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 ± 2°, similar to P(3-Bu)- 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)(η2-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)(η2-C2H4)]. 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)(η2-COD)]. As precursors primed for reactivity, labile arene-
ligated Ni(0) compounds have also been established using this system - [Ni(dtbpe)](η^6-C₆H₆), has been used as a source of reactive ‘[Ni(d’tbpe)]’ by a number of researchers. For instance, Hillhouse and co-workers published several seminal reports using this scaffold, accessing some of the first late metal imides (NR²)⁹,¹⁰ and phosphinidenes (PR²)¹¹,¹² – reactive molecules of relevance to pnictogen-transfer chemistry. Love and co-workers have additionally reported on the reactivity of ‘[Ni(d’tbpe)]’ with esters, thioesters,¹³ epoxides,¹⁴,¹⁵ and oxaziridines¹⁶ to give reactive nickellacycles of relevance to catalysis.

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

![Chart 1. A. Probing diphosphine ligand and metal design space. B. A timeline of [n]-boranyl diphosphines ligands (n = 4, 2, 1)](chart1.png)
Results and discussion:

A reasonable retrosynthesis was outlined using (±)-1-(di-tert-butyl-phosphino)-2-(tert-butyl-iodo-phosphino)ethane (±)-2, (first prepared by Fryzuk and co-workers as a pincer-synthon) as a modular source of electrophilic diphosphine. This compound was readily accessed on a gram scale via phosphorus-phosphorus bond cleavage of 1 using 1,2-diodoethane. With (±)-2 in-hand, a metathesis reaction was carried out using allyl magnesium chloride at 0 °C, providing tri-tert-butylallyldiphosphoethane (tbbape, (±)-3) as a viscous oil in 95% yield, following work-up (Figure 1). Consistent with alkylation, two sets of mutually-coupled doublets were observed in the $^{31}$P NMR spectrum at $\delta_P = 34.8$ and 2.25 ppm ($\delta_P$ = 30.3 Hz); the most deshielded-resonance corresponding to that bearing the di-tert-butyl-phosphine arm. This precursor was amenable to hydroboration; treatment of (±)-3 with a moderately electrophilic borane, HBCy: (Cy = cyclohexyl) permitted access to the monoboranyl ligand, tri-tert-butylboranyldiphosphoethane (tbbpe, (±)-4) (Figure 1). Alkene reduction was characterized by 1) disappearance of alkene signals in the $^1$H NMR spectrum; 2) a shift in $^{31}$P NMR resonance to $\delta_P = 35.9$ and 29.0 ppm ($\delta_P$ = 29.7 Hz); and 3) a broad borane signal in the $^{11}$B NMR spectrum at $\delta_B = 2.61$ ppm ($\Delta\delta_B = 286$ Hz), suggestive of an intramolecular B—P interaction.

![Diagram](image)

**Figure 1.** Accessing the targeted ligands tbbape (±)-3 and borane derivative, tbbpe (±)-4. Inset shows the DFT-optimized structures of (±)-3/4 using BP86-D3(BJ)/def2-TZVP.
Seeking to access a monoboranyl diphosphine nickel(0) synthon, we considered two routes: 1) post-coordination hydroboration of the pendant allyl group of '[Ni(t³bape)]⁻' or 2) direct insertion of Ni(0) into the B—P bond of (±)-4 (Figure 2). Such methods have previously proven fruitful using related P,B-ligands prepared in our laboratory.²²

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

As a primary route, t³bape ((±)-3) was reacted with [Ni(COD)]₂ in an aim to produce [Ni(t³bape)(COD)] (Figure 3). On inspection by 'H NMR spectroscopy, however, no resonance attributable to a coordinated COD ligand was observed c.f., an averaged signal of δ_H = 4.26 ppm for [Ni(d⁵bpe)(η²-COD)]; nor were signals observed for the free allyl group. Instead, several multiplets between 3.00 and 1.50 ppm were observed, consistent with a C₃-symmetric reduced π-nickel allyl moiety, '[Ni(d⁵bpe)]⁻'. By ³¹P NMR spectroscopy, two sets of second order AA'XX' multiplets were observed at δ_P = 94.5 and 65.5 ppm in a 1:1 ratio with 2J_P,P = 72.2 Hz, 4J_P,P = 21.0 Hz and 5J_P,P = 4.1 Hz, suggestive of an oligomer in solution. Strikingly, this result contrasts with a related ligand recently disseminated by our group, (±)-rac/meso-(Allyl)BuP-CH₂-CH₂-P(Bu)Allyl (Allyl = CH₂CHCH₂) which when reacted with [Ni(COD)]₂ gives [[(κ²-diphosphine)Ni(η²:η²-COD)]], highlighting the effect of substituting a single allyl substituent for a bulkier t-Bu group.²²
Figure 3. A. Reaction of (±)-3 with [Ni(COD)] (COD = 1,5-cyclooctadiene). Energies have been calculated from DFT-optimized structures using DLPNO-CCSD(T) (see ESI). B. Mercury depiction of the solid-state molecular structure of 5 (displacement ellipsoids are shown at the 50% probability, hydrogens omitted for clarity). C. Mercury depiction of the core ring structure of 5.

Crystals of 5, suitable for analysis by X-ray diffraction, corroborated the results observed in solution—a [Ni(tbape)] trimer connected by η2-alkene interactions that self-assemble to produce a cyclododecane ring (Figure 3). The conformation of 12-membered cycloalkane rings has been studied in detail with the D4-symmetric square [3333] (3 atoms per side) being the most stable, according to strain-energy calculations, solution-, and solid-state measurements.26-27 The conformation of 5, however, most closely resembles the higher-energy S6-symmetric structure of cyclododecane. The three nickel centers form an equilateral triangle with uniform Ni-Ni separations of 5.88 Å. In terms of the bound π-allyl group, elongated C-C alkene bond 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
bond lengths are equivalent (2.157 ± 0.007 Å). Remarkably, the mononuclear [Ni-η²-ethylene analogue, [Ni(dfpe)(η²-CH₂CH₂)] has similar bond metrics: an ethylene C-C bond length of 1.4189(6) Å, Ni-C bond lengths of 1.9708(4)/1.9715(4) Å, and Ni-P bond lengths of 2.16550(11)/2.16811(11) Å, suggesting little structural deformation due to cyclization. The <P-Ni-P and <C-Ni-C bite angles are additionally similar (93.456(5) vs. 90.88 ± 0.28° for 5 and 42.19(2) vs. 42.37 ± 0.32° for 5).

To gain a deeper understanding into the formation of 5, we sought to obtain information pertaining to the thermodynamics of some putative intermediates. Beginning with [Ni(COD)₂] and t'bape, formation of [Ni(t'bape)(η²-η²-COD)] is exothermic with $\Delta G^\circ = -8.6$ kcal mol⁻¹. COD rearrangement was determined to be uphill, giving [Ni(t'bape)(η²-COD)] ($\Delta G^\circ = +2.6$ kcal mol⁻¹). By comparison, the conversion of [Ni(dfpe)(η²-η²-COD)] to [Ni(dfpe)(η²-COD)] was calculated to be thermoneutral ($\Delta G^\circ = 0$ kcal mol⁻¹); the experimentally-observed COD isomer for this ligand is η²-COD. Finally, loss of 1,5-cyclooctadiene from [Ni(t'bape)(η²-COD)] and trimerization to give 5 was found to be highly exergonic ($\Delta G^\circ = -21.1$ kcal mol⁻¹) (Figure 3).

To assess the electrochemical properties of 5, cyclic voltammetry was performed (Figure 4). Compound 5 displays two peaks at $E_{1/2} = -1.27$ V ($\Delta E_p = 150$ mV) and -0.72 V ($\Delta E_p = 130$ mV) in THF (vs. Fe/Fe³⁺), assigned 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, this oxidation behavior is similar to [Ni(dcype)(COD)] (dcype = 1,2-bis-(dicyclohexylphosphino)ethane, which undergoes oxidation at $E_{1/2} = -0.95$ V (Ni(0)/Ni(I)) ²⁹, ³⁰ consistent with the weaker electron-releasing ability of dcype vs. t'bape.
Figure 4. Cyclic Voltammetry of 5 depicting Ni^{0II} and Ni^{III} couples at $E_{1/2} = -1.27$ and -0.72 V, respectively vs. \( \text{Fc/Fc}^+ \) (0.4 M \([\text{N}^4\text{Bu}_4]\)PF$_6$ in THF using a scan rate of 200 mV/s).

Consistent with strong Ni(d)$\pi$/C=C(\( \pi^* \)) overlap, benzene solutions of 5 do not react with HBCy2 to provide [Ni(d'tbape)](\( \eta^2-\text{C}_6\text{H}_6 \)). We thus endeavored to prepare the targeted monoboranyl nickel(0) diphosphine compound, (\( \pm \))-6 by direct reaction of [Ni(COD)] with (\( \pm \))4 (Figure 5). Unlike the d'bpe Ni complex, which coordinates COD in an \( \eta^2 \)-mode, compound (\( \pm \))-6 was observed to coordinate in an \( \eta^2:\eta^2 \)-fashion; four multiplets are observed in the \( ^1 \)H NMR spectrum at \( \delta_H = 4.75, 4.54, 4.47, \) and 4.27 ppm (accompanying signals at \( \delta_C = 90.6, 77.3, 90.3, \) and 78.8 by \( ^1 \)H-$^13 \)C HSQC NMR spectroscopy), consistent with a static bound diolefin of \( \text{C}_1 \)-symmetry (for comparison, \( \delta_H = 4.30, \delta_C = 89.8 \) ppm for [Ni(COD)] in \( \text{C}_6\text{D}_6 \)).\(^6\) Using \( ^31 \)P NMR spectroscopy, a pair of [AB] doublets were also observed at \( \delta_P = 88.9 \) and 60.1 ppm (\( ^2 \)J$_{PP} = 41.6$ 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 P:2B\(^3\)4 only undergo ring-opening under thermal conditions (in low conversion).\(^{20} \)
Figure 5. Reaction of \((\pm)-4\) with \([\text{Ni}(\text{COD})_2]\) (COD = 1,5-cyclooctadiene) to give \((\pm)-6\).

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'tbpe \((\pm)-3\), a stable 12-membered \([\text{Ni}]_3\) complex 5 self-assembles. This compound does not undergo hydroboration-induced ring-opening. For the borane analogue, t'bbpe \((\pm)-4\), however, facile phosphorus-boron ring-opening permits access to a Lewis-acid containing Ni precursor, \((\pm)-6\) – a singly substituted boron analogue of the well-known d'bpe ligand. Studies that draw upon the cooperative reactivity of \((\pm)-6\) will be reported in due course.

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

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The authors declare no competing financial interest.
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Notes and References


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