

A Monoboranyl Analogue of 1,2-*bis*(di-*tert*-butylphosphino)ethane

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Abstract:

Examples of unsymmetric diphosphines, especially those with customized secondary coordination spheres, are rare. Herein, we provide an approach towards a Lewis acid-containing analogue of the bulky diphosphine, 1,2-*bis*(di-*tert*-butylphosphino)ethane that contains a single boron moiety. The coordination chemistry of this ligand and its allyl precursor have been explored using nickel(0).

Keywords: Boron | Phosphorus | Nickel | Ligand design | Secondary coordination sphere (SCS)

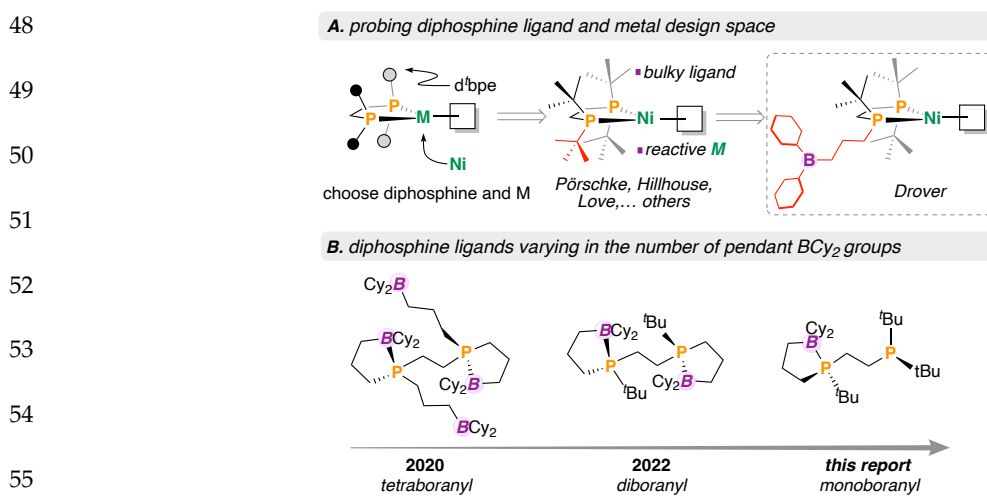
Introduction:

Metal-mediated reactivity offers a general means to perform challenging organic transformations that rely on the formation and/or cleavage of inert chemical bonds.^{1,2} In most cases, such reactions are performed using a specific ligand to confer control of metal accessibility, electron-richness, chirality, etc. In this realm, phosphines have occupied a privileged role, mostly due to the ease by which they are modified and readily installed. As a class of phosphine, bidentate diphosphines have enjoyed great popularity – they benefit from the chelate effect and are not easily displaced during catalysis. Further, they offer facile steric and electronic tuning by alteration of R group and/or backbone tether length; features that have been previously manipulated to enhance reactivity and/or selectivity.^{3,4,5} Of ligands in this class, 1,2-*bis*(di-*tert*-butylphosphino)ethane (d^tbpe) has been shown to serve as a bulky, sterically-shielding ligand with a cone angle of $184 \pm 2^\circ$, similar to P(^tBu)₃ - a quality that has contributed to its distinctive coordination chemistry.⁶

Of reported [M(d^tbpe)] compounds, those having M = Ni stand-out for their scope of controlled and novel reactivity (**Chart 1A**). The chemistry of [Ni(d^tbpe)(η^2 -alkene)] starting precursors was established by Pörschke and co-workers in the 1990s.^{7,8} These studies showed that alkene- and diene-containing Ni(0) species reacted with d^tbpe to give three-coordinate 16-electron Ni(0) compounds, e.g., for ethylene, [Ni(d^tbpe)(η^2 -CH₂CH₂)]. As a prototypical Ni(0) starting material, [Ni(COD)₂] (COD = 1,5-cyclooctadiene) maintains this trend, reacting with d^tbpe to afford [Ni(d^tbpe)(η^2 -COD)]. As precursors primed for reactivity, labile arene-

31 ligated Ni(0) compounds have also been established using this system - $[\text{Ni}(\text{dtbpe})]_2(\eta^6\text{-C}_6\text{H}_6)$, has been used
 32 as a source of reactive “[Ni(d^tbpe)]” by a number of researchers. For instance, Hillhouse and co-workers
 33 published several seminal reports using this scaffold, accessing some of the first late metal imides (NR²⁻)^{9,10}
 34 and phosphinidenes (PR²⁻)^{11,12} – reactive molecules of relevance to pnictogen-transfer chemistry. Love and co-
 35 workers have additionally reported on the reactivity of ‘[Ni(d^tbpe)]’ with esters, thioesters,¹³ epoxides,^{14,15} and
 36 oxaziridines¹⁶ to give reactive nickellacycles of relevance to catalysis.

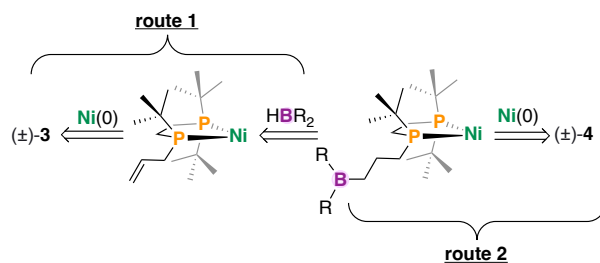
37 Recent work in our laboratory has concentrated on the preparation of diphosphine ligands having
 38 ligands featuring borane groups in the secondary coordination sphere (SCS) (**Chart 1B**).^{17,18,19,20} We and others
 39 have shown that these groups are participatory in chemical transformations, offering stabilization to Lewis
 40 basic substrates such as amides, sulfides, hydroxides, alkyl anions, hydrides, pyridines, and more.²¹ With the
 41 aim of expanding the ‘diphosphine ligand toolbox’ our initial reports focused on symmetrical diphosphine
 42 compounds with four²⁰ or two²² boranes. As an extension of our work, we were interested in preparing an
 43 unsymmetrical diphosphinoethane ligand that contained a single borane unit – a hitherto unreported ligand
 44 motif. More precisely, we wished to prepare a monoboranyl analogue of the 1,2-bis(di-*tert*-
 45 butylphosphino)ethane (d^tbpe) ligand discussed above to determine the effect of boron SCS inclusion.
 46 Inherent to this aim, this report provides access to this target and develops its downstream coordination
 47 chemistry with nickel(0).



56 **Chart 1. A.** Probing ligand design space. **B.** A timeline of [n]-boranyl diphosphines ligands (n = 4, 2, 1)

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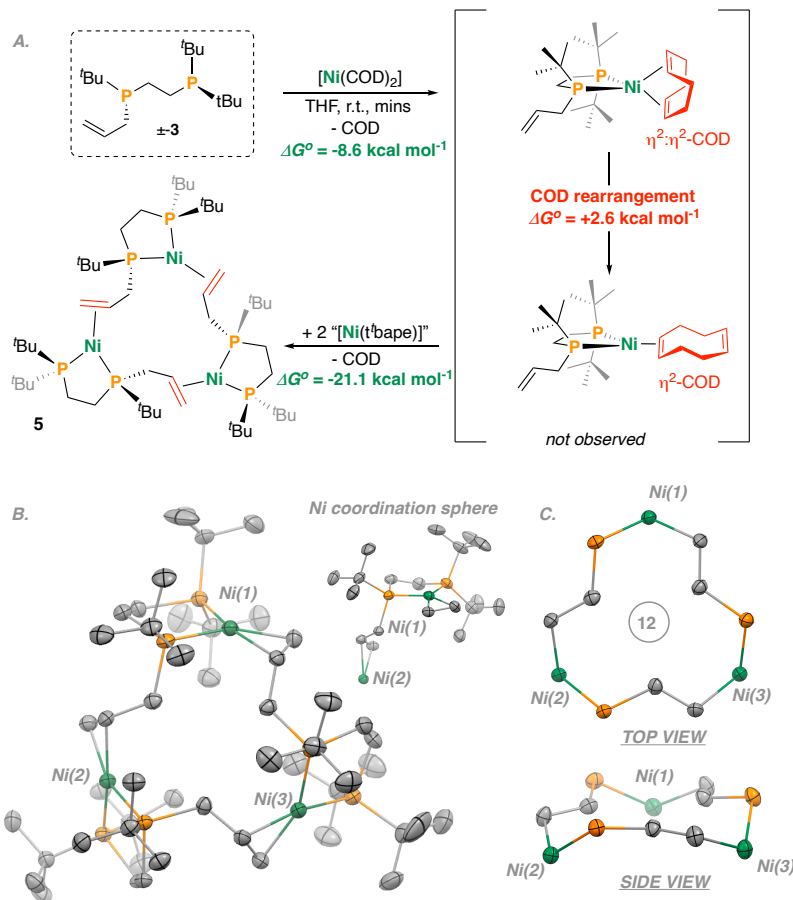
88 Seeking to access a monoboranyl diphosphine nickel(0) synthon, we considered two routes: 1) post-
 89 coordination hydroboration of the pendant allyl group of '[Ni(*t*bape)]' or 2) direct insertion of Ni(0) into the
 90 B—P bond of (\pm)-4 (**Figure 2**). Such methods have previously proven fruitful using related *P,B*-ligands
 91 prepared in our laboratory.²²



97 **Figure 2.** Retrosynthetic analysis for the targeted Ni(0) monoboranyl compound.

99 As a primary route, *t*bape ((\pm)-3) was reacted with [Ni(COD)]₂ in an aim to produce [Ni(*t*bape)(COD)]
 100 (**Figure 3**). On inspection by ¹H NMR spectroscopy, however, no resonance attributable to a coordinated COD
 101 ligand was observed *c.f.*, an averaged signal of $\delta_{\text{H}} = 4.26$ ppm for [Ni(*d*'bpe)(η^2 -COD)]; nor were signals
 102 observed for the free allyl group. Instead, several multiplets between 3.00 and 1.50 ppm were observed,
 103 consistent with a *C_i*-symmetric reduced π -nickel allyl moiety, '[Ni(*d*'bpe)]'. By ³¹P NMR spectroscopy, two
 104 sets of second order AA'XX' multiplets were observed at $\delta_{\text{P}} = 94.5$ and 65.5 ppm in a 1:1 ratio with ²*J*_{P,P} = 72.2
 105 Hz, ⁴*J*_{P,P} = 21.0 Hz and ⁵*J*_{P,P} = 4.1 Hz, suggestive of an oligomer in solution. Strikingly, this result contrasts with
 106 a related ligand recently disseminated by our group, (\pm)-*rac/meso*-(Allyl)^{*t*}BuP-CH₂-CH₂-P(^{*t*}Bu)Allyl (Allyl =
 107 CH₂CHCH₂) which when reacted with [Ni(COD)]₂ gives [(κ^2 -diphosphine)Ni(η^2 : η^2 -COD)], highlighting the
 108 effect of substituting a single allyl substituent for a bulkier *t*-Bu group.²²

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131 **Figure 3. A.** Reaction of (\pm)-**3** with $[\text{Ni}(\text{COD})_2]$ (COD = 1,5-cyclooctadiene). Energies have been calculated from
132 DFT-optimized structures using DLPNO-CCSD(T) (see ESI). **B.** Mercury depiction of the solid-state molecular
133 structure of **5** (displacement ellipsoids are shown at the 50% probability, hydrogens omitted for clarity). **C.**
134 Mercury depiction of the core ring structure of **5**.

136 Crystals of **5**, suitable for analysis by X-ray diffraction, corroborated the results observed in solution –
137 a $[\text{Ni}(\text{t}'\text{bape})]$ trimer connected by η^2 -alkene interactions that self-assemble to produce a cyclododecane ring
138 (**Figure 3**). The conformation of 12-membered cycloalkane rings has been studied in detail with the D_4 -
139 symmetric square [3333] (3 atoms per side) being the most stable, according to strain-energy calculations,
140 solution-, and solid-state measurements.^{26,27} The conformation of **5**, however, most closely resembles the
141 higher-energy S_6 -symmetric structure of cyclododecane. The three nickel centers form an equilateral triangle
142 with uniform Ni-Ni separations of 5.88 Å. In terms of the bound π -allyl group, elongated C-C alkene bond
143 lengths of 1.42 ± 0.01 Å (taken as an average) are supported by Ni-C bond lengths of 1.967 ± 0.008 Å; Ni-P

144 bond lengths are equivalent ($2.157 \pm 0.007 \text{ \AA}$). Remarkably, the mononuclear [Ni]- η^2 -ethylene analogue,
145 [Ni(d^tbpe)(η^2 -CH₂CH₂)] has similar bond metrics: an ethylene C-C bond length of 1.4189(6) \AA , Ni-C bond
146 lengths of 1.9708(4)/1.9715(4) \AA , and Ni-P bond lengths of 2.16550(11)/2.16811(11) \AA , suggesting little
147 structural deformation due to cyclization.²⁸ The <P-Ni-P and <C-Ni-C bite angles are additionally similar
148 (93.456(5) vs. $90.88 \pm 0.28^\circ$ for **5** and 42.19(2) vs. $42.37 \pm 0.32^\circ$ for **5**).

149 To gain a deeper understanding into the formation of **5**, we sought to obtain information pertaining to
150 the thermodynamics of some putative intermediates. Beginning with [Ni(COD)₂] and t^tbape, formation of
151 [Ni(t^tbape)(η^2 : η^2 -COD)] is exothermic with $\Delta G^\circ = -8.6 \text{ kcal mol}^{-1}$. COD rearrangement was determined to be
152 uphill, giving [Ni(t^tbape)(η^2 -COD)] ($\Delta G^\circ = +2.6 \text{ kcal mol}^{-1}$). By comparison, the conversion of [Ni(d^tbpe)(η^2 : η^2 -
153 COD)] to [Ni(d^tbpe)(η^2 -COD)] was calculated to be thermoneutral ($\Delta G^\circ \approx 0 \text{ kcal mol}^{-1}$); the experimentally-
154 observed COD isomer for this ligand is η^2 -COD.⁸ Finally, loss of 1,5-cyclooctadiene from [Ni(t^tbape)(η^2 -COD)]
155 and trimerization to give **5** was found to be highly exergonic ($\Delta G^\circ = -21.1 \text{ kcal mol}^{-1}$) (**Figure 3**).

156 To assess the electrochemical properties of **5**, cyclic voltammetry was performed (**Figure 4**). Compound
157 **5** displays two peaks at $E_{1/2} = -1.27 \text{ V}$ ($\Delta E_p = 150 \text{ mV}$) and -0.72 V ($\Delta E_p = 130 \text{ mV}$) in THF (vs. Fc/Fc⁺), assigned
158 as Ni(0)/Ni(I) and Ni(I)/Ni(II) redox couples, respectively; the open-circuit potential for **5** was -1.40 V . Of note,
159 this oxidation behavior is similar to [Ni(dcype)(COD)] (dcype = 1,2-bis-(dicyclohexylphosphino)ethane, which
160 undergoes oxidation at $E_{1/2} = -0.95 \text{ V}$ (Ni(0)/Ni(I)),^{29,30} consistent with the weaker electron-releasing ability of
161 dcype vs. t^tbape.

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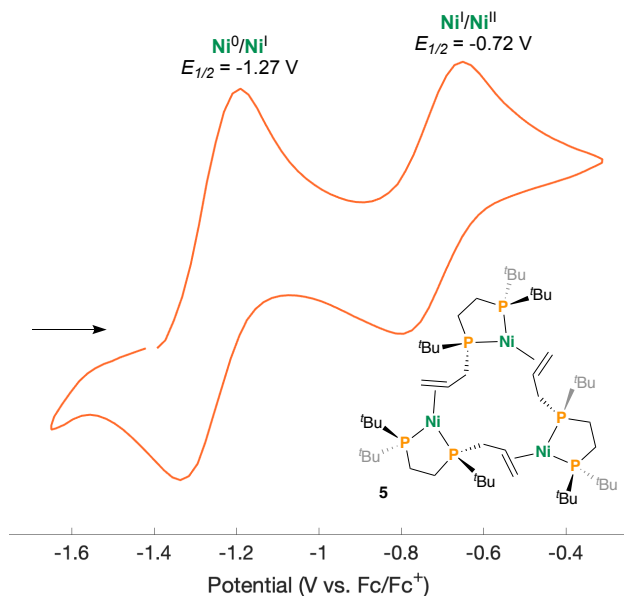


Figure 4. Cyclic Voltammetry of **5** depicting Ni⁰/I and Ni^I/II couples at $E_{1/2} = -1.27$ and -0.72 V, respectively vs. Fc/Fc⁺ (0.4 M [NⁿBu₄]PF₆ in THF using a scan rate of 200 mV/s).

Consistent with strong Ni($d\pi$)/C=C(π^*) overlap, benzene solutions of **5** do not react with HBCy₂ to provide [Ni(*d*'bape)]₂(η^6 -C₆H₆). We thus endeavored to prepare the targeted monoboranyl nickel(0) diphosphine compound, (\pm)-**6** by direct reaction of [Ni(COD)]₂ with (\pm)-**4** (**Figure 5**). Unlike the *d*'bpe Ni complex, which coordinates COD in an η^2 -mode, compound (\pm)-**6** was observed to coordinate in an η^2 : η^2 -fashion; four multiplets are observed in the ¹H NMR spectrum at $\delta_{\text{H}} = 4.75, 4.54, 4.47,$ and 4.27 ppm (accompanying signals at $\delta_{\text{C}} = 90.6, 77.3, 90.3,$ and 78.8 by ¹H-¹³C HSQC NMR spectroscopy), consistent with a static bound diolefin of C₁-symmetry (for comparison, $\delta_{\text{H}} = 4.30, \delta_{\text{C}} = 89.8$ ppm for [Ni(COD)]₂ in C₆D₆).⁸ Using ³¹P NMR spectroscopy, a pair of [AB] doublets were also observed at $\delta_{\text{P}} = 88.9$ and 60.1 ppm ($^2J_{\text{P,P}} = 41.6$ Hz). Notably, the ability of (\pm)-**4** to undergo facile ring-opening is a consequence of its bulky *t*-Bu phosphorus substituents – related analogues, such as P₂BCy₄ only undergo ring-opening under thermal conditions (in low conversion).²⁰

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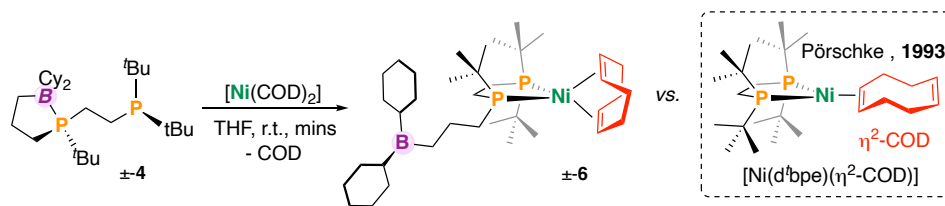


Figure 5. Reaction of (±)-4 with [Ni(COD)₂] (COD = 1,5-cyclooctadiene) to give (±)-6.

Conclusion:

In summary, we have translated the chemistry of a bulky diphosphine synthon into derivatives bearing a sole secondary borane moiety. In the case of d'bape ((±)-3), a stable 12-membered {Ni}₃ complex 5 self-assembles. This compound does not undergo hydroboration-induced ring-opening. For the borane analogue, t'bbpe ((±)-4), however, facile phosphorus-boron ring-opening permits access to a Lewis-acid containing Ni precursor, (±)-6 – a singly substituted boron analogue of the well-known d'bpe ligand. Studies that draw upon the cooperative reactivity of (±)-6 will be reported in due course.

Supplementary material:

¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹¹B{¹H} NMR spectra for all complexes. XYZ coordinates for DFT calculations. CCDC 2189205 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements:

The authors are grateful to the University of Windsor, the Council of Ontario Universities for a John C. Polanyi award to M.W.D., the Natural Sciences and Engineering Research Council of Canada (Discovery Grant, RGPIN-2020-04480, Discovery Launch Supplement, DGEGR-2020-00183), the American Chemical Petroleum Research Fund (PRF # 62284-ND3), and the Canadian Foundation for Innovation (Project # 41099).

Disclosure statement:

The authors declare no competing financial interest.

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299 **Table of Contents Entry:**

