Chemistry–A European Journal
Full Paper
doi.org/10.1002/chem.202001218

Boraneyl Complexes |*Hot Paper*|

Octaboraneyl Complexes of Nickel: Monomers for Redox-Active Coordination Polymers

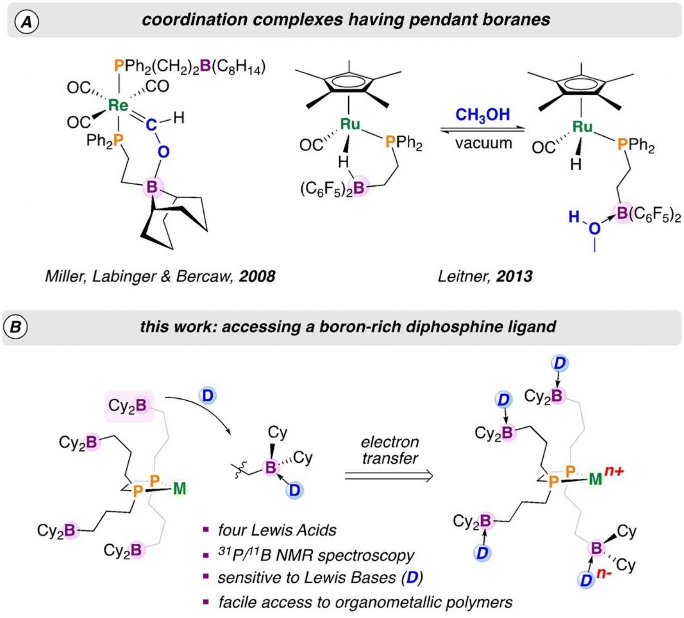
Marcus W. Drover,*[a] Maeve C. Dufour,[a] Lindsay A. Lesperance-Nantau,[a] Rayni P. Noriega,[a] Kirill Levin,[a] and Robert W. Schurko[a, b]

Abstract: Herein, we establish the preparation, characterization, and reactivity of a new diphosphine ligand, 1,2-bis(di(3-dicyclohexylboraneyl)propylphosphino)ethane ($P_2B^{Cy}{}_4$), a scaffold that contains four pendant boranes. An entryway into the coordination chemistry of $P_2B^{Cy}{}_4$ is established by using nickel, providing the octaboraneyl complex $[Ni(P_2B^{Cy}{}_4)_2]$—this species contains a boron-rich secondary coordination sphere that reacts readily with Lewis bases. In the case of 4,4′-bipyridine, an air-sensitive coordination polymer is obtained. Characterization of this material by solid-state NMR and EPR spectroscopy reveals the presence of a charge-transfer polymer, which forms as a function of intramolecular Ni→4,4′-bpy electron transfer (ET), providing an array of oxidized nickel sites and reduced 4,4′-bpy radical anion sites. Notably, the related intermolecular reaction between the model fragments $[Ni(dnppe)_2]$ (dnppe = 1,2-bis(di-*n*-propylphosphino)ethane) and a bis(boraneyl)-protected 4,4′-bpy, provides no ET. Overall, the $P_2B^{Cy}{}_4$ fragment provides a unique opportunity for Lewis base activation, in one case allowing for the facile construction of monomers for incorporation into redox-active macromolecules.

Introduction

In the context of ligand design, phosphines occupy a privileged role, owing to the ease by which they are modified and reliably coordinated to elements spanning the periodic table.[1] Amongst this class, diphosphine ligands have found great applicability, with modifications to the backbone length and R substituent leading to dramatic improvements in performance, selectivity, and net reactivity.[2] From a design perspective, these ligands represent a blank canvas on which a number of creative elements can be painted. In the realm of phosphine coordination chemistry, one area of notice is represented by the design of ambiphilic ligands that support both Lewis acid and base functionality—the first derivatives of which appeared as early as 1960;[3] since then, such species have been the subject of invested interest.[4]

With an eye toward designing such platforms for use in ligand-assisted activation, emphasis has been placed on the use of peripheral groups, which are positioned to engage substrates through secondary sphere interactions (Scheme 1).[5] For example, Miller et al. showed that a phosphine-tethered 9-borabicyclo[3.3.1]nonane (9-BBN) fragment could be employed for the cooperative activation of CO at rhenium.[6] In a similar



Scheme 1. A) Coordination complexes having pendant boranes. B) This work: introducing a borane-rich bis(diboraneylphosphine) ligand.

---

[a] Prof. M. W. Drover, M. C. Dufour, L. A. Lesperance-Nantau, R. P. Noriega,
Dr. K. Levin, Prof. R. W. Schurko
Department of Chemistry and Biochemistry
The University of Windsor
401 Sunset Avenue, Windsor, ON, N9B 3P4 (Canada)
E-mail: marcus.drover@uwindsor.ca

[b] Prof. R. W. Schurko
Department of Chemistry and Biochemistry
The Florida State University
102 Varsity Way, Tallahassee, FL, 32306-4390 (USA)

Supporting information (containing ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR spectra (solution and solid state) for the complexes as well as crystallographic data for ***2*** *and* ***3****) and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.202001218.*

way, Klankermeyer and co-workers showed that a bis(pentafluorophenyl)boraneyl ruthenium(II) hydride permits the activation of small Lewis basic moieties through reversible binding at the boron center (Scheme 1 A).[7] In our approach, we envisaged stitching boraneyl functionality into a tethered (diphosphino)ethane ligand with the goal of carving out new space in the design of P,B-ambiphilic ligands. The proposed framework (Scheme 1 B) is appealing as it provides a means by which a dense borane canopy can be quickly and straightforwardly draped around a transition-metal center, enabling the activation of several Lewis bases, providing molecular or indeed, macromolecular architectures, based on judicious choice of substrate.

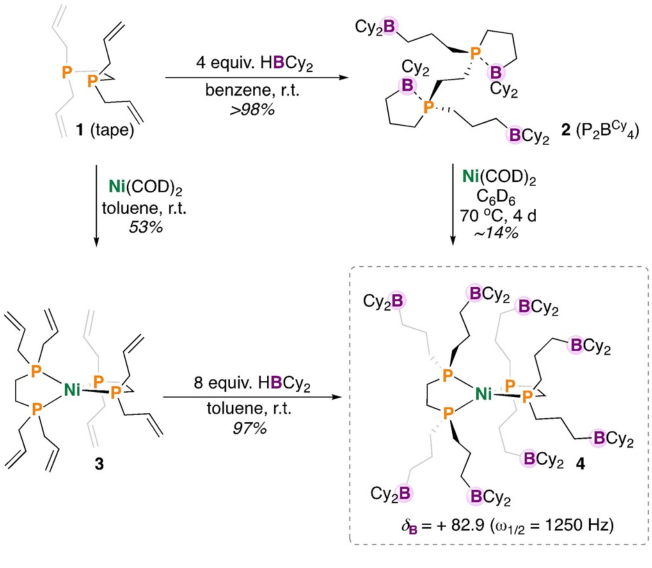
Herein, we disclose our initial endeavors with this new ambiphilic 1,2-bis(di(3-dicyclohexylboraneyl)-propylphosphino)ethane ($P_2B^{Cy}{}_4$) ligand, uncover its coordination chemistry by using nickel, and showcase the reactivity of the resulting complexes with Lewis bases. In one example, an open-shell charge-transfer polymer is prepared—an electron transfer reaction that is also reversible.

Results and Discussion

Entry into the system of present interest is as follows: allylation of 1,2-bis(dichlorophosphino)ethane by using five equivalents of allyl magnesium bromide provides the starting ligand precursor, 1,2-bis(diallylphosphino)ethane (tape),[8] which is isolated as a colorless oil.[9] With four allyl groups in-hand, we next sought to functionalize this substrate (**1**) by using hydroboration.

Reaction of an $HBCy_2$[10] (Cy = cyclohexyl) slurry and **1** in benzene or toluene provides a clear colorless solution after 5 min (Scheme 2).[11] Resulting from alkene reduction, the ^1H NMR spectrum of **2** provides signals in the $C(sp^3)$–H aliphatic region with $2.13 \geq \delta_H \geq 1.02$ ppm. More informatively, acquisition of a ^{31}P NMR spectrum shows consumption of the starting material and a new resonance at $\delta_P = +14.4$ ppm ($\Delta\delta_P = +43.1$ ppm cf. **1**), consistent with P(lp)→B(p) dative-bond formation. The ^{11}B NMR spectrum of **2** displays a broad signal at $\delta_B = 80.4$ ppm ($\Delta_{1/2} = 1500$ Hz).[12] Ultimately, cooling a saturated solution of **2** in hexane at −30 °C provides colorless blocks suitable for analysis by single-crystal X-ray diffraction (Figure 1). The core structure features a bis(diboraneylphosphino)ethane, which engages two of the four BCy_2R units in twisted five-membered rings.

Armed with a high-yielding route toward the desired ligand, $P_2B^{Cy}{}_4$ (**2**), we next wished to assess the propensity of this system to undergo ring-opening in the presence of an electron-rich d^{10} transition metal, $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene). Reaction of these two components in C_6D_6 at room temperature shows little conversion of the ligand precursor (by NMR spectroscopy). However, warming the mixture in a J. Young NMR tube at 70 °C (C_6D_6) proved more successful, providing two new ^{31}P resonances at $\delta_P = 39.2$ and 44.8 ppm along with uncoordinated COD ligand ($\delta_H = 5.57$ and 2.22 ppm—see the Supporting Information).[13] Although this transformation was low-yielding (≈14% conversion of **2** to **4** after 89 h), proof-of-coordination prompted us to devise an alternative route toward complex **4** (Scheme 2).



Scheme 2. Generation of the (diphosphino)ethane ligand **2** and ensuing Ni coordination chemistry.

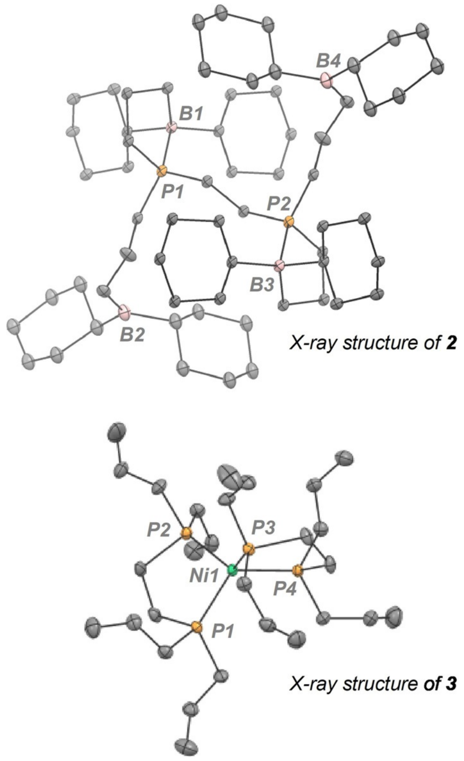


Figure 1. Mercury depiction of the solid-state molecular structures of **2** and **3** (displacement ellipsoids are shown at 50% probability, hydrogen atoms are omitted for clarity). The structure of compound **2** establishes connectivity only. Deposition numbers 1970972 (**2**) and 1970973 (**3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

To avoid the thermodynamic penalty associated with disruption of the P(lp)→B(p) bonding interaction in **2**, we sought to "protect" **1** by virtue of pre-coordination, with the desired B–C bond-forming steps being performed afterwards. Thus, a toluene solution of $[Ni(COD)_2]$ was slowly added to a solution of **1** (2 equiv), immediately causing a change in color from yellow to dark orange with concomitant formation of a ruby red precipitate. Following workup, $[Ni(tape)_2]$ (**3**) could be separated as a pale orange solid; crystals of **3** were grown from a saturated hexane solution at −30 °C. Owing to symmetry, the ^1H NMR spectrum displays three distinct signals: $\delta_H = 5.96$, 5.02, and 2.44 ppm for the allyl fragment and a single resonance at $\delta_P = 30.3$ ppm is observed by ^{31}P NMR spectroscopy. The crystal structure of **3** (Figure 1) corroborates formation of a tetrahedral Ni^0 complex ($\tau_4 = 0.89$)[14] having eight terminal C=C groups.

With eight sites ripe for modification, we next turned our sight to hydrofunctionalization. Treatment of a benzene solution of **3** with a slurry of $HBCy_2$ (8 equiv) results in a change in color from cloudy pale yellow to clear dark orange within a matter of seconds. Analysis by $^1H/^{13}C$ NMR spectroscopy confirms reaction of **3** as noted by the absence of olefinic $C(sp^2)$–H signals. In the ^1H NMR spectrum, and as observed for the ligand **2**, only a cluster of signals in the $C(sp^3)$–H aliphatic region ($1.94 \geq \delta_H \geq 1.30$ ppm) are apparent. Furthermore, a single resonance at $\delta_P = 39.2$ ppm fully supports formation of a symmetric compound, whereas an ^{11}B NMR resonance at $\delta_B = 82.9$ ppm ($\Delta_{1/2} = 1250$ Hz) confirms the incorporation of boraneyl functionality. ESI(+) MS also provides an $[M+H]^+$ signal at $m/z = 1992.734$ (calcd: 1992.737) for **4** of the appropriate isotope pattern. The speed and cleanliness of this reaction are notable given that **3** has undergone eight hydroboration reactions.

We next wished to examine if the secondary coordination sphere of **4** could be modified by exposure to Lewis basic moieties, and if so, which spectroscopic signatures might best reflect the nature of these interactions. Toward this aim, we monitored the reaction of **4** with 1–8 equivalents of the strong donor, 4-*N*,*N*-dimethylaminopyridine (DMAP) in C_6D_6 (Figure 2). Upon addition of one equivalent, the ^{31}P NMR spectrum broadens appreciably, indicating rapid fluxional behavior in solution (given that four distinct ^{31}P environments are not observed). At 2–4 equivalents of DMAP, the ^{31}P NMR signal further broadens (due to the presumed presence of multiple coordination isomers) and at five equivalents of DMAP, the signal sharpens considerably, approaching $\delta_P = 35.0$ ppm—the signal that is observed for isolated $Ni(P_2B^{Cy}{}_4)_2(DMAP)_8$ (**5**) (see below). Following this titration by ^1H NMR spectroscopy evidences gradual downfield-shifting of the DMAP $C{-}\underline{H}_{ortho}$, $C{-}\underline{H}_{meta}$, and $N(CH_3)_2$ signals as a function of added DMAP. Of note, addition of excess DMAP (9 equiv) shows ^1H NMR signals for both free and bound donor of integration 1:8 (see the Supporting Information), indicating that owing to its octaboraneyl secondary coordination sphere, complex **4** uptakes eight equivalents of DMAP. In an effort to access complex **5** cleanly, the reaction mixture can be washed with hexane to remove excess DMAP. The ^1H and ^{31}P NMR spectra for the isolated compound are as discussed previously. In terms of ^{11}B NMR spectroscopy, addition of 1–7 equivalents DMAP causes baseline broadening of the ^{11}B NMR signal for **4** ($\delta_B = 82.9$ ppm) and no signal for the DMAP-coordinated borane is observed. However, upon addition of excess DMAP and/or following isolation of **5**, a new up-

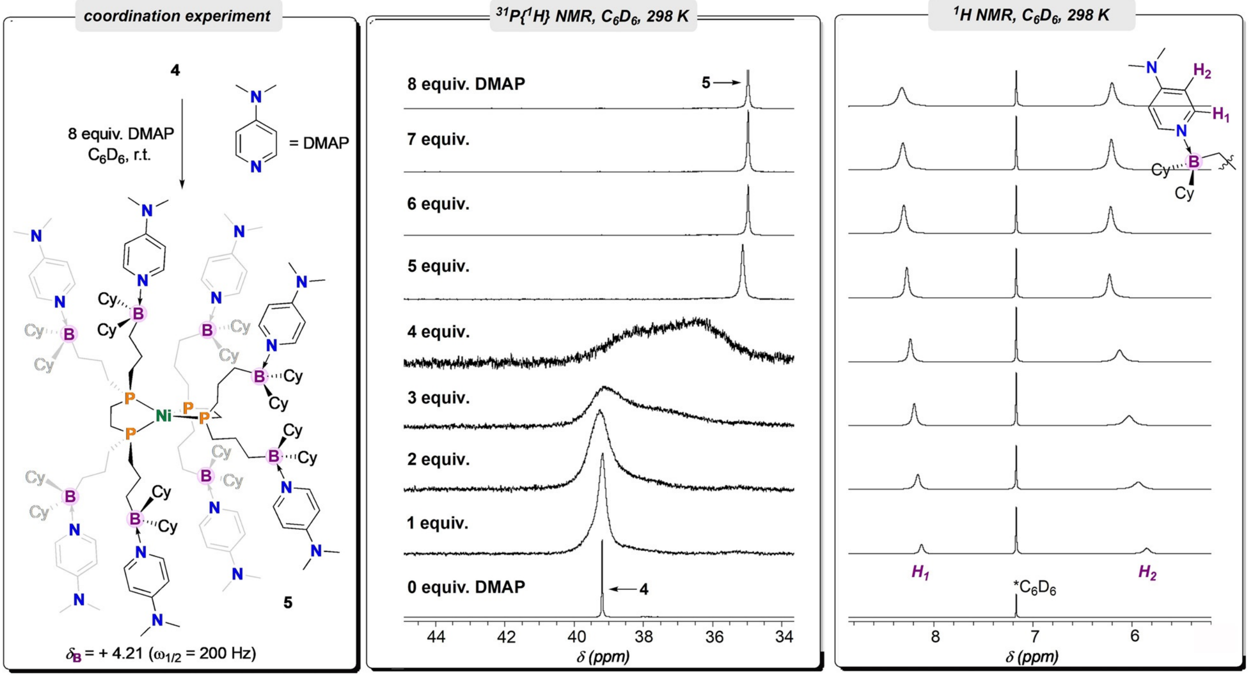
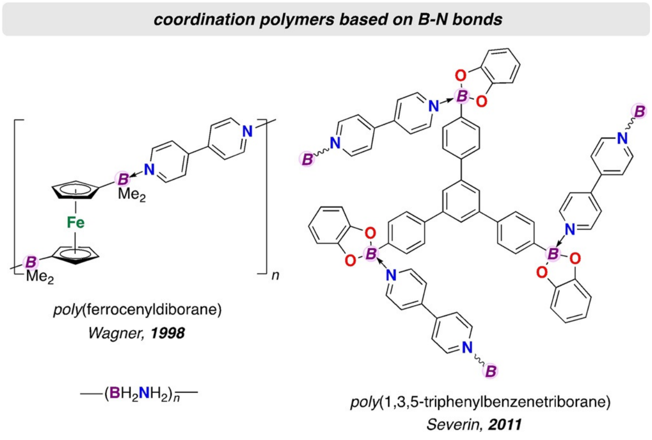


Figure 2. A) Reaction of **4** with eight equivalents 4-*N*,*N*-dimethylaminopyridine (DMAP). B) $^{31}P\{^1H\}$ NMR spectra (C_6D_6, 203 MHz, 298 K) as a function of added DMAP. C) ^1H NMR spectra (C_6D_6, 500 MHz, 298 K) as a function of added DMAP. $\delta_H(C_6D_6) = 7.16$ ppm.

field-shifted signal at $\delta_B = 4.21$ ppm ($\Delta_{1/2} = 200$ Hz, $\Delta\delta_B = -78.7$ ppm *cf.* **4**), is observed, consistent with formation of eight DMAP→B(Cy_2)R units. Of note, binding of THF or Et_2O by **4** (or **2**) is not observed (by $^1H/^{31}P/^{11}B$ NMR spectroscopy).

Given the strong affinity of the $P_2B^{Cy}_4$ framework for Lewis bases, we wondered if combination of **4** with a linking reagent, for example, a disubstituted donor, would provide an entry point into organometallic [Ni]-based coordination polymers.[15] Such arrays represent materials of particular interest, owing to potential applications in functional materials, for example, for electrical conductivity, magnetism, and/or optical applications, to name a few (Scheme 3).[16] This methodology would also furnish a new route towards Ni (and main-group)-rich macromolecules, which could be assembled and disassembled facilely—an ongoing area of interest. In this vein, combination of **4** with four equivalents of 4,4′-bipyridine (4,4′-bpy) in THF or C_6H_6 at room temperature results in immediate precipitation of a dark green amorphous solid in 89% yield (Figure 3A); this material is insoluble in hydrocarbon and ethereal solvents and is highly air/moisture sensitive, changing from green to yellow in less than 1 min on exposure to air (Figure 3B). Analysis of this yellow solid by NMR spectroscopy ($CDCl_3$) evidences formation of free 4,4′-bpy and decomposed ligand.



Scheme 3. Coordination polymers based on B–N bonds.

The connectivity of **6** was first investigated using solid-state NMR spectroscopy.[17] Contrary to our original supposition that **6** is a diamagnetic material comprising Ni^0 sites, acquisition of a standard ^1H magic-angle spinning (MAS) NMR spectrum revealed an extremely fast longitudinal (T_1) relaxation rate, as expected for a paramagnetic sample. Acquisition of a ^{13}C Hahn-echo MAS NMR spectrum further corroborated this observation (the failure of $^1H–^{13}C/^{31}P$ cross-polarization MAS (CP/MAS) experiments provided further evidence of the presence of unpaired electron spin density). Experiments performed with half- and full-echo acquisition by using two different relaxation delays demonstrate a significant difference in relaxation between the two sets of resonances centered at $\delta_C = 150$ and 25 ppm associated with the polymer C(sp^2) and C(sp^3) groups,

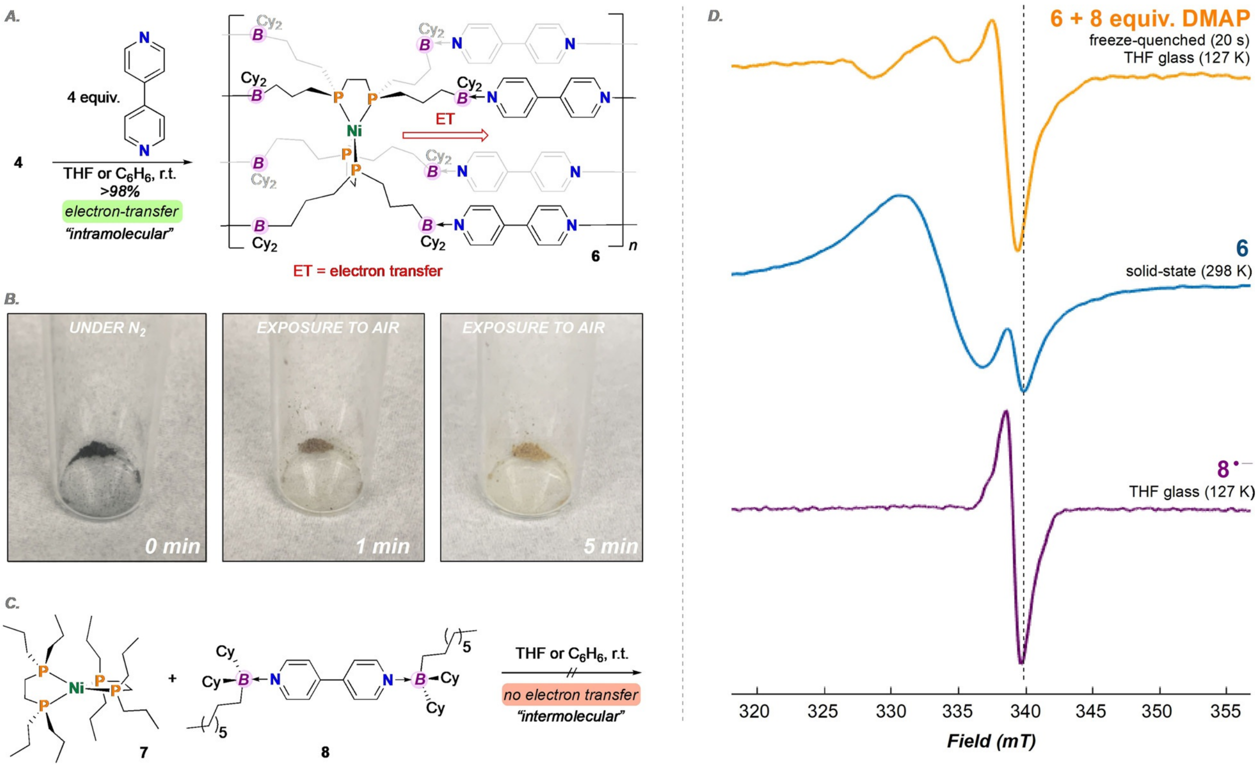


Figure 3. A) Reaction of **4** with 4,4′-bpy to generate the linked coordination polymer **6** (proposed structure). B) Exposure of solid **6** to air for 0, 1, and 5 min showing decomposition. C) Attempted reaction between **7** and **8** illustrating that intermolecular electron transfer is disfavored. D) EPR spectra (9.50 GHz) of $\mathbf{8}^{\bullet-}$ as a THF glass at 127 K (bottom), **6** in the solid-state at 298 K (middle), and the freeze-quenched spectrum of **6**+**8** equiv of DMAP after 20 s as a THF glass at 127 K (top).

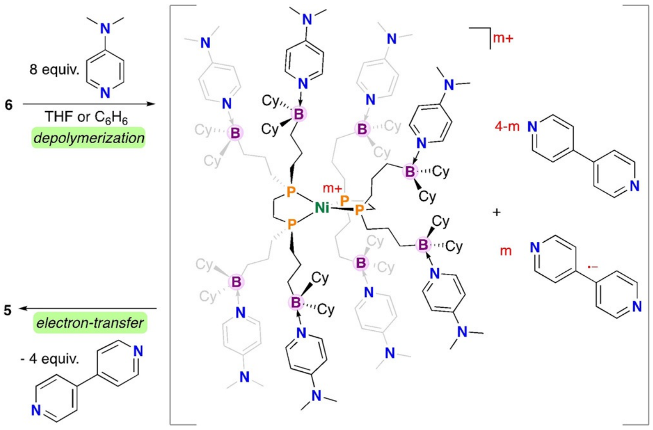
respectively (see the Supporting Information). Given that the dominant contributor to T_1 relaxation in a paramagnetic solid system originates from direct dipolar electron-nuclear coupling, the difference observed in T_1 for these different carbon groups suggests the presence of unpaired-electron spin density at or near the C(sp^2) bipyridine ring carbon atoms. In the ^{11}B MAS NMR spectrum, a center-of-gravity shift (cgs), $\delta_{cgs} = -6(2)$ ppm is observed ($\Delta_{1/2} = 2.5(3)$ kHz), whereas the ^{31}P Hahn-echo MAS NMR spectrum of **6** provides a weak signal at $\delta_P = 40(5)$ ppm; these signals are similar to those observed in **5**. Given that this ^{31}P NMR signal is not paramagnetically-shifted (and is visible at all, in spite of its rapid relaxation delay), might suggest an $S=0$ Ni spin state (i.e., there are no unpaired electrons at Ni). Acquisition of a solid-state FTIR spectrum corroborates coordination of the 4,4′-bpy N(lp) to the B(p)Cy$_2$R units of **4**, providing C=C/C=N resonances at $\tilde{\nu} = 1620$, 1536, and 1485 cm^{-1} for **6**, which are different from those of free 4,4′-bpy ($\tilde{\nu} = 1590$, 1531, and 1487 cm^{-1} [KBr disk]).[16a]

Altogether, these data are consistent with 1) 4,4′-bpy coordination and 2) electron transfer (ET), providing an array of oxidized nickel and reduced 4,4′-bpy sites. To contextualize this result and to emphasize the necessity of the $P_2B^{Cy}{}_4$ ligand framework to ET, we prepared the new compounds, Ni(d*n*ppe)$_2$; d*n*ppe = 1,2-bis(di-*n*-propylphosphino)ethane (**7**) and bis(*n*-octyldicyclohexylboraneyl)-4,4′-bipyridine (**8**) as models for the nickel- and boron-containing sites within **6** (Figure 3 C). Reaction of these species in [D$_8$]THF or C$_6$D$_6$ at room temperature reveals no ET as judged by NMR spectroscopy, indicating that ET must occur intramolecularly (once the 4,4′-bpy is captured within the confines of the polymer network), and not intermolecularly. To buttress this proposal, redox potentials for related compounds can be compared: for [Ni(dmpe)$_2$] (dmpe = 1,2-bis(dimethylphosphino)ethane) a single wave at $E_{1/2}$(II/0) = −1.39 V (CH$_3$CN) has been observed (all values are vs. ferrocene/ferrocenium (Fc/Fc$^+$)), whereas for [Ni(depe)$_2$] (depe = 1,2-*bis*(diethylphosphino)ethane), values of $E_{1/2}$(II/I) = −1.16 and $E_{1/2}$(I/0) = −1.29 V have been reported.[18] These values can be compared to the reduction potentials for some borane-protected 4,4′-bipyridines. For Et$_3$B(N-π-N)BEt$_3$ ((N-π-N) = 4,4′-bpy), a value of $E_{1/2}$(red) = −1.72 V has been reported in dichloroethane,[19] whereas for the ferrocenyl derivative, FcMe$_2$B(N-π-N)BMe$_2$Fc (Fc = ferrocene), a similar value of $E_{1/2}$(red) = −1.69 V (DMF) has been reported.[16a] From these data, ET from **4** or **7** to 4,4′-bpy ($E_{1/2}$(red) = −2.33 V in DMF)[16a] should not be feasible. Likewise, ET from **7** to **8** should not be feasible; experimentally, no reaction is observed. We suggest, however, that on formation of polymer **6** (where four 4,4′-bpy units are linked) that the value of E(II/0) for **4** becomes slightly more cathodic (by a few hundred millivolts) or that π–π stacking anodically shifts the 4,4′-bpy $E_{1/2}$(red) value, resulting in productive ET. Indeed, a similar cathodic shift of a donor unit (upon Lewis base binding) has been observed previously.[16a]

The solid-state EPR spectrum of **6** was next acquired (Figure 3 D, middle).[20] The signature at 298 K consists of a broadened signal with two prominent features (an identical signal is observed at 127 K). Importantly, this signal does not appear in the diamagnetic starting materials (**4** or 4,4′-bpy) and is consistent in signal intensity between batches. In addition, acquisition of a diluted solid-state EPR spectrum of **6** in KBr shows the same signal pattern. Attempts to model this resonance have not been successful thus far. We assign the first feature at $g \approx 2.0$ to the formation of a reduced 4,4′-bpy radical anion. For comparison, the radical anion, $\mathbf{8}^{\bullet -}$ was prepared as a dark green solution (see the Supporting Information) and analyzed by EPR spectroscopy (THF, 127 K), providing an isotropic absorbance at $g_{iso} = 2.00182$, in good agreement with the signal observed for **6** (Figure 3 D, bottom). The secondary resonance at low field ($g \approx 2.03$) seems inconsistent with an organic radical ($g > 2$), but not large enough to be attributable to a paramagnetic $S = {}^1\!/_2$ Ni$^{\rm I}$ center. For instance, larger g_{max} values of 2.332–2.104 have been reported for related Ni$^{\rm I}$ bis(diphosphine) fragments.[21] Given the presumed similarity in reduction potentials between **4** and the trapped R$_3$B(N-π-N)BR$_3$ units, a redox equilibrium between the two (resulting in an array of mixed oxidation-state Ni centers), resulting in significant line shape broadening, cannot be ruled out.

A solid-state UV/Vis spectrum of **6** was also acquired, providing features similar to those in the solution spectrum of $\mathbf{8}^{\bullet -}$ (see the Supporting Information), lending further credence to the presence of radical 4,4′-bpy units within **6**.

To further emphasize that ET occurs only in the polymer network and not between free molecules; the fate of these unpaired spins following depolymerization was investigated. Treatment of **6** with excess DMAP showcases the lability of these B–N linkages, providing a deep purple solution that quickly fades to yellow (Scheme 4). Freeze-quenched EPR studies (20 s after DMAP addition) evidences the formation of fragments bearing unpaired electrons, namely free 4,4′-bpy radical anion (which is anecdotally purple)[22] (Figure 3 D, top); annealing this mixture results in rapid radical quenching and the formation of **5** and four equivalents of free bipyridine, as judged by NMR spectroscopy. In this instance, the $P_2B^{Cy}{}_4$ fragment provides a unique opportunity for Lewis base activation, enabling the facile construction of monomers for incorporation into redox-active coordination polymers—a reversible process.



Scheme 4. Depolymerization of **6** by using DMAP.

Conclusions

We have provided here the synthesis and spectroscopic characterization of a new bis(diboraneylphosphino)ethane ligand. In our primary foray, the synthesis of a new nickel $P_2B^{Cy}_4$ complex has been achieved—a species bearing eight pendant borane moieties. The electrophilic nature of these units is highlighted by step-wise reaction with eight equivalents of the pyridine derivative DMAP, which generates a canopy of Lewis acid–base pairs. In addition, reaction of **4** with 4,4′-bpy, links a series of "$Ni(P_2B^{Cy}_4)_2$" monomers to provide a *Ni*,*P*,*B*,*N*-based coordination polymer that features charge transfer between donor and acceptor sites as revealed by solid-state NMR and EPR spectroscopy. ET in this system was observed only to occur in **6**, with no reaction ocurring between the free molecules **7** and **8**. Future investigations will harness the modularity of this $P_2B^{Cy}_4$ compound (and the electron deficiency of the pendant borane units) for new opportunities in polymer synthesis (including applications thereof), small molecule activation, and more.

Acknowledgements

The authors are grateful to the University of Windsor for start-up funds (M.W.D.). M.C.D and L.A.L.-N. thank the University of Windsor IGNITE work-study program. The authors thank the Canadian Foundation for Innovation, the Ontario Innovation Trust, and the University of Windsor for funding the solid-state NMR facilities. The authors also thank the Natural Sciences and Engineering Research Council of Canada (Discovery Grant, RGPIN-2020-04480 (M.W.D) RGPIN-2016-06642 (R.W.S)), Genentech, the Florida State University, and the National High Magnetic Field Laboratory for funding this research. The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1644779* and the State of Florida. Dr. Louise N. Dawe and Jason Mercer are thanked for the refinement of structure **2**. Dr. Janeen Auld is thanked for help with the acquisition of ESI(+) MS. Dr. Matthew Revington is thanked for help with the acquisition of NMR spectroscopy. Dr. Bulent Mutus is thanked for help with the acquisition of UV/Vis spectroscopy. Dr. Jeremy Rawson is thanked for helpful discussions. Chelsea Ymana (SmartUWINDSOR) is thanked for assistance with the graphical abstract and cover image.

Conflict of interest

The authors declare no conflict of interest.

Keywords: ambiphiles · borane · diphosphine ligands · electron transfer · Lewis acids · Lewis bases

[1] See Chapter 1 of D. W. Allen, *Phosphines and related P–C bonded compounds, Vol. 43* **2014**, RSC Publishing, London.

[2] For representative examples, see: a) J. J. Carbó, F. Maseras, C. Bo, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2001**, *123*, 7630; b) A. B. Chaplin, J. F. Hooper, A. S. Weller, M. C. Willis, *J. Am. Chem. Soc.* **2012**, *134*, 4885; c) J. W. Raebiger, A. Miedaner, C. J. Curtis, S. M. Miller, O. P. Anderson, D. L. DuBois, *J. Am. Chem. Soc.* **2004**, *126*, 5502; d) J. Liu, K. Dong, R. Franke, H. Neumann, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2018**, *140*, 10282.

[3] For an overview, see: a) R. West, A. Hill, M. J. Fink, *Advances in Organometallic Chemistry, Vol. 55* **2007**, Academic Press, Cambridge; b) G. Bouhadir, D. Bourissou, *Chem. Soc. Rev.* **2016**, *45*, 1065.

[4] For representative examples, see: a) M.-H. Thibault, J. Boudreau, S. Mathiotte, F. Drouin, O. Sigouin, A. Michaud, F.-G. Fontaine, *Organometallics* **2007**, *26*, 3807; b) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* **2008**, *130*, 16729; c) M.-A. Courtemanche, M.-A. Légaré, L. Maron, F.-G. Fontaine, *J. Am. Chem. Soc.* **2013**, *135*, 9326; d) M. Joost, A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 14654; e) M. A. Nesbit, D. L. M. Suess, J. C. Peters, *Organometallics* **2015**, *34*, 4741; f) B. E. Cowie, D. J. H. Emslie, *Organometallics* **2015**, *34*, 2737; g) J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2017**, *139*, 6074.

[5] For representative examples, see: a) C. P. Casey, G. A. Bikzhanova, Q. Cui, I. A. Guzei, *J. Am. Chem. Soc.* **2005**, *127*, 14062; b) A. D. Wilson, K. Fraze, B. Twamley, S. M. Miller, D. L. DuBois, M. R. DuBois, *J. Am. Chem. Soc.* **2008**, *130*, 1061; c) R. L. Shook, A. S. Borovik, *Inorg. Chem.* **2010**, *49*, 3646; d) T. J. Schmeier, G. E. Dobereiner, R. H. Crabtree, N. Hazari, *J. Am. Chem. Soc.* **2011**, *133*, 9274; e) C. Ford, Y. J. Park, E. M. Matson, Z. Gordon, A. Fout, *Science* **2016**, *354*, 741; f) J. J. Kiernicki, M. Zeller, N. K. Szymczak, *J. Am. Chem. Soc.* **2017**, *139*, 18194; g) J. J. Kiernicki, M. Zeller, N. K. Szymczak, *Inorg. Chem.* **2019**, *58*, 1147; h) S. Sung, X. Li, L. M. Wolf, J. R. Meeder, N. S. Bhuvanesh, K. A. Grice, J. A. Panetier, M. Nippe, *J. Am. Chem. Soc.* **2019**, *141*, 6569.

[6] A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2008**, *130*, 11874.

[7] T. G. Ostapowicz, C. Merkens, M. Holscher, J. Klankermayer, W. Leitner, *J. Am. Chem. Soc.* **2013**, *135*, 2104.

[8] The abbreviation, "tape" is used in reference [9] and refers to tetraallylbisphosphinoethane.

[9] The coordination chemistry of this ligand has not been extensively examined, for examples, see: a) P. G. Edwards, A. Harrison, P. D. Newman, W. Zhang, *Inorg. Chim. Acta.* **2006**, *359*, 3549; b) A. R. Battle, P. G. Edwards, R. Haigh, D. E. Hibbs, D. Li, S. M. Liddiard, P. D. Newman, *Organometallics* **2007**, *26*, 377; c) J. W. Gohdes, L. N. Zakharov, D. R. Tyler, *Polyhedron* **2013**, *52*, 1169; d) M. Schuman, M. Trevitt, A. Redd, V. Gouverneur, *Angew. Chem. Int. Ed.* **2000**, *39*, 2491; *Angew. Chem.* **2000**, *112*, 2604.

[10] A. Abiko, *Org. Synth.* **2002**, *79*, 103.

[11] $HBCy_2$ was chosen due to its facile and high-yielding synthesis as provided in reference [10]. Hydroboration of **3** by using other monohydroboranes is ongoing.

[12] A similar monophosphine has been reported, but the coordination chemistry has not been explored, see: L. A. Körte, S. Blomeyer, S. Heidemeyer, J. H. Nissen, A. Mix, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Dalton Trans.* **2016**, *45*, 17319.

[13] The signal at $\delta_P = 39.2$ ppm was later found to be complex **4**; the identity of the species at $\delta_P = 44.4$ ppm remains unknown, but could be attributable to $[Ni(P_2B^{Cy}_4)(COD)]$.

[14] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955.

[15] For a review on coordination polymers by using 4,4′-bipyridine, see: K. Biradha, M. Sarkar, L. Rajput, *Chem. Commun.* **2006**, 4169.

[16] a) M. Fontani, F. Peters, W. Scherer, W. Wachter, M. Wagner, P. Zanello, *Eur. J. Inorg. Chem.* **1998**, 1453; b) E. Sheepwash, V. Krampl, R. Scopelliti, O. Sereda, A. Neels, K. Severin, *Angew. Chem. Int. Ed.* **2011**, *50*, 3034; *Angew. Chem.* **2011**, *123*, 3090; c) A. L. Colebatch, A. S. Weller, *Chem. Eur. J.* **2019**, *25*, 1379; d) S. Baljak, A. D. Russell, S. C. Binding, M. F. Haddow, D. O'Hare, I. Manners, *J. Am. Chem. Soc.* **2014**, *136*, 5864; e) M. Yang, L. Zhang, Z. Lei, P. Ye, J. Si, Q. Yang, Y. Wang, *J. Appl. Polym. Sci.* **1998**, *70*, 1165; f) J. A. Paquette, E. R. Sauvé, J. B. Gilroy, *Macromol. Rapid Commun.* **2015**, *36*, 621.

[17] Solid-state (SS) NMR spectroscopy has been previously employed to confirm the presence of unpaired spin density, see: a) I. Bertini, C. Luchinat, G. Parigi, E. Ravera, *NMR of Paramagnetic Molecules: Applications to Metallobiomolecules and Models*, Elsevier, Amsterdam, **2016**; b) A. J. Pell, G. Pintacuda, C. P. Grey, *Prog. Nucl. Magn. Reson. Spectrosc.* **2019**, *111*, 1.

[18] D. E. Berning, B. C. Noll, D. L. DuBois, *J. Am. Chem. Soc.* **1999**, *121*, 11432.

[19] A. Lichtblau, W. Kaim, A. Schulz, T. Stahl, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1497.

[20] For a review on EPR of paramagnetic polymers, see K. R. Naveed, L. Wang, H. Yu, R. S. Ullah, M. Haroon, S. Fahad, J. Li, T. Elshaarani, R. U. Khan, A. Nazir, *Polym. Chem.* **2018**, *9*, 3306.

[21] a) J. Niklas, M. Westwood, K. L. Mardis, T. L. Brown, A. M. Pitts-McCoy, M. D. Hopkins, O. G. Poluektov, *Inorg. Chem.* **2015**, *54*, 6226; b) A. Kochem, F. Neese, M. van Gastel, *J. Phys. Chem. C* **2014**, *118*, 2350; c) G. Pilloni, A. Toffoletti, G. Bandoli, B. Longato, *Inorg. Chem.* **2006**, *45*, 10321.

[22] M. S. Denning, M. Irwin, J. M. Goicoechea, *Inorg. Chem.* **2008**, *47*, 6118.

Manuscript received: March 10, 2020
Revised manuscript received: April 17, 2020
Accepted manuscript online: April 21, 2020
Version of record online: August 6, 2020