donor substituents on HBEt$_2$ leading to a strong B−H bond, that in fact exhibits the shortest bond length of the three center core (1.23(5) Å).[19] This is remarkable, considering the d^{10} configuration exhibited by the nickel center, which might well have been expected to undergo oxidative addition of the B−H bond.

Molecular Structure Analysis of Complex 8. In the solid-state structure of complex **8**, two of the three hydrides are bridging, while the third appears as a terminal hydride over one of the two nickel atoms in the dimeric structure (Figure 2). The result contrasts with the ^{1}H and ^{31}P{^{1}H} NMR spectra of this complex, suggesting either a triply bridged structure in solution or rapid exchange of the hydrides in solution on the NMR time scale. In fact, the fluxional behavior of the analogous complexes [(dippe)$_2$Ni$_2$H$_3$][BPh$_4$],[20] [(dcype)$_2$Ni$_2$H$_3$][BPh$_4$],[20] [(dtbpe)$_2$Pt$_2$H$_3$][BPh$_4$],[21] [(dtbpp)$_2$Pt$_2$H$_3$]X (X = BPh$_4$, OMe),[21] [{Ph(t-Bu)(CH$_2$)$_2$PPh(t-Bu)}$_2$Pt$_2$H$_3$]X (X = BPh$_4$, OMe),[21] [(dppe)$_2$Pt$_2$H$_3$]X (X = BF$_4$, I, NO$_3$, BPh$_4$],[22] [(dppp)$_2$Pt$_2$H$_3$][BF$_4$],[22] [(dppb)$_2$Pt$_2$H$_3$]X (X = BF$_4$, NO$_3$),[22] and [(cis-Ph$_2$P(CH)$_2$PPh$_2$)Pt$_2$H$_3$][BF$_4$][22] in solution has been reported by several groups. From these complexes, [(dippe)$_2$Ni$_2$H$_3$][BPh$_4$][20] is the one that has been found to be directly comparable to complex **8**. The ^{1}H NMR spectrum of [(dippe)$_2$Ni$_2$(H)$_3$][BPh$_4$] exhibits only one hydride signal at δ −13.357 with multiplicity of a quintet ($^2J_{H-P}$ of 26.6 Hz); the ^{31}P{^{1}H} NMR spectrum displays a sharp singlet at δ 97.3. In the solid state, the dinuclear cations of both complexes exhibit the same Ni−Ni separation of 2.3 Å. The Ni$_2$H$_3$ core in complex **8** shows a marked asymmetry with the following distances: Ni(2)−H(100) (1.73 Å), Ni(2)−H(101) (1.50 Å), and Ni(2)−H(102) (1.40 Å), closely resembling the case of [(dppe)$_2$Pt$_2$H$_3$][BPh$_4$].[23]

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(19) A very similar effect has also been reported by Hartwig's group, on comparing the core geometries of a series of σ-coordinated HBcat, HBpin, and HBCy$_2$ complexes, in which the increase in hydridic character of the B−H bond in the HBCy$_2$ complex, due to an increased σ-donation from the alkyl substituents, was also seen to shorten the M−H bond distance, apparently resulting in a pivoting of the borane about the B−H bond (see ref 6d).

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(22) Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Bandittelli, G.; Bonati, F. *Inorg. Chem.* **1983**, *22*, 2324.

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Further examination of the marked asymmetry in the positions of the hydrides in complex **8** was performed, since this asymmetry reflects the greater steric constraint around Ni(2), imposed by the terminal hydride. In this instance, the angles H(100)−Ni(2)−H(102) (69.4°), H(101)−Ni(2)−H(102) (77.5°), and P(3)−Ni(2)−P(4) (89.75°), all seem to prove this premise.

Reactions of the Nickel (I) Hydrides with $(HBEt_2)_2$: in Situ Preparation of 4−6. Stoichiometric amounts of **1**, **2**, and **3** were added at ambient temperature to $(HBEt_2)_2$ solutions independently prepared in THF, following Wrackmeyer's procedure.[11] The reaction is spontaneous as verified by ^{1}H, ^{31}P, and ^{11}B NMR spectroscopies; the signals of the corresponding *σ*-alkylborane complexes **4**, **5**, and **6** all appear at their respective chemical shifts. None of the Ni(II) trihydride complexes **7**, **8**, or **9** was formed in this preparation. Isolated yields of the *σ*-alkylborane complexes, after workup, obtained by this route (10−15%) are lower than the corresponding yields obtained for these complexes, when the $[BEt_4]^-$ trihydride complexes are concomitantly formed. In turn, these results suggest that the formation of the *σ*-alkylborane complexes is favored under the latter route; the concomitant formation of **7**, **8**, and **9** is likely to be the driving force for such reactions.

Conclusions

We have shown that complexes of the type [(diphosphine)-NiH]$_2$ are effective precursors to generate (diphosphine)Ni(0) species able to coordinate a *σ*-borane, using of a blend of boranes easily formed in situ, with the coformation of ionic hydride dimers of Ni(II). Studies are currently underway to extend the scope of this reaction to related systems.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were carried out using standard Schlenk and glovebox techniques, under argon. All the solvents used were dried and distilled from dark-purple solutions of sodium/benzophenone ketyl. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in an MBraun glovebox (<1 ppm H_2O and O_2). Super-Hydride (1.0 M $LiHBEt_3$ in THF), BEt_3, and BH_3·THF were purchased from Aldrich and stored in the glovebox prior to their use. $(HBEt_2)_2$ was prepared in situ following the literature procedure.[11] [(dippe)NiH]$_2$ (**2**) was prepared from Super-Hydride and [(dippe)NiCl$_2$][24] suspended in hexane, similarly to the literature procedure;[17a] [(dcype)NiH]$_2$ (**1**) and [(dtbpe)NiH]$_2$ (**3**) were prepared analogously. The chelating bisphosphine ligands, dippe and dtbpe, were synthesized[25] from 1,2-bis(dichlorophosphino)ethane (Strem) and the corresponding Grignard alkyls (Aldrich), and dcype was purchased from Strem. Neutral alumina and silica were heated to 200 °C under vacuum for 2 days and stored in the glovebox. All other chemicals and filter aids were reagent grade and were used as received. Isolated complexes were purified by crystallization or column chromatography. ^{1}H, ^{11}B, and ^{31}P NMR spectra were recorded at ambient temperature on a 300 MHz Varian Unity spectrometer in THF-d_8, unless otherwise stated, and all ^{1}H chemical shifts (δ, ppm) are reported relative to the residual proton resonance in the deuterated solvent (δ 3.58, m, THF). ^{31}P NMR spectra were recorded relative to external 85% H_3PO_4. ^{11}B NMR spectra were recorded relative to external $BF_3 \cdot Et_2O$ in $CDCl_3$. All NMR spectra were obtained using thin wall (0.38 mm) WILMAD NMR tubes with Youngs valves. A Bruker APEX CCD diffractometer with monochromatized Mo Kα radiation ($\lambda = 0.71073$Å) was used for X-ray structure determinations. Elemental analyses for complexes **4**−**9** were carried out by USAI-UNAM. Complexes **4**−**6** were found to give irreproducible results due to their extreme sensitivity.

Reaction of BEt_3 with $LiHBEt_3$: Concomitant Formation of $(HBEt_2)_2$ and $LiBEt_4$. A stoichiometric amount of BEt_3 (0.014 mL, 0.096 mmol) was added to a colorless solution of Super-Hydride (0.0115 mL, 0.096 mmol) in THF-d_8. Reactants were mixed at ambient temperature in an NMR tube, and the mixture was stirred for over a minute. ^{1}H NMR: δ 1.02−0.95 (br, BEt_3), 0.95−0.78 (br, $(HBEt_2)_2$), 0.59 (*t* of 1:1:1:1 *q*, 12H, B-CH_2-CH_3, $J(CH_3B) = 3$ Hz), −0.195 (*q* of 1:1:1:1 *q*, 8H, B-CH_2, , $J(CH_2B) = 4.2$ Hz). ^{11}B{^{1}H} NMR: δ 70.7 (br, BEt_3), 37.72 (br, $(HBEt_2)_2$), −17.5 (s, $LiBEt_4$).

Reaction of [(dcype)NiH]$_2$ (1) with an $LiHBEt_3/BEt_3$ Mixture: Concomitant Formation of [(dcype)Ni(*σ*-HBEt$_2$)] (4) and [(dcype)$_2$Ni$_2$-(H)$_3$][BEt$_4$] (7). In the glovebox, two equivalents of [(dcype)NiH]$_2$ (**1**) (92.6 mg, 0.096 mmol) was added at room temperature to a mixture of BEt_3 (0.014 mL, 0.096 mmol) and Super-Hydride (0.0115 mL, 0.096 mmol) in THF. The mixture changed from colorless to a deep-red solution upon addition of the Ni(I) complex. The mixture was allowed to react for 1 h, after which time it was evaporated to dryness on the vacuum line, leaving a deep-red oily residue. The residue was dried on the vacuum line for 4 h, after which time hexane was added to it. The products were separated from the hexane solution via a short alumina column (5 cm); **4** was recovered as a deep-red solution as the first fraction, eluting with hexane, while **7** was recovered as the second fraction as a brick-red solution, eluting only with THF. The solvent was removed from both fractions on the vacuum line, and the residues were vacuum-dried overnight ($P < 10^{-4}$ mmHg). Yield of **4**, after workup: 30%. Yield of **7**, after workup: 84%. Anal. Calcd for **7**, $C_{60}H_{119}BNi_2P_4$: C, 65.95; H, 10.97. Found: C, 65.75; H, 10.89. NMR spectra for **4**: ^{1}H, δ −7.0 (br, *σ*-bonded B−H proton), 1.1−2.1 (m, 48H, cyclohexyl); ^{31}P{^{1}H}, δ 72.16 (d, $^2J_{P-P} = 77.8$ Hz), 58.27 (d, $^2J_{P-P} = 77.8$ Hz); ^{11}B, δ 43.32 (br). NMR spectra for **7**: ^{1}H, δ −13.42 (*q*, 3H, H$^-$; $^2J_{H-P} = 26.7$ Hz), 1.2−2.1 (m, 96H, cyclohexyl); ^{31}P-{^{1}H}, δ 88.5 (s); ^{31}P, δ 88.5 (*q*, $^2J_{P-H} = 26.7$ Hz);^{11}B, δ −17.5 (s).

Reaction of [(dippe)NiH]$_2$ (2) with an $LiHBEt_3/BEt_3$ Mixture: Concomitant Formation of [(dippe)Ni(*σ*-HBEt$_2$)] (5) and [(dippe)$_2$Ni$_2$-(H)$_3$][BEt$_4$] (8). The experiment was performed following the same procedure described for **1**, adding two equivalents of [(dippe)NiH]$_2$ (**2**) (61.8 mg, 0.096 mmol) to a mixture of BEt_3 (0.014 mL, 0.096 mmol) and Super-Hydride (0.0115 mL, 0.096 mmol) in THF. After column separation, **5** was recovered as a deep-red solution as the first fraction, eluting with hexane, while **8** was recovered as the second fraction as a brick-red solution, eluting only with THF. The solvent was removed from both fractions on the vacuum line and the residues were vacuum-dried overnight ($P < 10^{-4}$ mmHg). Yield of **5**, after workup: 26%. Yield of **8**, after workup: 83%. Anal. Calcd for **8**, $C_{36}H_{87}BNi_2P_4$: C, 55.99; H, 11.35. Found: C, 55.8; H, 11.3. NMR spectra for **5**: ^{1}H, δ −6.96 (br, *σ*-bonded B-H proton), 1.07−1.12 (m, 12H, CH_3), 1.14−1.24 (m, 12H, CH_3), 1.54−1.58 (m, 4H, CH_2), 2.10−2.15 (m, 4H, CH); ^{31}P{^{1}H}, δ 77.52 (d, $^2J_{P-P} = 67.8$ Hz), 66.43 (d, $^2J_{P-P} = 67.8$ Hz); ^{11}B, δ 45.38 (br). NMR spectra for **8**: ^{1}H, δ −13.31 (*q*, 3H, H$^-$; $^2J_{H-P} = 26.7$ Hz), 1.14−1.21 (m, 48H, CH_3), 1.94−2.03 (m, 8H, CH_2), 2.10−2.18 (m, 8H, CH); ^{31}P{^{1}H}, δ 98.92 (s); ^{31}P, δ 98.92 (*q*, $^2J_{P-H} = 26.7$ Hz);^{11}B, δ −17.5 (s).

Reaction of [(dtbpe)NiH]$_2$ (3) with an $LiHBEt_3/BEt_3$ Mixture: Concomitant Formation of [(dtbpe)Ni(*σ*-HBEt$_2$)] (6) and [(dtbpe)$_2$Ni$_2$-(H)$_3$][BEt$_4$] (9). The experiment was performed following the same procedure described for **1**, adding two equivalents of [(dtbpe)NiH]$_2$ (**3**) (72.6 mg, 0.096 mmol) to a mixture of BEt_3 (0.014 mL, 0.096 mmol) and Super-Hydride (0.0115 mL, 0.096 mmol) in THF. After column separation, **6** was recovered as a deep-red solution, being the first fraction, eluting with hexane, while **9** was recovered as a brick-red solution, as the second fraction, eluting only with THF. The solvent was removed from both fractions on the vacuum line, and the residues were vacuum-dried overnight ($P < 10^{-4}$ mmHg). Yield of **6**, after

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workup: 21%. Yield of **9**, after workup: 83%. Anal. Calcd for **9**, $C_{44}H_{103}BNi_2P_4$: C, 59.75; H, 11.73. Found: C, 59.63; H, 11.71. NMR spectra for **6**: ^{1}H, δ -7.5 (br, σ-bonded B$-$H proton), 1.3 (s, 36H, CH_3), 1.5$-$1.6 (m, 4H, CH_2); $^{31}P\{^1H\}$, δ 95.90 (d, $^2J_{P-P} = 63.9$ Hz), 84.12 (d, $^2J_{P-P} = 63.9$ Hz); ^{11}B, δ 48. NMR spectra for **9**: ^{1}H, δ -15.5 (*q*, 2H, H$^-$; $^2J_{H-P} = 26.5$ Hz), 1.3 (s, 72H, CH_3), 1.5$-$1.6 (m, 8H, CH_2); $^{31}P\{^1H\}$, δ 110.1 (s); ^{31}P, δ 110.1 (*q*, $^2J_{H-P} = 26.5$ Hz); ^{11}B, δ -17.5 (s).

Reaction of [(dcype)NiH]$_2$ (1) with (HBEt$_2$)$_2$: Preparation of [(dcype)Ni(σ-HBEt$_2$)] (4). Three equivalents of [(dcype)NiH]$_2$ (**1**) (280.7 mg, 0.3 mmol) was added at room temperature to a mixture of BEt_3 (0.058 mL, 0.4 mmol) and BH_3·THF (0.019 mL, 0.2 mmol) in THF. The mixture changed from colorless to a deep-red solution upon addition of the Ni(I) complex. The mixture was allowed to react for 1 h, after which time it was filtered through a small alumina column (5 cm). Complex **4** was recovered as deep-red solution, which was evaporated to dryness on the vacuum line; the residue was vacuum-dried overnight ($P < 10^{-4}$ mmHg). Yield of **4**, after workup: 15%.

Reaction of [(dippe)NiH]$_2$ (2) with (HBEt$_2$)$_2$: Preparation of [(dippe)Ni(σ-HBEt$_2$)] (5). The experiment was performed following the same procedure described for **1**, adding three equivalents of [(dippe)-NiH]$_2$ (**2**) (187.4 mg, 0.3 mmol) at room temperature to a mixture of BEt_3 (0.058 mL, 0.4 mmol) and BH_3·THF (0.019 mL, 0.2 mmol) in THF. Yield of **5**, after workup: 12%.

Reaction of [(dtbpe)NiH]$_2$ (3) with (HBEt$_2$)$_2$: Preparation of [(dtbpe)Ni(σ-HBEt$_2$)] (6). The experiment was performed following the same procedure described for **1**, adding three equivalents of [(dtbpe)-NiH]$_2$ (**3**) (220.1 mg, 0.3 mmol) at room temperature to a mixture of BEt_3 (0.058 mL, 0.4 mmol) and BH_3·THF (0.019 mL, 0.2 mmol) in THF. Yield of **6**, after workup: 10%.

Reaction of [(dcype)NiCl$_2$] with Super-Hydride: Concomitant Preparation of [(dcype)Ni(σ-HBEt$_2$)] (4) and [(dcype)$_2$Ni$_2$(H)$_3$][BEt$_4$] (7). In addition to the concomitant preparation of **4** and **7** described above that started from complex **1**, the concomitant preparation of **4** and **7** starting from the precursor complex [(dcype)NiCl$_2$] and Super-Hydride in a one-pot reaction was also performed. A stirred slurry of 4 equiv of [(dcype)NiCl$_2$] (1 g, 1.81 mmol) in THF was prepared in the glovebox, and to this was added dropwise at room temperature 10 equiv of Super-Hydride (4.5 mL, 4.5 mmol). The slurry gradually changed from an orange to a dark-red solution, with constant evolution of hydrogen gas all of which was vented to the glovebox. The mixture was allowed to react for 1 h, after which time the solution was filtered through a frit packed with a small amount (2 cm) of neutral alumina already eluted with THF. The solvent was then removed from the filtrate on the vacuum line, leaving a deep-red oily residue. The residue was dried on the vacuum line for 4 h, after which time hexane was added to it. The products were separated from the hexane solution via a small alumina column (5 cm); **4** was recovered as a deep-red solution as the first fraction, eluted with the hexane, and **7** was recovered as a brick-red solution as the second fraction, eluting only with THF. The solvent was removed from both fractions on the vacuum line, and the residues were vacuum-dried overnight ($P < 10^{-4}$ mmHg). Yield of **4**, after workup: 10%. Yield of **7**, after workup: 65%.

Reaction of [(dippe)NiCl$_2$] (2) with Super-Hydride: Preparation of [(dippe)Ni(σ-HBEt$_2$)] (5) and [(dippe)$_2$Ni$_2$(H)$_3$][BEt$_4$] (8). The preparations of **5** and **8** were analogous to those of **4** and **7**, using a THF slurry of [(dippe)NiCl$_2$] (1 g, 2.551 mmol) and Super-Hydride (6.4 mL, 6.4 mmol). After the column separation, **5** was recovered as a deep-red solution as the first fraction, eluting with hexane, and **8** was recovered as a brick-red solution as the second fraction, eluting only with THF. The solvent was removed from both fractions on the vacuum line, and the residues were vacuum-dried overnight ($P < 10^{-4}$ mmHg). Yield of **5**, after workup: 7%. Yield of **8**, after workup: 58%.

Reaction of [(dtbpe)NiCl$_2$] (3) with Super-Hydride: Preparation of [(dtbpe)Ni(σ-HBEt$_2$)] (6) and [(dtbpe)$_2$Ni$_2$(H)$_3$][BEt$_4$] (9). The preparation of **6** and **9** was also made analogously to the preparation of **4** and **7**, using a THF slurry of [(dtbpe)NiCl$_2$] (1 g, 2.231 mmol) and Super-Hydride (5.6 mL, 5.6 mmol). After the column separation, **6** was recovered as a deep-red solution as the first fraction, eluting with hexane, and **9** was recovered as a brick-red solution as the second fraction, eluting only with THF. The solvent was removed from both fractions on the vacuum line, and the residues were vacuum-dried overnight ($P < 10^{-4}$ mmHg). Yield of **6**, after workup: 6%. Yield of **9**, after workup: 60%.

Crystallographic Studies The X-ray diffraction data for both **4** and **8** were collected with the use of the program SMART[26] on a Bruker APEX CCD diffractometer with monochromatized Mo Kα radiation ($\lambda = 0.71073$). Space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program. Cell refinement and data reduction were carried out with the use of the program SAINT; the program SADABS was employed to make incident beam, decay, and absorption corrections in the SAINT-Plus v. 6.0 suite.[27] Then the structures of **4** and **8** were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL v. 6.1 suite.[28]

Crystallographic Analysis of 4. Brown single crystals of **4**, suitable for X-ray diffraction studies, were obtained by cooling a concentrated solution of **4** in hexane at -30 °C for 5 d in the glovebox. The crystals of **4** were mounted under Paratone 8277 on glass fibers and immediately placed under a cold nitrogen stream at 100 K on the X-ray diffractometer. Crystal data for **4** are provided in Table 2. A total of 5403 reflections were collected, 3350 of which were unique ($R_{int} = 3.33\%$). The space group was determined to be *Cc*. For $Z = 4$ and a formula weight of 551.23, the calculated density was 1.191 Mg/m^3. No absorption correction was applied. The structure was solved by direct methods and was expanded using Fourier techniques. H31 was located on the difference Fourier map. Remaining hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final model involved anisotropic displacement parameters for all non-hydrogen atoms. The final cycle of full-matrix least-squares refinement on F^2 was based on 3350 observed reflections ($I > 2\sigma(I)$) and 313 variable parameters and converged with unweighted and weighted agreement factors of $R = 4.25\%$ and $R_w = 9.33\%$. The goodness-of-fit on F^2 after refinement was found to be 1.054. The complete crystal data for **4**, as the rest of the experimental details of the X-ray diffraction studies for it, are provided in Table 2. Positional parameters for all atoms, anisotropic thermal parameters, and all bond lengths and angles, as well as fixed hydrogen positional parameters, are given in the Supporting Information for **4**.

Crystallographic Analysis of 8. Red single crystals of **8**, suitable for X-ray diffraction studies, were obtained by cooling a concentrated solution of **8** in THF at -30 °C for 5 d in the glovebox. The crystals of **8** were mounted under LVAC FOMBLIN Y on glass fibers and immediately placed under the cold nitrogen stream at 100 K on the X-ray diffractometer. A total of 16089 reflections were collected, 9949 of which were unique ($R_{int} = 4.45\%$). The space group was determined to be $P\bar{1}$. For $Z = 2$ and a formula weight of 772.17, the calculated density was 1.153 Mg/m^3. No absorption correction was applied. The structure was solved by direct methods and was expanded using Fourier techniques. H100, H101, and H102 were located on the difference Fourier map. Remaining hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final model involved anisotropic displacement parameters for all non-hydrogen atoms. The final cycle of full-matrix least-squares refinement on F^2 was based on 9949 observed reflections ($I > 2\sigma(I)$) and 420 variable parameters and converged with unweighted and weighted agreement factors of $R = 4.99\%$ and $R_w = 9.37\%$. The goodness-of-

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(26) Sheldrick, G. M. *SMART*; Bruker AXS, Inc.: Madison, WI, 2000.
(27) Sheldrick, G. M. *SAINT-Plus 6.0*; Bruker AXS, Inc.: Madison, WI, 2000.
(28) Sheldrick, G. M. *SHELXTL 6.10*; Bruker AXS, Inc.: Madison, WI, 2000.

fit on F^2 after refinement was found to be 0.895. The complete crystal data for **8**, as the rest of the experimental details of the X-ray diffraction studies for it, are provided in Table 2. Positional parameters for all atoms, anisotropic thermal parameters, and all bond lengths and angles, as well as fixed hydrogen positional parameters, are given in the Supporting Information for **8**.

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Supporting Information Available: Tables of complete crystallographic data for **4** and **8**. X-ray crystallographic data in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.

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