

Late 3d-Transition Metal Complexes Bearing a *Bis*-Phosphine Borane Ligand, $\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2$

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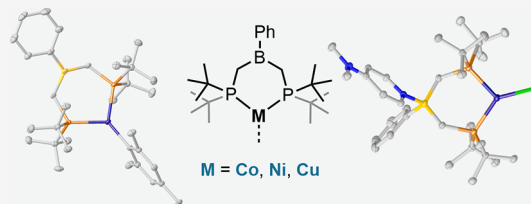


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ABSTRACT: The coordination chemistry of a bidentate ambiphilic ligand, $\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2$ ($[\text{BP}_2^t\text{Bu}]$), is established for a series of Co, Ni, and Cu compounds. The chloride starting materials $[\text{BP}_2^t\text{Bu}]\text{MCl}_2$ [$\text{M} = \text{Co}$ (1_{Co}), Ni (1_{Ni})] and $[\text{BP}_2^t\text{Bu}]\text{CuCl}$ (2_{Cu}) are readily accessed in high yields by the treatment of the corresponding metal chloride salts with $[\text{BP}_2^t\text{Bu}]$ in THF solution. The reduction of 1_{Ni} to $[\text{BP}_2^t\text{Bu}]\text{NiCl}$ (2_{Ni}) was affected by treatment with KC_8 . In contrast, the corresponding Co^{I} species was not isolable under similar reaction conditions. However, monovalent mesityl complexes of the form $[\text{BP}_2^t\text{Bu}]\text{M}(\text{Mes})$ [$\text{M} = \text{Co}$ (3_{Co}), Ni (3_{Ni}), Cu (3_{Cu})] were prepared by the treatment of 1_{Co} with one equiv of $\text{Mes}_2\text{Mg}(\text{THF})_2$ or by the reaction of 2_{M} ($\text{M} = \text{Ni}$, Cu) with 0.5 equiv of $\text{Mes}_2\text{Mg}(\text{THF})_2$. Modification of the borane moiety in 2_{Ni} was explored by the treatment of this complex with 4-dimethylaminopyridine (DMAP) to produce $[\text{PhB}(\text{DMAP})(\text{CH}_2\text{P}^t\text{Bu}_2)_2]\text{NiCl}$ (**4**), which displays distinct features in its UV–visible spectrum compared to 2_{Ni} . The solid-state molecular structures of most complexes have been determined by single-crystal X-ray diffraction analysis.



INTRODUCTION

Transition-metal complexes bearing ambiphilic ligands (with both donor and acceptor centers) are of interest as such species provide new pathways for substrate activations involving the metal and acceptor sites.^{1–4} Prominent examples are *bis*- and *tris*-phosphinoborane ligands which allow close contact of the metal and boron centers and formation of $\text{M} \rightarrow \text{B}$ (Z-type) interactions.^{1,4–8} The latter bonding feature is particularly common in complexes of low-valent metal centers, where additional electron density from the metal center can be shared with boron.⁸ For instance, close $\text{M}–\text{B}$ contacts are observed in $[\text{PhB}(\text{o}-\text{C}_6\text{H}_4\text{P}^i\text{Pr}_2)_2]\text{Co}(\text{N}_2)^9$ and $[\text{MesB}(\text{o}-\text{C}_6\text{H}_4\text{P}^i\text{Pr}_2)_2]\text{Ni}$ ($\text{Mes} = \text{mesityl}$).¹⁰ The $\text{M}–\text{B}$ linkages in these species cooperatively participate in bond activations by accepting fragments of incoming substrates.^{11–15} For example, the reaction of these Co or Ni species with silanes results in the formation of $\text{M}–\text{Si}$ linkages and a $\text{M}(\mu_2\text{-H})\text{B}$ moiety (Figure 1a).^{9,10}

In this laboratory, *bis*-phosphinoborane complexes have been encountered as unexpected byproducts following the degradation of *tris*-phosphinoborate ligands. For example, the rhodium(I) complex $[\kappa^2\text{-BP}_3^i\text{Pr}]\text{Rh}(\text{PMe}_3)_2$ ($[\text{BP}_3^i\text{Pr}] = \text{PhB}(\text{CH}_2\text{P}^i\text{Pr}_2)_3^-$), undergoes reversible $-\text{CH}_2\text{P}^i\text{Pr}_2$ side-arm migration at elevated temperatures to generate $[\text{PhB}(\text{CH}_2\text{P}^i\text{Pr}_2)_2]\text{Rh}(\text{CH}_2\text{P}^i\text{Pr}_2)$.¹⁶ A related rearrangement of the $[\text{BP}_3^i\text{Pr}]$ ligand is observed in reactions of $\text{Na}(\text{THF})_6\{[\text{BP}_3^i\text{Pr}]\text{-CoI}\}$ with 1.5 equivs of RSiH_3 ($\text{R} = \text{H}$, Ph), in which 0.5 equiv of the respective silicide complexes $[\text{PhB}(\text{CH}_2\text{P}^i\text{Pr}_2)_2]\text{-(RSiH}_2)(\text{H})_2\text{Co}=\text{Si}=\text{Co}(\text{H})_2[\text{BP}_3^i\text{Pr}]$ are generated (Figure 1b).¹⁷ In these cases, the $-\text{CH}_2\text{P}^i\text{Pr}_2$ side-arm is expelled via coupling with 0.5 equiv of RSiH_3 to produce $^i\text{Pr}_2\text{PCH}_2\text{SiH}_2\text{R}$,

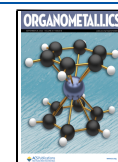
suggesting that the formation of the $[\text{PhB}(\text{CH}_2\text{P}^i\text{Pr}_2)_2]$ ligand is mechanistically important in generating the silicide product.

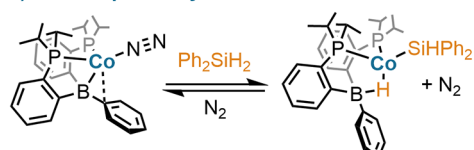
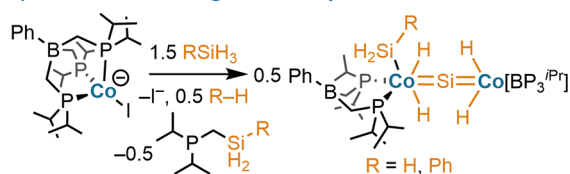
For *bis*-phosphine borane ligands of the type $[\text{PhB}(\text{CH}_2\text{PR}_2)_2]$, the P- and B-sites are in close proximity as they are linked by C_1 fragments. These ligands therefore offer greater rigidity than the more commonly employed examples incorporating C_2 linkers (frequently *o*-phenylene) which enable close $\text{M}–\text{B}$ contacts.^{5,6,18,19} However, the more structurally rigid frameworks might enforce separation of an electron-rich metal center from a nearby electrophilic boron to give a situation analogous to that of “frustrated” Lewis pairs (FLPs).^{20,21} In addition, isolation of the M- and B-centers may allow for these two sites to be independently modified (e.g., by selective coordination of a Lewis base to M or B), and should enable study of the influence of a remote electrophile on a transition metal center.

An interesting ligand in this context is $\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2$ ($[\text{BP}_2^t\text{Bu}]$), which should provide significant steric demand and rigidity when coordinated to a metal center. This molecule has previously been utilized in accessing an unsymmetrical borate ligand, $[\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)_2(\text{pyrazolyl})]^-$, which functions as a *P,P,N*-donor ligand when coordinated to a metal center.²² However, the coordination chemistry of complexes bearing this

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a) M–B cooperativity in substrate bond-activation:⁹b) Borate to borane ligand decomposition:¹⁷

c) Investigation of a structurally rigid borane ligand: (present work)

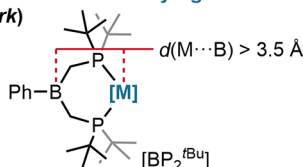


Figure 1. (a) Role of phosphine-borane ligands possessing close M–B contacts in substrate bond activation. (b) Spontaneous formation of a phosphine-borane ligand via borate ligand decomposition. (c) Structure of the structurally rigid phosphine-borane ligand investigated in this work.

bis-phosphino borane has not been separately examined. This work describes the synthesis, characterization, and chemical transformations of Co, Ni, and Cu complexes of the $[\text{BP}_2^{\text{tBu}}]$ ligand.

RESULTS AND DISCUSSION

Coordination Chemistry of $[\text{BP}_2^{\text{tBu}}]$. The $[\text{BP}_2^{\text{tBu}}]$ proligand was prepared via salt-metathesis of two equivs of $^t\text{Bu}_2\text{PCH}_2\text{Li}$ and one equiv of PhBCl_2 , as described by Thomas and Peters.²² Colorless block crystals of this compound were obtained by cooling a saturated pentane solution to -35°C for 12 h. The solid-state molecular structure reveals monomeric units of $[\text{BP}_2^{\text{tBu}}]$ with trigonal planar coordination about the boron atom [$\Sigma_\angle = 359.9(3)^\circ$; see [Supporting Information](#), Figure S1]. Furthermore, there are no apparent intermolecular interactions between P and B atoms of neighboring molecules, nor are there any intramolecular $\text{P}\cdots\text{B}$ interactions [$d(\text{P}–\text{B})_{\text{ave}} = 2.887(4) \text{ \AA}$].²³

The addition of solid $[\text{BP}_2^{\text{tBu}}]$ to THF suspensions of CoCl_2 , $\text{NiCl}_2(1,2\text{-dimethoxyethane})$, or CuCl results in rapid color changes to blue, purple, or yellow, respectively. The products of these reactions, $[\text{BP}_2^{\text{tBu}}]\text{CoCl}_2$ ($\mathbf{1}_{\text{Co}}$), $[\text{BP}_2^{\text{tBu}}]\text{NiCl}_2$ ($\mathbf{1}_{\text{Ni}}$), and $[\text{BP}_2^{\text{tBu}}]\text{CuCl}$ ($\mathbf{2}_{\text{Cu}}$) were obtained as bright blue, mauve, and yellow crystalline solids, respectively, after workup ([Scheme 1](#)). Complexes $\mathbf{1}_{\text{Co}}$ and $\mathbf{1}_{\text{Ni}}$ are paramagnetic with solution magnetic moments of $4.5 \mu_{\text{B}}$ and $3.0 \mu_{\text{B}}$ (Evans method), respectively; these values are consistent with $S = 3/2$ (Co^{II}) and $S = 1$ (Ni^{II}) centers in tetrahedral ligand fields. Interestingly, the ^1H NMR spectra of $\mathbf{1}_{\text{Co}}$ and $\mathbf{1}_{\text{Ni}}$ display only modest paramagnetic shifting of resonances for the hydrogen nuclei of the Ph ring, with discernible spin–spin ($^3J_{\text{HH}}$) couplings, in addition to paramagnetically shifted, broadened resonances due to the ^tBu and CH_2 groups. In contrast to complexes $\mathbf{1}_{\text{Co}}$ and $\mathbf{1}_{\text{Ni}}$, $\mathbf{2}_{\text{Cu}}$ is diamagnetic and its ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra displays sharp resonances ($\delta_{\text{P}} = 22.1$

Scheme 1. Syntheses of $[\text{BP}_2^{\text{tBu}}]\text{MCl}_2$ ($\text{M} = \text{Co}$, $\mathbf{1}_{\text{Co}}$; $\text{M} = \text{Ni}$, $\mathbf{1}_{\text{Ni}}$) and $[\text{BP}_2^{\text{tBu}}]\text{CuCl}$ ($\mathbf{2}_{\text{Cu}}$)

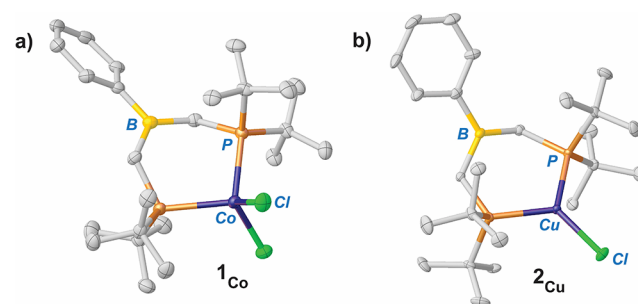
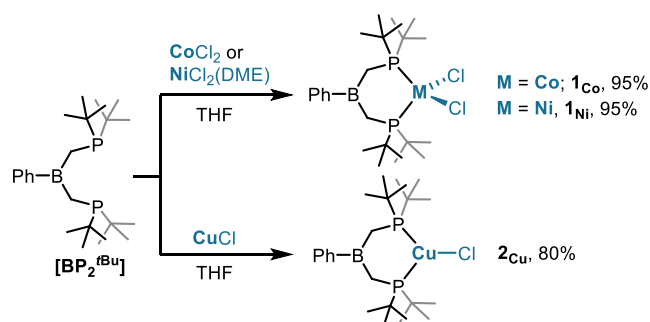


Figure 2. Solid-state molecular structures of $\mathbf{1}_{\text{Co}}$ (a) and $\mathbf{2}_{\text{Cu}}$ (b). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

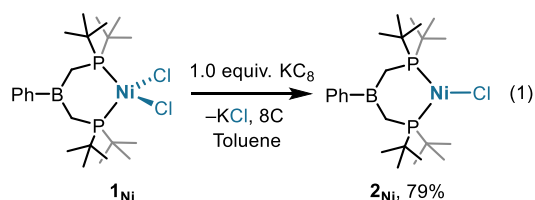
ppm) that are only modestly shifted compared to those of free $[\text{BP}_2^{\text{tBu}}]$ ($\delta_{\text{P}} = 38.4 \text{ ppm}^{22}$).

While both $\mathbf{1}_{\text{Co}}$ and $\mathbf{1}_{\text{Ni}}$ crystallize as long, thin needles, the crystals of $\mathbf{1}_{\text{Ni}}$ were not of sufficient size to allow for X-ray structural determination. Complex $\mathbf{1}_{\text{Co}}$ ([Figure 2a](#)) crystallizes with two molecules in the asymmetric unit that possess essentially identical coordination geometries about the Co centers, with the Co–P distances ranging from $2.379(2)$ – $2.404(2) \text{ \AA}$. As anticipated, the rigid $[\text{BP}_2^{\text{tBu}}]$ ligand enforces a long $\text{Co}\cdots\text{B}$ distance [$3.890(4)$ and $3.893(4) \text{ \AA}$], indicating no direct Co–B interaction. The boron centers of both molecules are rigorously planar, with $\Sigma_\angle = 360.0(5)^\circ$ (averaged across both molecules). The six-membered chelate ring of the $[\text{BP}_2^{\text{tBu}}]$ ligand is modestly puckered, with the P, Co, P and C, B, C atoms defining two planes with a torsion angle averaging $27.5(2)^\circ$ for the two molecules.

The crystallographic solid-state molecular structure of $\mathbf{2}_{\text{Cu}}$ ([Figure 2b](#)) reveals a monomeric unit possessing trigonal planar coordination at both the copper [$\Sigma_{\angle, \text{Cu}} = 359.81(9)^\circ$] and boron centers [$\Sigma_{\angle, \text{B}} = 359.1(5)^\circ$]. Unlike $\mathbf{1}_{\text{Co}}$, the $[\text{BP}_2^{\text{tBu}}]$ Cu ring of $\mathbf{2}_{\text{Cu}}$ adopts a half-chair conformation with the C, B, C fragment being puckered out of the mean plane defined by the C, P, Cu, P, C set of atoms [fold $\angle = 50.6(4)^\circ$]. The $\text{Cu}\cdots\text{B}$ separation of $3.639(5) \text{ \AA}$ is smaller than that of $\mathbf{1}_{\text{Co}}$, likely resulting from the differing conformations of the six-membered $[\text{BP}_2^{\text{tBu}}]\text{M}$ chelate rings.

The reduction of $\mathbf{1}_{\text{Ni}}$ was examined as a possible route to a nickel(I) complex. Nickel(I) species remain relatively uncommon, though their unique structural and magnetic properties have attracted considerable attention.^{24,25} The addition of KC_8 to $\mathbf{1}_{\text{Ni}}$ in toluene solution resulted in a color change from clear purple to orange over 24 h and the product, $[\text{BP}_2^{\text{tBu}}]\text{NiCl}$ ($\mathbf{2}_{\text{Ni}}$), was isolated as an analytically pure solid following a workup ([eq 1](#)). Crystals of $\mathbf{2}_{\text{Ni}}$ were grown by

maintaining a saturated THF solution layered with $(\text{Me}_3\text{Si})_2\text{O}$ at -35°C for 18 h.



The solid-state structure of 2_{Ni} (Figure 3a) resembles that of 2_{Cu} with a trigonal planar coordination geometry at the Ni and B centers. The Ni...B distance of 3.733(4) Å is in between the analogous metrical parameters of 1_{Co} and 2_{Cu} . The ^1H NMR spectrum of 2_{Ni} is dominated by broad, featureless resonances, and an Evans method measurement reveals a solution magnetic moment of $1.9 \mu_{\text{B}}$, consistent with an $S = 1/2$ spin state. Thus, 2_{Ni} likely retains a monomeric structure in solution. Dimeric species with $\text{Ni}_2(\mu\text{-Cl})_2$ cores often exhibit spin-pairing because of antiferromagnetic superexchange through the bridging chloride ligands, or potentially via direct Ni–Ni interactions.^{26–29}

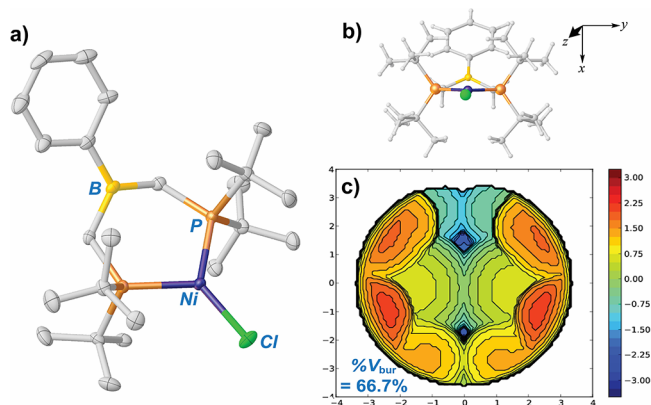


Figure 3. (a) Solid-state molecular structure of 2_{Ni} . Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. (b) View of 2_{Ni} along the Cl–Ni axis and coordinate system orientation. (c) Steric map of $[\text{BP}_2^{\text{tBu}}]$ in 2_{Ni} , viewed along the Cl–Ni axis.

The monomeric structure of 2_{Ni} reflects the larger size of $[\text{BP}_2^{\text{tBu}}]$ relative to other ligands commonly encountered in Ni^{I} species, such as dtbpe [dtbpe = 1,2-bis-(di-tert-butylphosphino)ethane] or IPr [IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene], both of which support $\text{Ni}_2(\mu\text{-Cl})_2$ -type dimers, namely, $[(\text{dtbpe})\text{NiCl}]_2$ ²⁶ and $[(\text{IPr})\text{NiCl}]_2$.²⁷ The buried volume ($\%V_{\text{bur}}$) provides a useful quantitative measure of the bulk of these ligands,^{30,31} with $[\text{BP}_2^{\text{tBu}}]$ ($\%V_{\text{bur}}$ = 66.7%; Figure 3c)³² encapsulating the metal center to a significantly greater extent than dtbpe ($\%V_{\text{bur}}$ = 58.4%)³³ or IPr ($\%V_{\text{bur}}$ = 40.8%).³⁴ As anticipated, the $[\text{BP}_2^{\text{tBu}}]$ ligand has steric properties very similar to those of dtbpp [dtbpp = 1,3-bis-(di-tert-butylphosphino)propane] ($\%V_{\text{bur}}$ = 62.8%).³⁵

The Ni–Cl bond length of 2.163(1) Å in 2_{Ni} is shorter than the analogous Cu–Cl distance of 2.213(1) Å in 2_{Cu} despite the small ionic radius of the copper atom.³⁶ A qualitative energy-level molecular orbital (MO) diagram of $[\text{L}_2]\text{M}^{\text{I}}\text{Cl}$ complexes under C_{2v} symmetry (Figure 4) indicates that this elongation

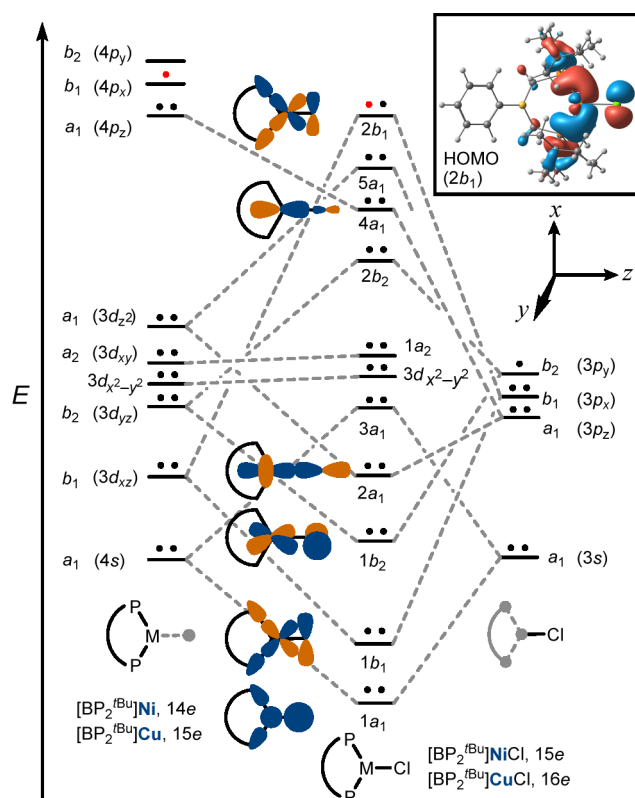
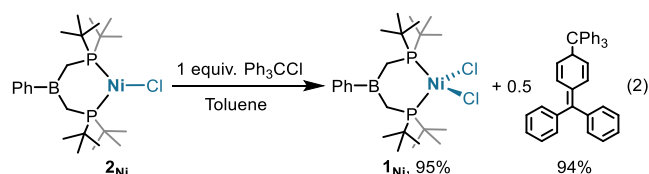


Figure 4. Qualitative MO energy-level diagram of $[\text{BP}_2^{\text{tBu}}]\text{MCl}$. Dots (•) represent electrons; the red dot is an additional electron from Cu. Atomic orbital labels on the left-hand side (in brackets) denote transition-metal orbital parentage for $[\text{BP}_2^{\text{tBu}}]\text{M}$ -fragment orbitals. Inset: rendering of HOMO from DFT calculations (isolevel 0.03) of 2_{Cu} at the $\omega\text{B97X-D3}$ level of theory.

results from additional filling of an antibonding $\pi^*(\text{M}–\text{Cl})$ orbital ($2b_1$) in 16-electron 2_{Cu} compared to 15-electron 2_{Ni} . The additional electron in 2_{Cu} is represented by a red-colored dot in Figure 4. Further theoretical confirmation of this hypothesis was provided by density functional theory (DFT) computations at the $\omega\text{B97X-D3}$ level of theory for 2_{Cu} . Consistent with the qualitative MO diagram shown in Figure 4, the calculated highest-occupied MO (HOMO) is of π -symmetry and is dominated by Cu–Cl antibonding character (Figure 4, inset).

Cyclic voltammetric studies of 2_{Ni} in 1,2-difluorobenzene solution (1 mM 2_{Ni} , 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ electrolyte) identified a quasi-reversible wave corresponding to the $\text{Ni}^{\text{I}}/\text{Ni}^{\text{II}}$ couple at -0.321 V, suggesting that the chemical oxidation of 2_{Ni} to regenerate 1_{Ni} should be possible. Indeed, the treatment of a toluene solution of 2_{Ni} with one equiv of trityl chloride resulted in a rapid color change from clear orange to purple, indicating the formation of dichloride complex 1_{Ni} . The ^1H NMR spectrum of the product mixture showed that 1_{Ni} and Gomberg's dimer are the exclusive products of this reaction (eq 2). The products were separated by extraction of Gomberg's dimer into pentane and each was isolated in nearly quantitative yields.

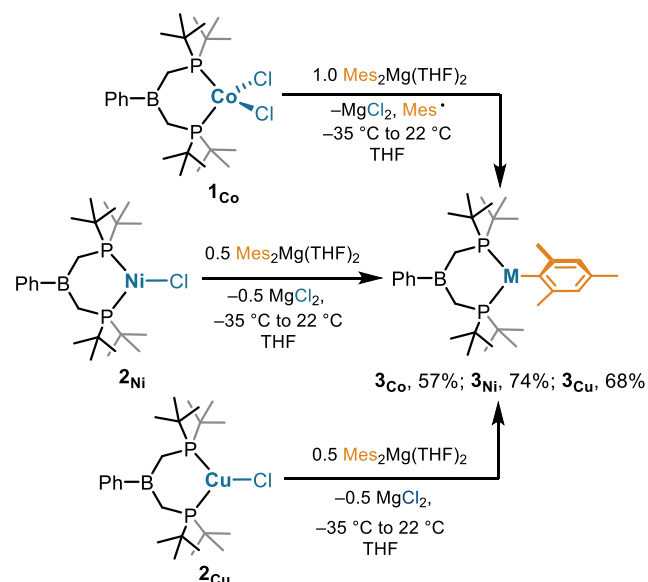
Synthesis of $[\text{BP}_2^{\text{tBu}}]\text{M}$ –Mesityl Derivatives. Attempts to affect the one electron reduction of 1_{Co} to generate $[\text{BP}_2^{\text{tBu}}]\text{CoCl}$ were frustrated by apparent disproportionation pathways. Treatment of toluene or THF solutions of 1_{Co} with KC_8 , NaHg , or zinc dust generated no tractable products, and



only trace quantities of 1_{Co} were recovered from the reaction mixtures in addition to a black powder (presumably Co^0) that was attracted to the poles of the magnetic stir bar. It seemed that a kinetically stable $[\text{BP}_2^{\text{tBu}}]\text{Co}^{\text{I}}\text{--X}$ species might be isolable if disproportionation pathways were inhibited by a sufficiently bulky X group (X = alkyl, aryl).

Treatment of 1_{Co} with one equiv of $\text{Mes}_2\text{Mg}(\text{THF})_2$ in THF solution at -35°C led to the formation of a dark green complex that was isolated as a crystalline solid following filtration and crystallization from toluene (Scheme 2). The ^1H

Scheme 2. Synthesis of $[\text{BP}_2^{\text{tBu}}]\text{M}(\text{Mes})$ Complexes (M = Co, 3_{Co} ; M = Ni, 3_{Ni} ; M = Cu, 3_{Cu})



NMR spectrum and Evans method magnetic moment ($3.7 \mu_{\text{B}}$) is consistent with its formulation as $[\text{BP}_2^{\text{tBu}}]\text{Co}(\text{Mes})$ (3_{Co}), and this was confirmed by single-crystal X-ray diffraction studies (Figure 5a). Complex 3_{Co} is stable in benzene- d_6 solution for at least 5 days and can be stored indefinitely as a solid at -35°C under an inert atmosphere. In this reaction, $\text{Mes}_2\text{Mg}(\text{THF})_2$ serves both to install Mes upon cobalt, and to reduce the metal center. Consistently, the ^1H NMR spectrum of the crude reaction mixture in THF solution indicates that upon reduction, an equiv of $\text{Mes}^\bullet$ is converted into bimesitylene [82% vs $\text{Mes}_2\text{Mg}(\text{THF})_2$] and mesitylene [16% vs $\text{Mes}_2\text{Mg}(\text{THF})_2$], as determined by integration against an internal standard of $(\text{Me}_3\text{Si})_2\text{O}$.

The congeneric Ni and Cu $[\text{BP}_2^{\text{tBu}}]\text{M}(\text{Mes})$ complexes (3_{Ni} , 3_{Cu} respectively) were readily generated by the treatment of monohalides 2_{Ni} and 2_{Cu} with 0.5 equiv $\text{Mes}_2\text{Mg}(\text{THF})_2$. Complexes 3_{Ni} and 3_{Cu} were isolated as dark orange- and orange-colored crystalline solids, respectively (Scheme 2). Complex 3_{Ni} is paramagnetic, as evidenced by the solution-state Evans method magnetic moment of $1.7 \mu_{\text{B}}$. Complex 3_{Cu} unlike its cobalt and nickel congeners, is diamagnetic and exhibits sharp, resolved resonances in its ^1H , $^{31}\text{P}\{^1\text{H}\}$, and

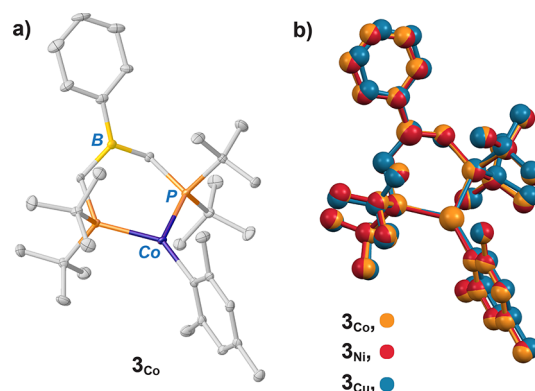


Figure 5. (a) Solid-state molecular structure of 3_{Co} . Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. (b) Overlay of solid-state molecular structures of 3_{Co} , 3_{Ni} , and 3_{Cu} .

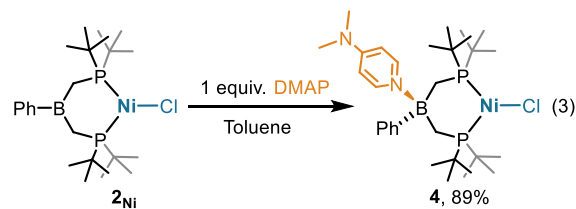
$^{13}\text{C}\{^1\text{H}\}$ NMR spectra, with chemical shifts that are not influenced by pseudocontact shifts ($\delta_{\text{P}} = 28.9$ ppm).

Complexes 3_{Co} , 3_{Ni} , and 3_{Cu} crystallize in triclinic space group $P\bar{1}$ and are essentially isostructural in the solid-state (Figure 5b). All three crystal structures exhibit twinning, suggesting that this is an inherent solid-state feature of $[\text{BP}_2^{\text{tBu}}]\text{M}(\text{Mes})$ molecules. In each molecule, the plane defined by the Mes ring is oriented perpendicular to the P, M, P plane.

The synthetic routes to complexes 3_{Co} , 3_{Ni} , and 3_{Cu} illustrate that the borane functionalities of the corresponding starting materials are resistant to nucleophilic attack by $\text{Mes}_2\text{Mg}(\text{THF})_2$. This feature is likely a function of the steric constraints imposed by Mes substituents, whose bulk precludes the formation of four-coordinate boron centers in this system. This is consistent with the observation that the attempted preparation of benzyl complexes of the form $[\text{BP}_2^{\text{tBu}}]\text{M}(\text{CH}_2\text{Ph})$ (M = Co, Ni, Cu) were unsuccessful when 1_{Co} , 2_{Ni} , and 2_{Cu} were treated with the corresponding quantities of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2$, resulting instead in the formation of intractable mixtures of products in THF solution.

Lewis Base Coordination to the $[\text{BP}_2^{\text{tBu}}]$ Ligand of 2_{Ni}

In addition to chemical transformations occurring at the transition-metal center, the boron centers represent a second potential reaction site in $[\text{BP}_2^{\text{tBu}}]$ -ligated complexes; thus, a straightforward transformation involves treatment of these complexes with a Lewis base. This type of functionalization may serve to alter the electronic properties of the complex in a remote fashion.



Addition of one equiv of 4-dimethylaminopyridine (DMAP) to 2_{Ni} in toluene solution resulted in rapid bleaching of the orange color, and deposition of an off-white solid after several minutes. The solid material, which is soluble in THF and 1,2-difluorobenzene, was crystallized from concentrated THF solution at -35°C . Single-crystal X-ray diffraction analysis

of the nearly colorless blocks confirms the identity of the product to be the adduct $[\text{PhB}(\text{DMAP})(\text{CH}_2\text{P}^t\text{Bu}_2)_2]\text{NiCl}$ (**4**; Figure 6).

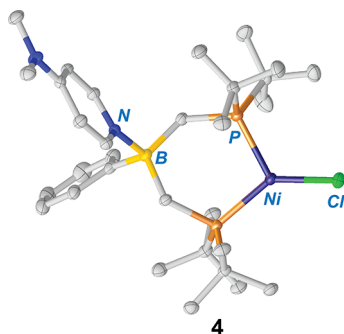


Figure 6. Solid-state molecular structure of **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

The solid-state molecular structure of **4** possesses a trigonal planar nickel center, while the boron atom is tetrahedrally coordinated with $\tau_4 = 0.93$. The Ni–Cl bond in **4** [$d(\text{Ni}–\text{Cl}) = 2.1786(6)$ Å] is slightly elongated (by ~ 0.02 Å) relative to that in **2**_{Ni}. This minor structural change may be the result of the somewhat greater steric demands of $[\text{PhB}(\text{DMAP})(\text{CH}_2\text{P}^t\text{Bu}_2)_2]$ relative to the parent $[\text{BP}_2^t\text{Bu}]$ ligand. Another possibility is that the presumably highly electron releasing ligand sphere in **4** generates a more electron-rich nickel center that repels the chloride ligand.

To examine whether the DMAP-ligated boron center of **4** could be “deprotected”, **4** was treated with one equiv of a Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$. Analysis of the reaction mixture by ^1H NMR spectroscopy in the presence of an internal standard $[(\text{Me}_3\text{Si})_2\text{O}]$ indicated that **2**_{Ni} and $\text{DMAP}–\text{B}(\text{C}_6\text{F}_5)_3$ were formed in high yields (eq 4) as the sole products of the reaction.

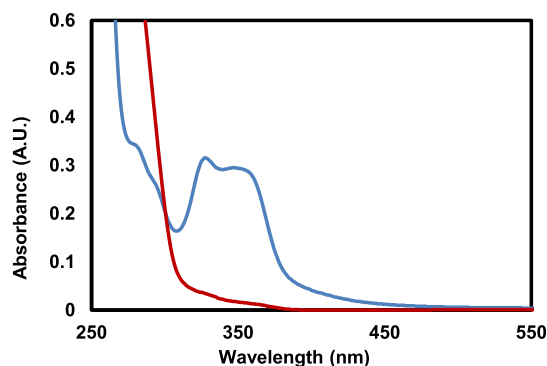
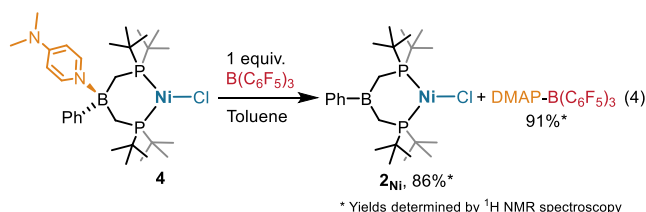


Figure 7. UV–visible spectra of **2**_{Ni} (blue trace) and **4** (red trace) recorded in THF solution.

potentially useful starting materials for accessing metal–element bonds via addition–elimination reactions with main-group element hydrides to eliminate mesitylene. The boron center of the $[\text{BP}_2^t\text{Bu}]$ ligand can be further modified by the coordination of a Lewis base, resulting in changes to the spectroscopic properties of the complex. This feature presents a method for tuning molecular properties by the modification of the metals’ secondary coordination sphere.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.2c00378>.

Atomic coordinates for **2**_{Cu} (XYZ)

Detailed descriptions of syntheses, crystallography, computations, UV–visible spectroscopy, electrochemistry, and NMR spectra (PDF)

Accession Codes

CCDC 2175406–2175413 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

The UV–visible spectra of **2**_{Ni} and **4** in THF solution (Figure 7) show significant differences that can be attributed to the coordination of DMAP. Notably, two major absorption features exhibited by **2**_{Ni} at 347 nm ($\epsilon = 2769 \text{ M}^{-1} \text{ cm}^{-1}$) and 328 nm ($\epsilon = 2956 \text{ M}^{-1} \text{ cm}^{-1}$) are absent in the spectrum for **4**, consistent with the observed colors of these complexes. On this basis, the transitions at 347 and 328 nm observed in the electronic spectrum of **2**_{Ni} are assigned to $\text{B} \leftarrow \text{Ni}$ charge transfer, a process which is quenched by coordinative and electronic saturation of the boron center of **4**.

■ CONCLUSIONS

Complexes bearing the $[\text{BP}_2^t\text{Bu}]$ ligand have been established for mono- and di-valent late 3d transition-metals. These studies illustrate that the $[\text{BP}_2^t\text{Bu}]$ ligand facilitates access to reduced organometallic species (namely, 3Co and 3Ni) without the degradation of the borane functionality, provided that an appropriate reductant is used. The mesityl derivatives are

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- (33) $\%V_{\text{bur}}$ was calculated for the (dtbpe)Ni fragment found in CCDC entry RUYMIH {corresponding to $[(\text{dtbpe})\text{NiCl}]_2$ } with the

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