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Reactions of nickel boranyl compounds with pnictogen–carbon triple bonds†

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The catalytic conversion of unsaturated small molecules such as nitriles into reduced products is of interest for the production of fine chemicals. In this vein, metal–ligand cooperativity has been leveraged to promote such reactivity, often conferring stability to bound substrate – a balancing act that may offer activation at the cost of turnover efficiency. This report describes the reactivity of a [(diphosphine)Ni] compound with pnictogen carbon triple bonds ($R-C\equiv E$; $E = N, P$), where the diphosphine contains two pendant borane groups. For $E = N$, cooperative nitrile coordination is observed to afford $\{Ni\}_2$ complexes displaying B–N interactions, whereas for $E = P$, B–P interactions are absent. This work additionally outlines a structure–activity relationship that uses nitrile dihydroboration as a model reaction to unveil the effect of SCS stabilization, employing [(diphosphine)Ni] where the diphosphine contains 0, 1, or 2 pendant Lewis acid groups.

Introduction

Metal–ligand cooperation (MLC), where both a metal and ligand participate in substrate activation has become an important tool relevant to small molecule conversion chemistry.^{1,2} Perhaps one of the best known examples is exemplified by compounds prepared by Milstein *et al.* where aromatization/dearomatization of a pyridine, fluorenyl, or acridine ligand component permits the addition of E–H bonds across both metal and ligand.^{3,4} Using this approach, polar substrates such as nitriles ($R-C\equiv N$) have been activated for hydration,^{5,6} as well as Michael addition-type reactivity (Fig. 1).^{7–10} Cooperative nitrile activation is not limited to pincer-based ligand scaffolds – Beckhaus *et al.* recently described a vanadium pentafulvene complex that reduces 4-chlorobenzonitrile using both a $C_5H_5^-$ (Cp) ring and vanadium(v) (Fig. 1).¹¹ Despite nitrile Lewis basicity, the application of Lewis acidic ligand components to drive the activation and conversion of this substrate class remains relatively unexplored.¹² A unique example is provided by Williams *et al.* where a ruthenium bis(pyrazolyl)borate complex is shown to promote hydride transfer, permitting selective nitrile reduction to the corresponding amine or amide (Fig. 1).¹³

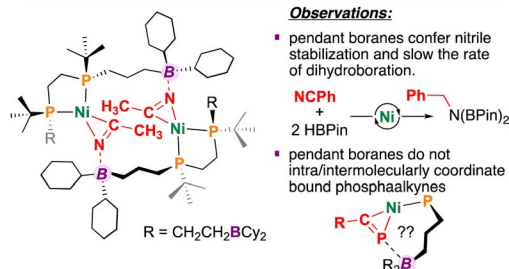
Incorporation of Lewis acidic groups into the secondary coordination sphere (SCS: atoms that are not directly bound to

the metal) has grown in popularity over recent years.^{14,15} Since 2020, our group has reported on several new ligand motifs featuring SCS Lewis acidic borane groups, asking general questions relevant to the effect of Lewis acid SCS incorporation on downstream reactivity.^{16–19} This work has focused on expanding the “diphosphine ligand toolbox”, offering scaffolds containing four,¹⁶ two,¹⁷ or one¹⁹ Lewis acidic SCS borane groups. Of relevance here, complexation of the mono (*t*bbpe: tri-*tert*-butylboranyldiphosphinoethane) and diboranyl (*d*’bbpe: di-*tert*-butylboranyldiphosphinoethane) diphosphine systems

A. examples of cooperative nitrile binding/functionalization



B. this work: cooperative nitrile coordination and reactivity studies



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Fig. 1 Literature precedent for cooperative nitrile coordination and this work.



to Ni(0) allowed for the isolation of the monophosphine-substituted starting materials [(diphosphine)Ni(COD)] (COD = 1,4-cyclooctadiene).^{17,19} For the monoboranyl Ni(0) complex, [Ni(t^lbbpe)(COD)], reaction with nitriles was found to form 14-membered {Ni}₂ dimers, with co-stabilization being provided by both boron and nickel (Fig. 1).¹⁹

In this report, we advance our understanding of the diborane-containing ligand set, d^lbbpe – studying the reactivity of (±)-*rac/meso*-[Ni(d^lbbpe)(COD)] with nitriles to assess SCS effects on product outcome. Moreover, we expand the scope of pnictogen coordination chemistry to phosphalkynes.²⁰ Finally, we provide a structure activity relationship that relates the concentration (*i.e.*, number) of SCS Lewis acid groups to reactivity by considering a model benzonitrile (PhCN) dihydroboration reaction.

Results and discussion

Reactivity with nitriles

To begin, a solution of (±)-*rac/meso*-[Ni(d^lbbpe)(COD)] (**1**) was reacted with an excess of CH₃CN in toluene (Fig. 2). Analysis by ³¹P{¹H} NMR spectroscopy showed a new set of [AB]-doublets at δ_p = 67.3 and 70.4 ppm (²J_{P,P} = 45.7 Hz), suggesting consumption of **1** and formation of a new nitrile-bound C₁-symmetric complex **2**, isolated as a yellow solid in 76% yield (Fig. 2). Consistent with nitrile coordination, the FT-IR spectrum also provided a signal at ν(C≡N) = 1777 cm⁻¹ (*c.f.*, ν(C≡N) = 2253 cm⁻¹ for unbound CH₃CN). Symmetry of the d^lbbpe ligand warrants comment – this ligand contains two isomers – *racemic* (*rac*) and *meso* (differing in the presence of a mirror plane). In the instance where nitrile coordination provides an intramolecular B–N interaction, three possible isomers (two enantiomers and a *meso* compound) are expected –

(±)-*rac/meso*-[Ni(d^lbbpe)(η²-NCCH₃)]. However, were an intermolecular B–N interaction to persist (as is the case here), matters become more complicated. In this instance, several variants could be produced, including: *meso/meso*-, (±)-*rac/meso*-, and (±)-*rac/rac*-pairings; these geometries all permit access to 14-membered {Ni}₂ dimers. In the current instance, single-crystal X-ray diffraction data obtained on “[Ni(d^lbbpe)(η²-NCCH₃)]₂ (*meso/meso*-2), corroborating the dimeric form of these products – metrics of **2** will be discussed later.

Under similar conditions, benzonitrile (PhCN) was added to a toluene solution of **1** and allowed to stir overnight. Following work-up, the PhCN-coordinated complex [Ni(d^lbbpe)(η²-NCPh)]₂ (**3**) was isolated as a yellow-brown oil in 97% yield (Fig. 2). Analysis by ³¹P{¹H} NMR spectroscopy provided several signatures, consistent with the stereogenic d^lbbpe ligand scaffold, as introduced earlier. The major isomer features two doublets at δ_p = 68.2 and 67.0 ppm (²J_{P,P} = 46.2 Hz). An additional broad signal at δ_p = 69.8 ppm corresponds to an additional minor isomeric component alongside a doublet at 66.7 ppm (²J_{P,P} = 48.7 Hz). Like **2**, compound **3** featured a signal at ν(C≡N) = 1771 cm⁻¹ (*c.f.*, ν(C≡N) = 2228 cm⁻¹ for unbound PhCN).

To investigate the effect of nitrile steric bulk on dimer formation, complex **1** was reacted with adamantyl nitrile (1-Ad)CN (Fig. 2). However, no reaction was concluded between **1** and (1-Ad)CN by ³¹P{¹H} NMR spectroscopy. Additional heating of the reaction mixture at 60 °C over 48 h likewise provided no evidence for (1-Ad)CN coordination or even decay of **1**, suggesting that the 1-Ad group inhibits nitrile binding, which is contrasted with the facile coordination observed for CH₃CN and PhCN.

Yellow crystals of complex **2**, suitable for X-ray crystallography, were grown from a saturated toluene solution layered with hexane at –35 °C overnight (Fig. 3). For the t^lbbpe system discussed previously, structural data was only available for the PhCN adduct – this represents the first crystallographically characterized CH₃CN derivative. Complex **2** features two

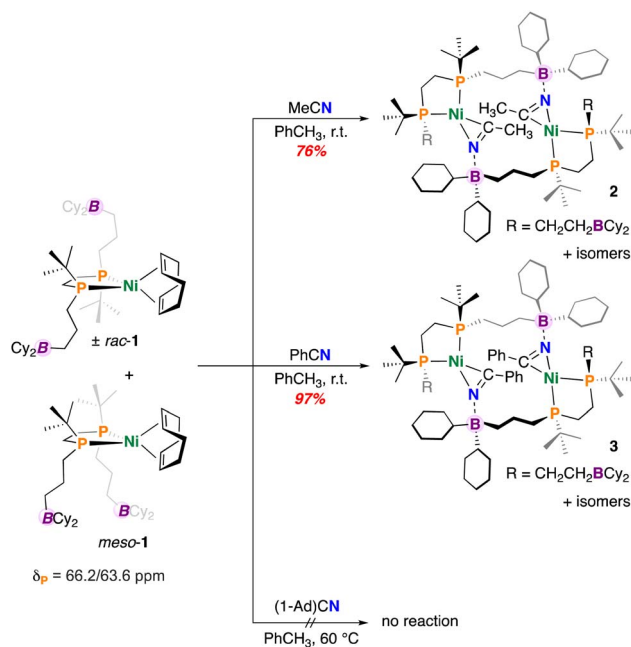


Fig. 2 Synthesis of Ni nitrile complexes.

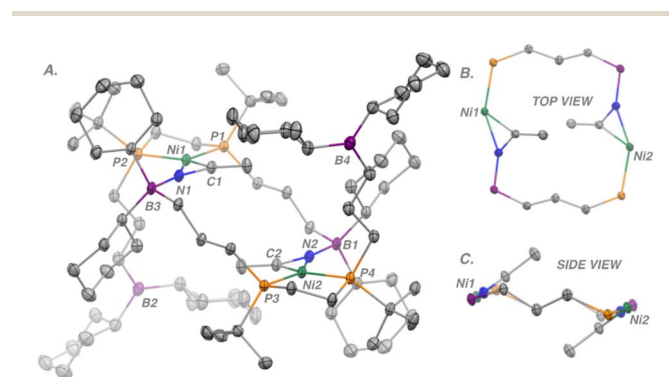


Fig. 3 (A) Molecular structure of **2**; (B) top view; (C) side view. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ni1–C1 1.236(2), Ni2–C2 1.236(2), Ni1–Ni2 6.484(8), B1–N2 1.629(2), B3–N1 1.629(2), Ni1–N1 1.907(14), Ni2–N2 1.907(14), Ni1–C1 1.856(17), Ni2–C2 1.856(17).



intermolecular B–N interactions resulting in a 14-membered $\{\text{Ni}\}_2$ ring system with a Ni...Ni separation of 6.484(8) Å. The average C–N bond length is 1.236(2) Å (*c.f.*, ~ 1.13 Å for a free nitrile).²¹ Two hybridizations, sp^2 and sp^3 , are assigned to the borane moieties, one for the non-interacting ($\Sigma_{\text{C-B-C}} = 360^\circ$) and one for the interacting ($\Sigma_{\text{C-B-C}} = 339^\circ$), respectively. This notion is also reflected in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum, which features two resonances at $\delta_{\text{B}} = 83.7$ (non-interacting) and 1.42 ppm (interacting); the B–N bond length for the interacting borane was observed to be 1.629(2) Å.

Reactivity with 1-adamantylphosphaethyne

The controlled activation and transformation of phosphalkynes, congeners of nitriles, but more closely resembling alkynes, is of interest for the synthesis of organophosphorus compounds.²⁰ Despite this, isolated examples of η^2 -bound R–C \equiv P units are far less common than their nitrile counterparts.^{22–29} To investigate the possibility of inter/intramolecular P...B interactions and inspired by some elegant [(diphosphine)Ni(η^2 -P \equiv CR)] chemistry from Jones and *et al.*,²⁸ we accordingly sought to examine the reactivity of **1** with a commercially available phosphalkyne, 1-adamantylphosphaethyne ((1-Ad)CP), a heavier analogue of (1-Ad)CN, described above. However, unlike in the above case of (1-Ad)CN, reaction of **1** with (1-Ad)CP in toluene resulted in an immediate colour change from light yellow to deep brown. Following work-up, complex (\pm)-*rac/meso*-[Ni(d⁴bbpe)(η^2 -PC(1-Ad))] (**4**) was isolated as a brown oily solid in 46% yield (Fig. 4). Analysis by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy corroborated loss of signals corresponding to **1** and the appearance of six additional resonances with doublet of doublet multiplicity, attributable to a mixture of *meso*- and (\pm)-*rac*-isomers. For the coordinated phosphalkyne, resonances were observed at $\delta_{\text{P}} = 133.3$ and 135.0 ppm for the minor and major isomers, respectively in a roughly 1:2 ratio, significantly downfield-shifted when compared to free (1-Ad)CP ($\delta_{\text{P}} = -67.9$ ppm). These values are consistent with previously reported η^2 -coordinated phosphalkyne complexes.^{26,29} For the diphosphine ligand scaffold, signals at $\delta_{\text{P}} = 76.8$ ppm (major/minor overlapping), 69.4 (minor), and 68.8 (major) ppm are consistent with two compounds. The presence of two (1-Ad)CP resonances clearly suggests the formation of a monomeric species, rather than a dimer, which would produce a more convoluted spectrum. Moreover, the lack of an upfield shifted boron resonance ($\delta_{\text{B}} = 83.7$ ppm only), suggests the absence of a persistent B...P interaction, which might be due to the lower electronegativity of P as compared to N.³⁰ Apparently, the difference in reactivity

between **1** and (1-Ad)CN/(1-Ad)CP is not attributable to sterics. With complexes **2**, **3**, and **4** in-hand, we next turned to density functional theory (DFT) to understand the thermodynamics associated with borane co-ordination in such [(diphosphine)Ni(η^2 -E \equiv CR)]_n (E = N, P) compounds.

Theoretical considerations

DFT analysis utilizing the BP86-D3(BJ)/def2-TZVP level of theory provided optimized structures for nickel complexes having bound CH₃CN and CH₃CP, as models (Fig. 5 and 6). Examination of the non-interacting geometries **2**_{none} and **4**_{none} provided stark differences in η^2 -bonding (Fig. 5). While in both cases, Ni–C bond lengths are similar (1.90 vs. 1.92 Å), the Ni–P bond length is 0.25 Å longer than that the corresponding Ni–N bond length (1.97 vs. 2.22 Å). The pnictogen–carbon multiple bond (E \equiv CR) lengths are also elongated due to Ni(d π)-to-E \equiv CR(π^*) back-bonding, giving values of 1.23 vs. 1.65 Å for E = N and P, respectively.

For the nitrile system, it was determined that intramolecular stabilization of the coordinated nitrile (**2**_{intra}) was favoured by 13.7 kcal mol^{−1} (Fig. 6). Dimer formation *via* intermolecular B–N coordination to give **2**_{inter} was also found to be favorable (−12.5 kcal mol^{−1}); the difference between them ($\Delta G_{\text{rel}} = 1.2$ kcal mol^{−1}) being close to the margin of calculation error. By contrast, an intramolecular variant of **4** (*e.g.*, **4**_{intra}) could not be located; a potential energy surface scan that varied the B–P distance from roughly 7.8 to 1.4 Å (see ESI†) provided no energy minimum. A dimeric complex **4**_{inter} was located, albeit this compound was found to be uphill ($G_{\text{rel}} = +4.6$ kcal mol^{−1}), consistent with experimental results.

Catalytic nitrile hydroboration

Catalytic hydroboration, the addition of a B–H unit across an unsaturated bond, is a useful tool for access to reduced products.^{31–33} Hypothesizing that co-ordination would be deleterious to turnover, we wished to quantize the effect of stabilization on nitrile reduction. Accordingly, 10 mol% [Ni(COD)₂], a diphosphine ligand, PhCN, and 2 equivs. of HBPIn in C₆D₆ were reacted over the period of 72 h (Fig. 7); three diphosphine ligands were tested having 0 (d⁴bpe: 1,2-bis(di-*tert*-

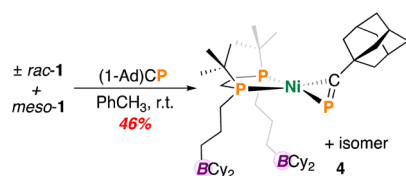


Fig. 4 Synthesis of phosphalkyne adduct, **4**.

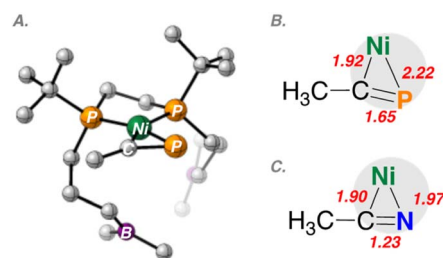


Fig. 5 DFT-optimized structures for CH₃CN/P-coordinated Ni compounds **2**_{none} and **4**_{none} showing differences in geometric parameters of bound substrate. Bond distances (Å) and angles (deg). (A) [Ni(d⁴bbpe)(η^2 -PCCH₃)]. (B) Core of [Ni(d⁴bbpe)(η^2 -PCCH₃)]: <C–Ni–P 46.2, <Ni–P–C 76.7, <Ni–C–P 57.1. (C) Core of [Ni(d⁴bbpe)(η^2 -NCCH₃)]: <C–Ni–N 37.0, <Ni–N–C 68.4, <Ni–C–N 74.5.



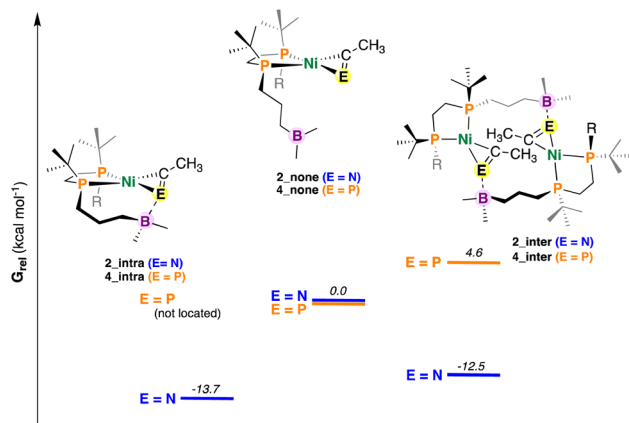


Fig. 6 DFT-optimized structures of **2** and **4** with differing $E\equiv CR$ ($E = N$ or P) coordination modes. Values in kcal mol^{-1} . Energies have been calculated from DFT-optimized structures using DLPNO-CCSD(T) (see ESI†). Note that for simplicity $E = N$ and P have been placed on the same graph – these energies cannot be directly compared.

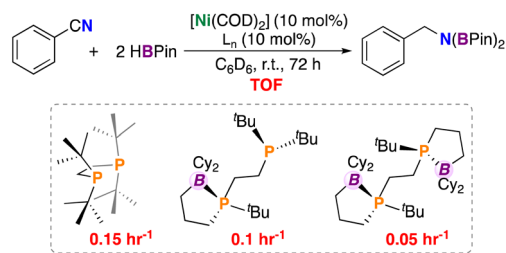


Fig. 7 Nitrile dihydroboration using a series of borane-containing ligands. Values in red are turnover frequencies after 72 h (h^{-1}). $d^t\text{bbpe}$ is used as a mixture of isomers.

butylphosphino)ethane), **1** ($t^t\text{bbpe}$), and **2** ($d^t\text{bbpe}$) pendant borane groups. The all-alkyl ligand, $d^t\text{bpe}$ provided the diborylated amine in 97% yield ($\text{TOF} = 0.15 \text{ h}^{-1}$), $t^t\text{bbpe}$ resulted in 80% ($\text{TOF} = 0.1 \text{ h}^{-1}$), and $d^t\text{bbpe}$ resulted in 40% ($\text{TOF} = 0.05 \text{ h}^{-1}$). These TOFs are lower than those found for related nickel-based systems. For example, Shimada *et al.* reported a nickel(II) bis(acetylacetonato) catalyst for the hydroboration of aryl nitriles with catecholborane (HBcat) (catalyst loading: 0.5 mol%, RT, 12 h, >99% yield),³⁴ while Baker *et al.* reported a $[\text{Ni}(\text{II})(2,5\text{-Me}_2\text{-pyrrolyl})(\kappa^3\text{-NNN})]$ complex for nitrile dihydroboration (catalyst loading: 2.0 mol%, RT, 10–18 h, >99% yield).³⁵

Conclusion

This study has explored the reactivity of (\pm)-*rac/meso*-[($d^t\text{bbpe}$) $\text{Ni}(\text{COD})$] (**1**) with two nitriles (PhCN and CH_3CN) and a phosphalkyne ((1-Ad)CP) to understand boron SCS effects on $R-C\equiv E$ ($E = N, P$) coordination and reduction chemistry (for $E = N$). We found that a Lewis acidic SCS can be used for the coordination of nitriles, providing 14-membered ring systems. Moreover, nickel coordination was found to depend on the nature of “E”: compound **1** does not react with (1-Ad)CN, but

readily reacts with (1-Ad)CP. For the phosphorus analogue, the SCS borane groups do not engage with the nickel-bound (1-Ad) CP unit, as shown by NMR spectroscopy and as supported by DFT calculations. Finally, this work shows that Ni/B-nitrile coordination comes at the cost of catalytic dihydroboration efficiency – speaking to the balance that must be achieved between coordination/stabilization and achieving turnover.

Experimental data

General considerations

The storage and manipulation of all compounds was carried out under an atmosphere of dry nitrogen either in an MBraun glovebox or employing standard Schlenk techniques under an atmosphere of dry nitrogen. Dried solvents were retrieved from a solvent purification system supplied by PPT, LLC. and stored over molecular sieves. Benzene- d_6 was dried over molecular sieves and degassed by three freeze–pump–thaw cycles prior to use. HBCy_2 ,³⁶ 1,2-bis(di-*tert*-butylphosphino)ethane ($d^t\text{bpe}$),³⁷ di-*tert*-butylboranyldiphosphinoethane ($d^t\text{bbpe}$),¹⁷ tri-*tert*-butylboranyldiphosphinoethane ($t^t\text{bbpe}$),¹⁹ and compound **1** (ref. 17) were prepared following literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

Physical methods

NMR spectra were collected on a Bruker Avance III 500 (BBFO probe, TOPSPIN 3.5). ^1H NMR spectra are reported in parts per million (ppm) and are referenced to residual solvent *e.g.*, $^1\text{H}(\text{C}_6\text{D}_6)$: $\delta = 7.16$; $^{13}\text{C}(\text{C}_6\text{D}_6)$: 128.06; coupling constants are reported in Hz. ^{13}C , ^{11}B , and ^{31}P NMR spectra were performed as proton-decoupled experiments and are reported in ppm. Infrared spectra were collected on a Bruker Alpha II FT-IR spectrophotometer with ATR module.

Preparation of compounds

Note: all compounds were isolated as mixtures of isomers. Where appropriate, data is listed in terms of major and minor isomers; ratios were determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

$[\text{Ni}(d^t\text{bbpe})(\eta^2\text{-MeCN})]_2$ [**2**: $\text{C}_{84}\text{H}_{162}\text{B}_4\text{N}_2\text{Ni}_2\text{P}_4$, $\text{Mw} = 1484.8 \text{ g mol}^{-1}$]: to a 20 mL scintillation vial equipped with a stir bar was added **1** (0.046 g, 0.057 mmol) and dissolved in 4 mL toluene. To the solution was added MeCN (5 mL). The mixture was stirred for 12 h and toluene removed *in vacuo*. The resulting residue was dissolved in hexane and filtered through Celite®. Hexane was removed under vacuum and the product redissolved in minimal toluene, layered with hexane, and allowed to crystallize at $-35 \text{ }^\circ\text{C}$, giving **2** (as the majority *meso/meso*-isomer) as yellow blocks in a 76% yield (0.032 g, 0.015 mmol). ^1H NMR (500 MHz, $\text{tol-}d_8$, 298 K, select signals for major isomer only): $\delta_{\text{H}} = 2.46$ (d, $^4J_{\text{P,H}} = 4.7 \text{ Hz}$, 6H; CH_3CN), 0.99 (d, $^3J_{\text{P,H}} = 12.7 \text{ Hz}$, 18H; *t*-Bu), 0.91 (d, $^3J_{\text{P,H}} = 13.3 \text{ Hz}$, 18H; *t*-Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $\text{tol-}d_8$, 298 K, select signal for major isomer only): $\delta_{\text{C}} = 164.5$ (dd, $^2J_{\text{P-C}} = 46.2 \text{ Hz}$, $^2J_{\text{P-C}} = 6.3 \text{ Hz}$; NC-CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, $\text{tol-}d_8$, 298 K): $\delta_{\text{P}} = 70.4$ (d, $^2J_{\text{P-P}} =$



45.7 Hz), 67.3 (d, $^2J_{P-P} = 45.7$ Hz). $^{11}B\{^1H\}$ NMR (160.5 MHz, *tol-d*₈, 298 K): $\delta_B = 83.7$ ($\Delta_{1/2} = 1002$ Hz; non-interacting), 1.42 (interacting). FT-IR: $\nu(C\equiv N)$: 1777 cm^{-1} .

$[Ni(d^4bbpe)(\eta^2-PhCN)]_2$ (3: $C_{94}H_{166}B_4N_2Ni_2P_4$, Mw = 1608.9 g mol^{-1}): to a 20 mL scintillation vial equipped with a stir bar was added 1 (0.028 g, 0.035 mmol) and dissolved in 4 mL toluene. PhCN (0.004 g, 0.035 mmol) was added to the reaction mixture and was stirred for 12 h before toluene was removed *in vacuo*. The resulting crude product was dissolved in hexane and filtered through Celite®, giving 3 (as a mixture of isomers) as a brown oil in 97% yield (0.027 g, 0.017 mmol). 1H NMR (500 MHz, *tol-d*₈, 298 K, select signals for major isomer only): $\delta_H = 7.52$ (d, $^3J_{H-H} = 7.6$ Hz, 4H; NC – \underline{Ph}_o), 7.21 (t, $^3J_{H-H} = 7.6$ Hz, 2H; NC – \underline{Ph}_p), 7.15 (t, $^3J_{H-H} = 7.6$ Hz, 4H; NC – \underline{Ph}_m), 1.05 (d, $^3J_{P,H} = 12.4$ Hz, 18H; *t*-Bu), 0.81 (d, $^3J_{P,H} = 13.3$ Hz, 18H; *t*-Bu). $^{13}C\{^1H\}$ NMR (125.8 MHz, *tol-d*₈, 298 K, select signals for major isomer only): $\delta_C = 168.8$ (dd, $^2J_{P-C} = 42.7$ Hz, $^2J_{P-C} = 7.2$ Hz; NC-Ph). $^{31}P\{^1H\}$ NMR (202.5 MHz, *tol-d*₈, 298 K): $\delta_P = 69.8$ (br; minor isomer), 68.2 (d, $^2J_{P-P} = 46.2$ Hz; major isomer), 67.0 (d, $^2J_{P-P} = 46.2$ Hz; major isomer), 66.7 (d, $^2J_{P-P} = 48.7$ Hz; minor isomer). [Major]:[Minor] = [1.00]:[0.41]. $^{11}B\{^1H\}$ NMR (160.5 MHz, *tol-d*₈, 298 K): $\delta_B = 83.7$ ($\Delta_{1/2} = 1367$ Hz; non-interacting), 2.85 (interacting). FT-IR: $\nu(C\equiv N)$: 1771 cm^{-1} .

(\pm) -*rac/meso*- $[Ni(d^4bbpe)(\eta^2-(1-Ad)CP)]$ ((\pm)-*rac/meso*-4: $C_{51}H_{93}B_2NiP_3$, Mw = 879.6 g mol^{-1}): To a 20 mL scintillation vial equipped with a stir bar was added 1 (0.038 g, 0.047 mmol) and (1-Ad)CP (0.084 mg, 0.047 mmol) and dissolved in 4 mL toluene. This mixture was stirred for 12 h and toluene removed *in vacuo*. The resulting crude product was dissolved in hexane and filtered through Celite®, giving (\pm)-*rac/meso*-4 as a brown oil in 46% yield (0.019 g, 0.01 mmol). $^1H\{^{31}P\}$ NMR (500 MHz, *tol-d*₈, 298 K, select signals only): $\delta_H = 1.21$ (s, *t*-Bu, major isomer), 1.16 (s, *t*-Bu, minor isomer), 1.13 (s, *t*-Bu, minor isomer), 1.12 (s, *t*-Bu, major isomer). $^{13}C\{^1H\}$ NMR (125.8 MHz, *tol-d*₈, 298 K, select signals only): $\delta_C = 255.0$ (from 1H - ^{13}C HMBC; PC-Ad), 48.0 (br, PC – Ad), 43.6 (br, PC – Ad), 37.6 (br, PC – Ad), 30.3 (br, PC – Ad). $^{31}P\{^1H\}$ NMR (202.5 MHz, *tol-d*₈, 298 K): $\delta_P = 135.1$ (br, PC-Ad; minor isomer), 133.5 (br, PC-Ad; major isomer), 77.09 (d, $^2J_{P-P} = 34.9$ Hz; minor isomer), 76.87 (d, $^2J_{P-P} = 33.3$ Hz; major isomer), 69.5 (dd, $^2J_{P-P} = 34.9$ Hz, $^2J_{P-P} = 16.0$ Hz; minor isomer), 68.9 (dd, $^2J_{P-P} = 33.3$ Hz, $^2J_{P-P} = 13.5$ Hz; major isomer). [Major]:[Minor] = [1.00]:[0.47]. $^{11}B\{^1H\}$ NMR (160.5 MHz, *tol-d*₈, 298 K): $\delta_B = 83.7$ ($\Delta_{1/2} = 1397$ Hz).

Conflicts of interest

There are no conflicts to declare.

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