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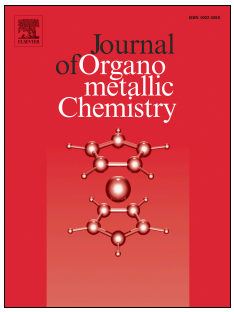

The Synthesis of an Anionic, Tetraphenylborate-Functionalized, [P,N]-Hybrid Phosphinobenzimidazole Ligand and its Hemilabile Behaviour in Ruthenium Zwitterion Chemistry

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The Synthesis of an Anionic, Tetraphenylborate-Functionalized, [P,N]-Hybrid Phosphinobenzimidazole Ligand and its Hemilabile Behaviour in Ruthenium Zwitterion Chemistry

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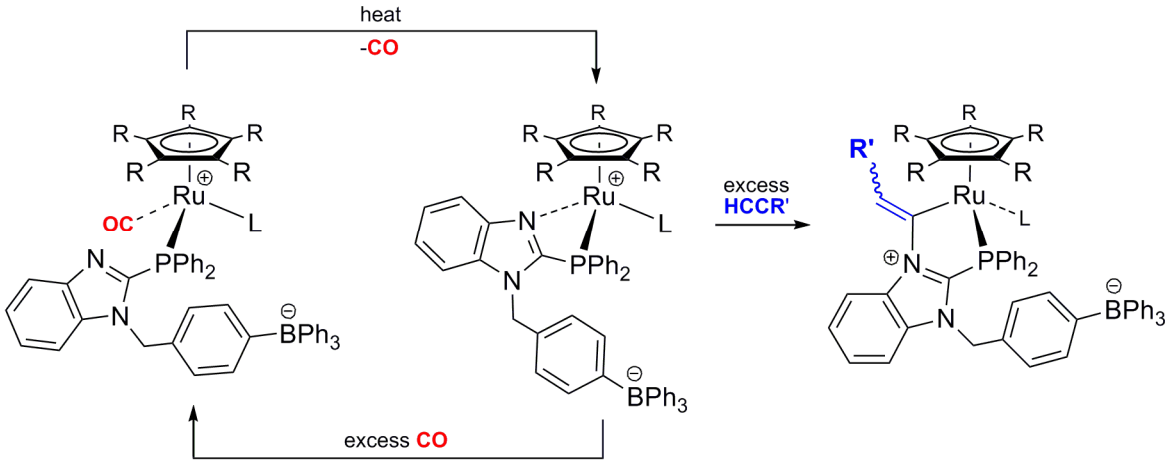
The synthesis of a new anionic [P,N]-hybrid ligand based on a phosphinobenzimidazole scaffold and functionalized with a tetraphenylborate substituent is described. The coordination chemistry and hemilability of this ligand when incorporated as an auxiliary ligand in zwitterionic ruthenium piano-stool complexes are examined and discussed.



The Synthesis of an Anionic, Tetraphenylborate-Functionalized, [P,N]-Hybrid Phosphinobenzimidazole Ligand and its Hemilabile Behaviour in Ruthenium Zwitterion Chemistry

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Abstract

A new anionic [P,N]-hybrid ligand based on a phosphinobenzimidazole scaffold and functionalized with a tetraphenylborate substituent is reported. This new anionic ligand readily chelates to a variety of ruthenium-cyclopentadienyl and -pentamethylcyclopentadienyl precursors to form a series of zwitterionic ruthenium piano-stool complexes (η^5-C_5R_5)Ru(L)(κ^2-P,N) (R = H or Me; L = CO or PPh_3). In the presence of excess CO or 1-alkynes, the chelate complexes undergo ring-opening of the κ^2-P,N ligand at the ruthenium-nitrogen bond (in some cases reversibly) under relatively mild conditions. In particular, the reactions with 1-alkynes proceed via vinylidene intermediates which subsequently insert into the ruthenium-nitrogen bond of the κ^2-P,N ligand.

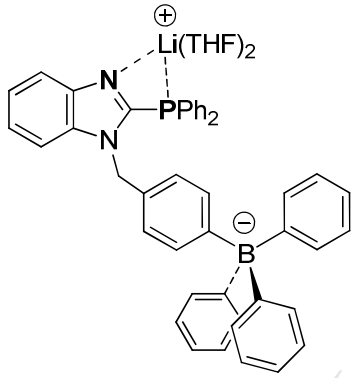
Keywords: ruthenium; zwitterionic; anionic phosphines; hybrid ligands; hemilabile; vinylidenes

Introduction

The continued expansion of anionic organophosphorus ligands in transition metal chemistry is linked, in part, to an increasing interest in investigating the impact of these phosphine ligands in applications which customarily employ conventional neutral phosphines. Several classes of anionic phosphine ligands employ a covalently bound borate group (either as a structural unit or as a pendant group) as a way of rendering the phosphine ligand anionic.[1-9] Interestingly, some of the anionic phosphine ligands modified in this way reportedly display enhanced donor powers over their neutral counterparts.[1-3,5e,7i,10] The anionic nature of these phosphines also allows access to the synthesis of zwitterionic complexes, and some zwitterionic catalysts have proven to be differently (sometimes more) reactive or selective than their cationic counterparts in a number of instances.[8,11] We recently reported on the synthesis of anionic and zwitterionic complexes of ruthenium containing the tetraphenylborate-modified monodentate phosphine ligands $[E][PR_2(p\text{-}Ph_3BC_6H_4)]$ ($E = Bu_4N^+$ or PNP^+) which contain, at least conceptually, a non-coordinating tetraphenylborate anion covalently tethered to a $–PR_2$ unit.[12] We have since wondered if this strategy could be expanded to include bidentate ligands,[8] especially heterobidentate hybrid ligands possessing hemilabile[13] properties. Thus, the key design features of these ligands should include a substitutionally inert anchor donor group, a substitutionally labile group, and a covalently tethered tetraphenylborate group, the latter of which would render the ligand negatively charged.

We report here on the synthesis of the tetraphenylborate-functionalized, heterobidentate phosphinobenzimidazole ligand **1** (Structure I). Ligand **1** readily chelates to ruthenium, but will ring-open at the ruthenium nitrogen-bond in the presence of various substrates. The contrasting pairing of the harder imidazole nitrogen with a comparatively softer ruthenium centre likely

promotes hemilability. Furthermore, as a bidentate ligand, the relative positions of the phosphino group and the imidazole nitrogen produce a strained bite angle, a feature that undoubtedly also favours ring-opening of the metallacycle.



1

Structure I

Results and Discussion

Synthesis and Characterization of Ligand 1. The anionic P,N-hybrid ligand **1** (abbreviated as $[Li(THF)_2][P^{Ph}NBPh_4]$) was prepared as illustrated in Scheme 1.[14] During the early stages of development, we initially attempted to use imidazole as a simpler building block; however, the subsequent phosphination step of the 1-(4-bromobenzyl)imidazole[15] precursor was complicated by reactions also occurring at the 4- and 5-positions of the imidazole backbone at the expense of the desired 2-position.[16] Alternatively, employing benzimidazole allowed us to circumvent these issues. Strict attention to reaction temperature, time and base was required for the synthesis of the precursor 1-(4-bromobenzyl)-2-(diphenylphosphino)benzimidazole from 1-(4-bromobenzyl)benzimidazole[15] and chlorodiphenylphosphine, otherwise tetraphenyldiphosphine monoxide[17] was observed to form as a by-product after work-up. Similarly, the final step in the synthesis of **1** from 1-(4-bromobenzyl)-2-(diphenylphosphino)benzimidazole also required special consideration. The

metalating agents *n*-BuLi, *i*-PrMgCl and *i*-PrMgClXLiCl[18] proved to be less effective than *t*-BuLi for the borane addition reaction. Furthermore, careful control of the reaction temperature, time and rate of addition of the BPh_3 to the metalated intermediate was required, since otherwise Li(*t*-$BuBPh_3$)[19] or the *N*-addition product[20] would contaminate the desired product. Typically, ligand **1** was isolated in 70-80% yields in this final step, and was sufficiently pure for further use. The $^{31}P\{^1H\}$ NMR spectrum of **1** displays a sharp singlet at δ -24.1 ppm, while the ^1H NMR spectrum reveals that two equivalents of THF are retained in the product. The ^{11}B NMR chemical shift for ligand **1** appears at δ -6.7 ppm, which is similar to that observed for $NaBPh_4$ (δ -6.2 ppm).[21] The Ph_4P^+ salt of ligand **1** can easily be prepared via cation metathesis using Ph_4PX (X = Cl or Br) in CH_2Cl_2. The ^{31}P chemical shift of the anion of $[Ph_4P][P^{Ph}NBPh_4]$ appears further upfield (δ -28.1 ppm) of that observed for **1**, suggesting that in the latter case the anion $[P^{Ph}NBPh_4]^-$ chelates to the $[Li(THF)_2]^+$ cation in solution. Indeed, the ^7Li NMR spectrum of **1** in $CDCl_3$ shows a sharp singlet at δ -0.35 ppm, and appears in a region observed for other similar systems;[22] at lower temperatures, however, this signal only broadens, and unfortunately no distinct coupling to phosphorus is observed. For synthetic applications involving transition metal precursors, the lithium salt is preferred as it assists in avoiding any issues which may arise involving the removal of a Ph_4P^+ salt that might be produced as a reaction by-product.

Reactions of Ligand 1 with Ruthenium Piano-Stool Precursors. With a reliable ligand synthesis in hand, we next turned our attention towards exploring its coordination chemistry with ruthenium. Our initial efforts focussed on installing ligand **1** on ruthenium-cyclopentadienyl precursors (Scheme 2). For example, stirring a 1:1 mixture of $CpRuCl(PPh_3)_2$ and ligand **1** in refluxing 1,2-dichloroethane leads to the substitution of the chloride ligand and one PPh_3 ligand, and yields the yellow, air-stable, chelated zwitterionic complex **2** in 88% yield. The corresponding

reaction with Cp*RuCl(PPh_3)$_2$ occurs under milder conditions (*i.e.*, at room temperature), and produces yellow-orange complex **3** in very similar yields. These results contrast most other reactions between (η^5-C_5R_5)RuCl(PPh_3)$_2$ (R = H or Me) and neutral bidentate phosphine ligands, where often both PPh_3 ligands are displaced, and the chloride is retained as a ligand in the product.[23] The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** each reveal two doublets of an AX pattern corresponding to the PPh_3 ligand (δ_A 49.7 ppm for **2**, δ_A 50.1 ppm for **3**) and the -PPh_2 group (δ_X 17.6 ppm for **2**, δ_X 20.1 ppm for **3**) of the chelated ligand **1**, with *cis* $^2J_{PP}$ coupling constants of 36 Hz and 33 Hz, respectively. The chiral ruthenium centres of **2** and **3** cause the protons of the ligand's bridging methylene group to be diastereotopic, with each group appearing as two doublets of an AB spin pattern (δ_A 5.09 ppm and δ_B 4.71 ppm for **2**, δ_A 5.00 ppm and δ_B 4.57 ppm for **3**, both with $^2J_{HH}$ = 16 Hz) in their respective ^1H NMR spectra. *In situ* monitoring of each reaction by $^{31}P\{^1H\}$ NMR spectroscopy at regular intervals showed only a steady increase in the concentrations of **2**, **3** and free PPh_3, and a decrease in concentrations of CpRuCl(PPh_3)$_2$ or Cp*RuCl(PPh_3)$_2$. No monodentate intermediates were observed, suggesting chelation rapidly occurs following initial ligand displacement in the formation of **2** and **3**. For comparison, reactions between CpRuCl(PPh_3)$_2$ and either 2-(diphenylphosphino)pyridine[24] or 4-(diphenylphosphino)-2-isopropylimidazole[25] result in the displacement of only one ligand – the PPh_3 ligand – to yield the monodentate products; ring-closing only occurs once a halide abstractor has been added. In these cases, formation of the strained four-membered chelate ring only occurs on irreversible removal of a ligand, in this case the chloride. This also seems to be the case for **2** and **3** since both PPh_3 and LiCl are formed as by-products. Interestingly, when either CpRuCl(PPh_3)$_2$ or Cp*RuCl(PPh_3)$_2$ is mixed with the Ph_4P^+ salt of ligand **1** in 1,2-dichloroethane, no reaction is observed, even under reflux conditions. Indeed, LiCl is much less soluble in

1,2-dichloroethane than Ph_4PCl, and these results suggest halide displacement is likely the first step in the reaction towards the formation of **2**, and not phosphine displacement.

Crystals of **2**•$2CH_2Cl_2$•$(CH_3CH_2)_2O$ suitable for a crystallographic study were obtained from a CH_2Cl_2/diethyl ether mixture. The solid-state structure reveals several interesting features. As expected, complex **2** adopts a three-legged piano-stool structure typically observed for η^5-Cp and -Cp* complexes of ruthenium, with the remaining octahedral sites occupied by a PPh_3 ligand, and the κ^2-$P^{Ph}NBPh_4$ ligand (Figure 1). Several structural features of the κ^2-P,N ligand clearly show the strain of the chelate. The angles around the C(6) carbon atom of the benzimidazole moiety bearing the -PPh_2 group reveal a substantial amount of bending in order to accommodate the chelate (*i.e.*, P(1)-C(6)-N(1) = 104.4(4)° *vs.* P(1)-C(6)-N(2) = 142.0(4)°). Moreover, the -PPh_2 group is pulled out of the plane of the planar benzimidazole group by about 13°. The N(1)-Ru(1)-P(1) chelate bite angle of 67.6(1)° is small, but not unusual.[26] The distance between the ruthenium and the -PPh_2 group (Ru(1)-P(1) = 2.342(2) Å) is slightly longer than that observed between the ruthenium and the PPh_3 ligand (Ru(1)-P(2) = 2.316(2) Å), and this is undoubtedly attributed to the strained chelate. The different ruthenium-phosphorus distances seem to impact the distances between the ruthenium and the carbon atoms of the cyclopentadienyl ligand. For example, the PPh_3 ligand adopts a position that is roughly *trans* to the C(1)-C(2) bond of the cyclopentadienyl ligand, with the plane containing the ruthenium-PPh_3 vector Ru(1)-P(2) approximately bisecting C(1)-C(2). The ruthenium-carbon distances here are the longest (Ru(1)-C(1) = 2.233(7) Å and Ru(1)-C(2) = 2.217(7) Å). In contrast, the position of the -PPh_2 moiety is roughly *trans* to the C(3)-C(4) bond of the cyclopentadienyl ligand, with the Ru(1)-P(1) plane approximately bisecting C(3)-C(4). Here, the ruthenium-carbon distances are the shortest (Ru(1)-C(3) = 2.178(8) Å and Ru(1)-C(4) = 2.167(8) Å). The remaining Ru(1)-C(5) distance

(2.193(6) Å) is intermediate between the two sets. Perhaps these differences in Ru-C(cyclopentadienyl) distances may be linked to the inability of the -PPh_2 group to exert its *trans* influence to the same extent as the PPh_3 ligand as a result of the strained metallacycle.

One of the original intentions of this work was to establish whether or not ligand **1** would display hemilabile character when coordinated to ruthenium. To test for this, the chelated complexes **2** and **3** were treated with CO under various conditions.[27] Unfortunately, in all cases, the NMR spectra revealed a number of compounds had formed, including free PPh_3. Considering the complexity of the NMR spectra, and the production of PPh_3, the formation of ring-opened, including bridged-species,[25,26a] cannot be ruled out in these reactions. We therefore considered other precursors to test for hemilability. Since the synthesis of **2** and **3** likely proceeds via initial halide displacement, we reasoned that the complex $Cp^*RuCl(CO)_2$[28] would be a good candidate to examine in reactions with ligand **1**. When equimolar amounts of $Cp^*RuCl(CO)_2$ and ligand **1** are refluxed together in 1,2-dichloroethane over 24 hours (Scheme 3), a mixture of the monodentate (**4**) and ring-closed (**5**) zwitterionic complexes are formed in an approximately 3:2 ratio. *In situ* monitoring of the reaction progress at regular intervals by $^{31}P\{^1H\}$ NMR spectroscopy revealed complex **4** forms first, and it is slowly converted to the chelated complex **5** before ligand **1** is completely consumed. Unfortunately, complex **5** slowly decomposes with prolonged heating (*i.e.*, to ensure complete conversion from complex **4**), and this prevented its isolation in pure form. Complex **4** exhibits a singlet at δ 36.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum, while the singlet for **5** appears at δ 19.4 ppm. These results are consistent with the large chemical shift differences invariably observed between chelated phosphine ligands forming four-membered rings with a metal, and their corresponding ring-opened structures.[29] As was observed for complexes **2** and **3**, the ^1H NMR spectrum of **5** provides strong evidence for chelation. Consistent with the chirality of

5, two distinct doublets of an AB spin pattern (δ_A 5.15 ppm and δ_B 4.99 ppm, $^2J_{HH}$ = 16 Hz) are observed, which correspond to the diastereotopic protons of the methylene group bridging the tetraphenyborate group to the phosphinobenzimidazole moiety. In contrast, C_{2v}-symmetric **4** displays a singlet at δ 4.75 ppm for the bridging methylene group of the κ^1-ligand. Importantly, Scheme 3 also illustrates the hemilabile nature of ligand **1** as part of complexes **4** and **5**. Thus, pure complex **4** in CH_2Cl_2 slowly evolves CO when heated, and undergoes ring-closing to produce complex **5**. When complex **5** is dissolved in CH_2Cl_2 and allowed to stir under CO, it undergoes ring-opening and adds a second CO ligand to yield the monodentate complex **4**.

Reactions of Complexes 2 and 3 with Alkynes. We have had a long-standing interest in the synthesis and chemistry of ruthenium vinylidene and higher cumulene complexes, mainly because they may be employed as precursors to ruthenium carbyne complexes.[30] Encouraged by our observations from the reactions of **2** and **3** with CO, and the hemilabile properties displayed by **4** and **5**, we wondered if the chelated complexes **2** and **3** might serve as suitable precursors to vinylidene complexes if they, too, could undergo ring-opening in the presence of alkyne substrates.[31,32] As illustrated in Scheme 4, when complex **2** is stirred with a 10-fold excess of phenylacetylene in CH_2Cl_2 over 24 hours, a dark red-orange solution is produced from which a microcrystalline red-orange solid is obtained upon work-up. NMR spectroscopic analysis of the solid reveals the clean formation of a mixture of the *E*- and *Z*-isomers of the vinylidene insertion product **6** in approximately a 4:1 ratio. The $^{31}P\{^1H\}$ and ^1H NMR spectra clearly show that **6** contains inequivalent phosphine ligands and a chiral metal. The $^{13}C\{^1H\}$ NMR spectrum of **6** perhaps offers the most compelling evidence for insertion, and shows two sets of overlapping doublets at δ 159.6 ppm (major) and δ 155.0 ppm (minor) corresponding to C_α of the alkenyl ligands coupling with the PPh_3 ligand and -PPh_2 portion of coordinated ligand **1**.[31b] Interestingly,

when we repeated this reaction but instead using excess 1-hexyne, only *one* isomer (**7**) is produced. Moreover, the reactions between complex **3** and either excess phenylacetylene or 1-hexyne also preferentially produced only one isomer (complexes **8** and **9**, respectively).[33]

Scheme 5 illustrates a plausible mechanism by which the vinylidene insertion complexes **6-9** may form.[31] The precursors **2** or **3** first undergo ring-opening to yield unsaturated κ^1-$P^{Ph}NBPh_4$ intermediates that rapidly coordinate and isomerize the alkyne to an intermediate vinylidene complex. The vinylidene intermediate then undergoes attack at strongly electrophilic C_α by the pendant, nucleophilic benzimidazole nitrogen of the κ^1-$P^{Ph}NBPh_4$ ligand to yield the ring-closed product. The ring-closing process is especially facile since the nucleophilic attack occurs in an intramolecular, chelate-assisted fashion. Certainly, the relief in ring-strain upon switching from the 4-membered to the 5-membered metallacycle assists this process. We attempted to detect the vinylidene intermediates via *in situ* monitoring of the reactions by NMR spectroscopy, but saw no evidence of their formation. To establish the likelihood of this intermediate, the complex Cp*RuCl(CCHPh)(PPh_3)[34] – which contains a preformed vinylidene ligand – was reacted sequentially with AgOTf and ligand **1** in THF. NMR spectroscopic analysis of the red solid isolated from the reaction showed it to be complex **8**, thus suggesting the vinylidene intermediate in Scheme 5 is plausible.

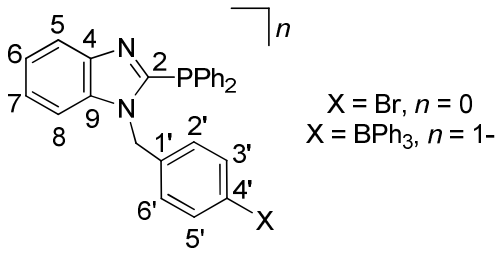
Summary

With careful control of the reaction conditions, the tetraphenyborate-functionalized, heterobidentate phosphinobenzimidazole ligand **1** can be prepared in good yield. Ligand **1** readily reacts with the ruthenium piano-stool precursors (η^5-C_5R_5)RuCl(PPh_3)$_2$ (R = H or Me) via a mechanism that appears to include initial chloride – and not phosphine – displacement. The hard/soft mismatch between the benzimidazole moiety and the ruthenium centre, and the strained

bite angle of the chelated complexes, undoubtedly encourage the hemilabile character of ligand **1**. Indeed, the metallacycle readily ring-opens at the ruthenium-nitrogen bond in the presence of π-acids such as CO and vinylidene ligands (in the latter case, via terminal alkynes).

Experimental

All experiments and manipulations were conducted under an inert atmosphere of prepurified nitrogen using standard Schlenk techniques. Hexanes, CH_2Cl_2 and 1,2-dichloroethane were pre-dried over activated 4Å molecular sieves, passed through a column of alumina, purged with N_2 and stored over 4Å molecular sieves in bulbs with Teflon taps.[35] Diethyl ether and THF were freshly distilled from sodium metal under nitrogen. $CDCl_3$ (dried over anhydrous $CaCl_2$) and CD_2Cl_2 (dried over CaH_2) were vacuum distilled, freeze-pump-thaw degassed three times, and stored in bulbs with Teflon taps. NMR spectra (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and ^7Li) were obtained using a Varian Unity INOVA 500 MHz spectrometer, with chemical shifts (in ppm) referenced to residual solvent peaks (^1H and ^{13}C), external 85% H_3PO_4 (^{31}P), external BF_3•OEt_2 solution (^{11}B), or external LiCl in D_2O. Infrared spectra were acquired using a Nicolet 380 FT-IR spectrometer. Elemental analyses were obtained from the Lakehead University Instrumentation Laboratory. $CpRuCl(PPh_3)_2$,[36] $Cp^*RuCl(PPh_3)_2$,[37] $Cp^*RuCl(CO)_2$,[28] $Cp^*RuCl(CCHPh)(PPh_3)$,[34] and 1-(4-bromobenzyl)benzimidazole[15] were synthesized using previously reported procedures.



Synthesis of 1-(4-bromobenzyl)-2-(diphenylphosphino)benzimidazole. Lithium diisopropylamide (LDA) was first synthesized by adding *n*-BuLi (6.97 mmol, 4.40 mL of a 1.6 M solution in hexanes) to diisopropylamine (6.97 mmol, 976 μL) in THF (5 mL) at -78EC. After 1 hour at -78EC, the LDA solution was then added via cannula to a THF (30 mL) solution of 1-(4-bromobenzyl)benzimidazole (2.00 g, 6.97 mmol) pre-cooled to -78EC. The bright orange solution was stirred at -78EC for 1 hour. Next, $ClPPh_2$ (6.97 mmol, 1.25 mL) was added to the cooled orange solution via syringe. The mixture was left in the cooling bath and allowed to warm slowly to room temperature over 2 hours. After this time, the volatiles were removed under reduced pressure to yield a tacky orange solid. The solid was extracted into CH_2Cl_2 (5 H 10 mL) and filtered through Celite. Removal of the volatiles under reduced pressure yielded a pale yellow solid. Yield: 3.16 g (96%). ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 7.85 (d, 1 H, $^2J_{HH}$ = 8.5 Hz, C^8H), 7.50-7.19 (overlapping m, 15 H, Ph of -PPh_2, C^5H-C^7H, $C^{3'}H$ and $C^{5'}H$), 6.80 (d, 2 H, $^2J_{HH}$ = 8.5 Hz, $C^{2'}H$, $C^{6'}H$), 5.55 (d, 2 H, $^4J_{PH}$ = 3 Hz, -CH_2-). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 154.4 (d, $^1J_{PC}$ = 9 Hz, C^2), 144.6-128.4 (Ph, $C^{1'}$-$C^{6'}$ and C^4, C^9), 123.5, 122.4 (both s, C^6 and C^7), 120.8 (s, C^5), 110.0 (s, C^8), 47.8 (d, $^3J_{PC}$ = 15 Hz, -CH_2-). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): -28.3 (s, -PPh_2).

Synthesis of $[Li(THF)_2][P^{Ph}NBPh_4]$, 1. The compound 1-(4-bromobenzyl)-2-(diphenylphosphino)benzimidazole (1.00 g, 2.13 mmol) was dissolved in THF (30 mL) and the solution was cooled to -80EC (isopropanol/LN_2). Next, *t*-BuLi (2.13 mmol, 1.25 mL of 1.7 M solution in pentane) was added dropwise via syringe to the cooled solution over about 2 minutes yielding a dark orange solution. The solution was stirred and kept between -80EC and -90EC for 1 hour. The solution was maintained at -90EC, and then BPh_3 (0.516 g, 2.13 mmol) in THF (8 mL) was added very slowly dropwise via syringe over 30 minutes. The orange solution

was stirred at -90EC for 2 hours, and then it was allowed to warm slowly to room temperature overnight while in the cooling bath. The next day, excess hexanes (~100 mL) were added to the light orange solution producing an orange oil. The mixture was allowed to stand for about 3 hours, and then the supernatant was decanted. The remaining orange oil was washed with hexanes (2 H 20 mL) and then dried under reduced pressure to yield a powdery pale yellow solid. Yield: 1.20 g (73%). ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 7.62 (d, 1 H, $^{2}J_{HH}$ = 8 Hz, C^{8}*H*), 7.47-6.89 (overlapping m, 30 H, Ph of -PPh_2 and BPh_3, C^{5}*H*-C^{7}*H* and C$^{3'}$*H*, C$^{5'}$*H*), 6.79 (d, 2 H, $^{2}J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 5.31 (s, 2 H, -CH_2-), 3.60 (m, 8 H, THF), 1.79 (m, 8 H, THF). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 165.0 (q, $^{1}J_{BC}$ = 48 Hz, *C*$^{4'}$), 163.9 (q, $^{1}J_{BC}$ = 50 Hz, *ipso C* of B-Ph), 155.7 (d, $^{1}J_{PC}$ = 16 Hz, *C*^{2}), 142.7-123.3 (Ph, *C*$^{1'}$-*C*$^{3'}$, *C*$^{5'}$, *C*$^{6'}$, *C*^{4} and *C*^{9}), 121.9 (s, *C*^{6}, *C*^{7}), 117.9 (s, *C*^{5}), 112.5 (s, *C*^{8}), 88.7 (s, C_5Me_5), 68.6 (s, THF), 50.0 (s, -CH_2-), 25.5 (s, THF). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): -24.1 (s, -*P*Ph_2). ^{11}B{^{1}H} NMR (160 MHz, 22EC, $CDCl_3$): -6.7 ppm (s). ^{7}Li NMR (195 MHz, 22EC, $CDCl_3$): -0.35 ppm (s).

Synthesis of [CpRu(PPh_3)(κ^2*P*,*N*-P^{Ph}NBPh_4)], 2. $CpRuCl(PPh_3)_2$ (0.139 g, 0.191 mmol) and ligand **1** (0.150 g, 0.191 mmol) were combined and dissolved in 1,2-dichloroethane (10 mL). The orange mixture was refluxed for 24 hours. The next day, the cloudy orange-yellow mixture was allowed to cool to room temperature and then it was filtered through Celite. The volatiles were removed from the filtrate and the orange-yellow solid that remained was washed with diethyl ether (4 H 20 mL) to remove the PPh_3. The yellow-orange product was dried under reduced pressure. Yield: 0.178 g (88%). Recrystallization from CH_2Cl_2/diethyl ether yielded analytically pure samples. Anal. Calcd. for $C_{67}H_{55}BN_2P_2Ru$•0.5CH_2Cl_2: C, 73.4; H, 5.11; N, 2.54. Found: C, 73.8; H, 5.11; N, 2.62. ^{1}H NMR (500 MHz, 22EC, CD_2Cl_2): 7.41-6.78 (overlapping m, 46 H, Ph of -PPh_2, PPh_3 and BPh_3, C^{5}*H*-C^{8}*H*, and C$^{3'}$*H*, C$^{5'}$*H*), 6.42 (d, 2 H, $^{2}J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 5.09 (d, 2

H, $^{2}J_{HH}$ = 16 Hz, -C*H*$_A$H$_B$-), 4.70 (d, 1 H, $^{2}J_{HH}$ = 16 Hz, -CH$_A$*H*$_B$-), 4.43 (s, 5 H, Cp). ^{13}C{^{1}H} NMR (125 MHz, 22EC, CD_2Cl_2): 165.9 (q, $^{1}J_{BC}$ = 49 Hz, *C*$^{4'}$), 164.0 (q, $^{1}J_{BC}$ = 49 Hz, *ipso C* of B-Ph), 156.6 (d, $^{1}J_{PC}$ = 31 Hz, *C*^{2}), 143.4-124.3 (Ph, *C*$^{1'}$-*C*$^{3'}$, *C*$^{5'}$, *C*$^{6'}$, *C*^{4} and *C*^{9}), 122.5 (s, *C*^{6}, *C*^{7}), 117.6 (s, *C*^{5}), 113.6 (s, *C*^{8}), 78.7 (s, *C*$_5$H$_5$), 50.2 (s, -*C*H$_2$-). ^{31}P{^{1}H} NMR (202 MHz, 22EC, CD_2Cl_2): 49.8 (d, $^{2}J_{PP}$ = 36 Hz, *P*Ph$_3$), 17.9 (d, $^{2}J_{PP}$ = 36 Hz, -*P*Ph$_2$). ^{11}B{^{1}H} NMR (160 MHz, 22EC, CD_2Cl_2): -6.6 ppm (s).

Synthesis of [Cp*Ru(PPh$_3$)(κ^2*P*,*N*-P^{Ph}NBPh$_4$)], 3. Cp*RuCl(PPh$_3$)$_2$ (0.100 g, 0.125 mmol) and ligand **1** (0.099 g, 0.125 mmol) were combined and dissolved in CH_2Cl_2 (10 mL). The orange solution was allowed to stir for 24 hours. The next day, the hazy, light orange mixture was filtered through Celite, and then the volatiles were removed from the filtrate under reduced pressure. The light orange solid was then washed with diethyl ether (4 H 20 mL) to remove the PPh_3. The yellow-orange product was dried under reduced pressure. Yield: 0.126 g (89%). Recrystallization from CH_2Cl_2/diethyl ether yielded analytically pure samples. Anal. Calcd. for $C_{75}H_{65}BN_2P_2Ru{\bullet}CH_2Cl_2$: C, 74.1; H, 5.66; N, 2.38. Found: C, 74.4; H, 5.69; N, 2.54. ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 7.72 (d, 1 H, $^{2}J_{HH}$ = 8 Hz, C^{8}*H*), 7.51-6.73 (overlapping m, 45 H, Ph of -PPh$_2$, PPh$_3$ and BPh$_3$, C^{5}*H*-C^{7}*H*, and C$^{3'}$*H*, C$^{5'}$*H*), 6.49 (d, 2 H, $^{2}J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 4.99 (d, 1 H, $^{2}J_{HH}$ = 16 Hz, -C*H*$_A$H$_B$-), 4.58 (d, 1 H, $^{2}J_{HH}$ = 16 Hz, -CH$_A$*H*$_B$-), 1.33 (s, 15 H, Cp*). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 166.2 (q, $^{1}J_{BC}$ = 49 Hz, *C*$^{4'}$), 163.6 (q, $^{1}J_{BC}$ = 50 Hz, *ipso C* of B-Ph), 156.4 (d, $^{1}J_{PC}$ = 33 Hz, *C*^{2}), 142.2-124.1 (Ph, *C*$^{1'}$-*C*$^{3'}$, *C*$^{5'}$, *C*$^{6'}$, *C*^{4} and *C*^{9}), 121.8 (s, *C*^{6}, *C*^{7}), 116.8 (s, *C*^{5}), 114.2 (s, *C*^{8}), 88.7 (s, *C*$_5$Me$_5$), 51.0 (s, -*C*H$_2$-), 10.8 (s, -*C*H$_3$ of Cp*). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 50.1 (d, $^{2}J_{PP}$ = 33 Hz, *P*Ph$_3$), 20.1 (d, $^{2}J_{PP}$ = 33 Hz, -*P*Ph$_2$). ^{11}B{^{1}H} NMR (160 MHz, 22EC, $CDCl_3$): -6.6 ppm (s).

Synthesis of [Cp*Ru(CO)$_2$(κ^1*P*-P^{Ph}NBPh$_4$)], 4, and [Cp*Ru(CO)(κ^2*P*,*N*-P^{Ph}NBPh$_4$)],

5. $Cp^*RuCl(CO)_2$ (0.0500 g, 0.153 mmol) and ligand **1** (0.120 g, 0.153 mmol) were combined, dissolved in 1,2-dichloroethane (5 mL), and refluxed for 24 hours. The next day, the cloudy yellow mixture was allowed to cool to room temperature, and then it was filtered through Celite. The volatiles were removed from the filtrate and the yellow solid was washed with diethyl ether (10 mL) before drying under reduced pressure. NMR spectroscopic analysis of the product revealed it to be a mixture of complexes **4** and **5** in an approximately 3:2 ratio. Complete NMR data of complex **4** is given below; selected NMR data for complex **5** follows: ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 6.56 (d, 2 H, $^2J_{HH}$ = 7.5 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 5.15 (d, 1 H, $^2J_{HH}$ = 15 Hz, -C*H*$_A$H$_B$-), 4.99 (d, 1 H, $^2J_{HH}$ = 16 Hz, -CH$_A$*H*$_B$-), 1.72 (s, 15 H, Cp*). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 19.4 (s, -*P*Ph_2). ^{11}B{^{1}H} NMR (160 MHz, 22EC, $CDCl_3$): -6.6 ppm (s).

Synthesis of [Cp*Ru(CO)$_2$(κ^1*P*-P^{Ph}NBPh$_4$)], 4. $Cp^*RuCl(CO)_2$ (0.0500 g, 0.153 mmol) and ligand **1** (0.120 g, 0.153 mmol) were combined, dissolved in 1,2-dichloroethane (5 mL), and refluxed for 24 hours. After cooling to room temperature, the cloudy yellow mixture was then filtered through Celite. The volatiles were removed from the filtrate under reduced pressure yielding a yellow solid. The flask was then backfilled with CO, and then CH_2Cl_2 (5 mL) was added. The dark yellow solution was allowed to stir under CO for 24 hours. After this time, the volatiles were removed under reduced pressure yielding a pale yellow solid. The solid was washed with diethyl ether (20 mL) before drying under reduced pressure. Yield: 0.120 g (85%). Recrystallization from CH_2Cl_2/diethyl ether yielded analytically pure samples. Anal. Calcd. for $C_{59}H_{61}BN_2O_2PRu$: C, 72.8; H, 6.32; N, 2.88. Found: C, 72.3; H, 5.90; N, 3.21. IR (Nujol): 2044 (s), 1994 (s). ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 7.83 (d, 1 H, $^2J_{HH}$ = 8 Hz, C^8*H*), 7.37-6.81 (overlapping m, 30 H, Ph of -PPh_2 and BPh_3, C^5*H*-C^7*H* and C$^{3'}$*H*, C$^{5'}$*H*), 6.11 (d, 2 H, $^2J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 4.76 (s, 2 H, -C*H*$_2$-), 1.68 (s, 15 H, Cp*). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$):

198.1 (d, $^{2}J_{PC}$ = 15 Hz, *C*O), 164.5 (q, $^{1}J_{BC}$ = 49 Hz, $C^{4'}$), 163.8 (q, $^{1}J_{BC}$ = 49 Hz, *ipso C* of B-Ph), 143.2 (d, $^{1}J_{PC}$ = 21 Hz, C^{2}), 138.6-123.0 (Ph, $C^{1'}$-$C^{3'}$, $C^{5'}$, $C^{6'}$, C^{4} and C^{9}), 121.8 (s, C^{6},C^{7}), 120.5 (s, C^{5}), 113.1 (s, C^{8}), 103.1 (s, C_5Me_5), 50.2 (s, -CH$_2$-), 9.75 (s, -CH$_3$ of Cp*). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 36.1 (s, -*P*Ph$_2$). ^{11}B{^{1}H} NMR (160 MHz, 22EC, $CDCl_3$): -6.7 ppm (s).

Synthesis of [CpRu(PPh$_3$)(κ^2*C*,*P*-(CCHPh)-P^{Ph}NBPh$_4$)], 6. Complex **2** (0.0500 g, 0.0471 mmol) was dissolved in CH_2Cl_2 (2 mL). Next, phenylacetylene (52 μL, 0.471 mmol) was added to the suspension via syringe, and the mixture was allowed to stir for 24 hours. The resulting clear red-orange solution was evaporated to dryness under reduced pressure, and the red solid that remained was washed with diethyl ether (2 H 15 mL). The product was recrystallized from THF/hexanes yielding a microcrystalline red-orange solid which was washed with diethyl ether and dried under reduced pressure. Yield: 0.0410 g (75%). Anal. Calcd. for $C_{75}H_{61}BN_2P_2Ru$: C, 77.4; H, 5.28; N, 2.41. Found: C, 76.7; H, 5.54; N, 2.61. NMR spectroscopy revealed two isomers of **6** had formed in approximately a 4:1 ratio. Selected NMR spectroscopic data for each isomer follows. **Major isomer:** ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 5.78 (d, 2 H, $^{2}J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 4.89 (d, 1 H, $^{2}J_{HH}$ = 16 Hz, -C*H*$_A$H$_B$-), 4.71 (d, 1 H, $^{2}J_{HH}$ = 16 Hz, -CH$_A$*H*$_B$-), 4.38 (s, 5 H, Cp). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 166.2 (q, $^{1}J_{BC}$ = 48 Hz, $C^{4'}$), 163.5 (q, $^{1}J_{BC}$ = 50 Hz, *ipso C* of B-Ph), 159.6 (dd, $^{2}J_{PC}$ = 18 Hz, $^{2}J_{PC}$ = 17 Hz, C_α), 152.2 (d, $^{1}J_{PC}$ = 22 Hz, C^{2}), 121.9 (s, C^{6}, C^{7}), 117.7 (s, C^{5}), 116.1 (s, C^{8}), 86.2 (s, C_5H_5), 52.7 (s, -CH$_2$-). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 69.0 (d, $^{2}J_{PP}$ = 35 Hz, *P*Ph$_3$), 49.1 (d, $^{2}J_{PP}$ = 35 Hz, -*P*Ph$_2$). **Minor isomer:** ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 6.00 (d, 2 H, $^{2}J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 5.15 (d, 1 H, $^{2}J_{HH}$ = 16 Hz, -C*H*$_A$H$_B$-), 4.98 (d, 1 H, $^{2}J_{HH}$ = 16 Hz, -CH$_A$*H*$_B$-), 4.62 (s, 5 H, Cp). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 166.4 (q, $^{1}J_{BC}$ = 49 Hz, $C^{4'}$), 163.5 (q, $^{1}J_{BC}$ = 50 Hz, *ipso C* of B-Ph), 155.0 (dd, $^{2}J_{PC}$ = 22 Hz, $^{2}J_{PC}$ = 12 Hz, C_α), 153.0 (d, $^{1}J_{PC}$ = 19 Hz, C^{2}), 121.9 (s, C^{6}, C^{7}), 118.4 (s, C^{5}), 114.2 (s,

C^8), 87.3 (s, C_5H_5), 53.5 (s, -CH$_2$-). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 69.6 (d, $^2J_{PP}$ = 35 Hz, PPh$_3$), 50.8 (d, $^2J_{PP}$ = 35 Hz, -PPh$_2$).

Synthesis of [CpRu(PPh$_3$)(κ^2*C*,*P*-(CCHBu)-P^{Ph}NBPh$_4$)], 7. Complex **2** (0.0600 g, 0.0565 mmol) was dissolved in CH_2Cl_2 (3 mL). Next, 1-hexyne (65 μL, 0.565 mmol) was added to the suspension via syringe, and the mixture was allowed to stir for 24 hours. The now clear orange solution was evaporated to dryness under reduced pressure, and the orange solid that remained was washed with diethyl ether (2 H 10 mL). The product was dried under reduced pressure. Yield: 0.0640 g (84%). Recrystallization from CH_2Cl_2/hexanes yielded analytically pure samples. Anal. Calcd. for $C_{73}H_{65}BN_2P_2Ru$•0.5CH_2Cl_2: C, 74.4; H, 5.61; N, 2.36. Found: C, 74.6; H, 5.79; N, 2.65. ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 7.87 (d, 1 H, $^2J_{HH}$ = 8 Hz, C^8*H*), 7.53-6.80 (overlapping m, 46 H, Ph of -PPh$_2$, PPh$_3$ and BPh$_3$, C^5*H*-C^7*H*, C$^{3'}$*H*, C$^{5'}$*H* and C$_\beta$*H*), 5.89 (d, 2 H, $^2J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 5.02 (d, 1 H, $^2J_{HH}$ = 15 Hz, -CH_AH$_B$-), 4.88 (d, 1 H, $^2J_{HH}$ = 16 Hz, -CH$_A$$H_B$-), 4.68 (s, 5 H, Cp), 2.45 (br m, 2 H, *n*-Bu), 1.67 (br m, 2 H, *n*-Bu), 1.55 (br m, 2 H, *n*-Bu), 1.10 (t, 3 H, $^3J_{HH}$ = 7 Hz, *n*-Bu). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 166.3 (q, $^1J_{BC}$ = 48 Hz, $C^{4'}$), 163.4 (q, $^1J_{BC}$ = 49 Hz, *ipso C* of B-Ph), 154.7 (dd, $^2J_{PC}$ = 16 Hz, $^2J_{PC}$ = 21 Hz, C_α), 150.8 (d, $^1J_{PC}$ = 23 Hz, C^2), 137.9-123.2 (Ph, $C^{1'}$-$C^{3'}$, $C^{5'}$, $C^{6'}$, C^4, C^9 and C_β), 121.9 (s, C^6, C^7), 117.9 (s, C^5), 115.5 (s, C^8), 84.8 (s, C_5H_5), 52.8 (s, -CH$_2$-), 33.8 (s, *n* -Bu), 33.2 (s, *n*-Bu), 23.3 (s, *n*-Bu), 14.4 (s, *n*-Bu). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 69.0 (d, $^2J_{PP}$ = 34 Hz, PPh$_3$), 52.2 (d, $^2J_{PP}$ = 34 Hz, -PPh$_2$). ^{11}B{^{1}H} NMR (160 MHz, 22EC, $CDCl_3$): -6.7 ppm (s).

Synthesis of [Cp*Ru(PPh$_3$)(κ^2*C*,*P*-(CCHPh)-P^{Ph}NBPh$_4$)], 8. (a) **Method A.** Complex **3** (0.0500 g, 0.0442 mmol) was dissolved in CH_2Cl_2 (4 mL). Next, phenylacetylene (49 μL, 0.442 mmol) was added to the solution via syringe, and the mixture was allowed to stir for 24 hours. The resulting clear dark red solution was evaporated to dryness under reduced pressure, and the red

solid that remained was washed with diethyl ether (2 H 15 mL).Yield: 0.031 g (60%). Recrystallization from CH_2Cl_2/hexanes yielded analytically pure samples. Anal. Calcd. for $C_{80}H_{71}BN_2P_2Ru•0.5CH_2Cl_2$: C, 75.7; H, 5.68; N, 2.19. Found: C, 75.3; H, 6.33; N, 2.04. ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 7.69-6.78 (overlapping m, 44 H, Ph of -PPh_2, PPh_3 and BPh_3, C^5*H*, C^8*H*, C$^{3'}$*H* and C$^{5'}$*H*), 6.76 (s, 1 H, C$_\beta$*H*), 6.64-6.37 (m, 5 H, Ph), 6.18 (br, 2 H, C^6*H*, C^7*H*), 5.83 (d, 2 H, $^2J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 5.05 (d, 1 H, $^2J_{HH}$ = 15 Hz, -C*H*$_A$H$_B$-), 4.74 (d, 1 H, $^2J_{HH}$ = 15 Hz, -CH$_A$*H*$_B$-), 1.30 (s, 15 H, Cp*). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 166.0 (q, $^1J_{BC}$ = 48 Hz, *C*$^{4'}$), 163.4 (q, $^1J_{BC}$ = 50 Hz, *ipso C* of B-Ph), 162.2 (dd, $^2J_{PC}$ = 18 Hz, $^2J_{PC}$ = 22 Hz, *C*$_\alpha$), 155.2 (d, $^1J_{PC}$ = 21 Hz, *C*^{2}), 139.4-123.1 (Ph, *C*$^{1'}$-*C*$^{3'}$, *C*$^{5'}$, *C*$^{6'}$, *C*^{4}, *C*^{9} and *C*$_\beta$), 121.9 (s, *C*^{6}, *C*^{7}), 119.1 (s, *C*^{5}), 114.4 (s, *C*^{8}), 95.6 (s, *C*$_5$Me$_5$), 53.2 (s, -*C*H$_2$-), 9.91 (s, -*C*H$_3$ of Cp*). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 67.1 (d, $^2J_{PP}$ = 32 Hz, *P*Ph_3), 51.9 (d, $^2J_{PP}$ = 32 Hz, -*P*Ph_2). ^{11}B{^{1}H} NMR (160 MHz, 22EC, $CDCl_3$): -6.7 ppm (s).

(b) **Method B.** Cp*RuCl(CCHPh)(PPh_3) (0.100 g, 0.157 mmol) and AgOTf (0.040 g, 0.157 mmol) were combined, dissolved in THF (10 mL) and allowed to stir for 30 minutes. Ligand **1** (0.124 g, 0.157 mmol) in THF was added via cannula to the deep, dark purple solution turning it cloudy, dark orange-red. The mixture was allowed to stir for 1 hour, and then the volatiles were removed under reduced pressure. The product was extracted into CH_2Cl_2 (20 mL) and filtered through Celite. The volatiles were removed from the deep, dark red filtrate yielding a red solid. The solid was washed with diethyl ether (15 mL) before drying under reduced pressure. Yield: 0.131 g (68%). The NMR spectroscopic data of the red solid were identical to that observed for the product isolated using Method A.

Synthesis of [Cp*Ru(PPh_3)(κ^2*C,P*-(CCHBu)-P^{Ph}NBPh$_4$)], 9. Complex **3** (0.0700 g, 0.0618 mmol) was dissolved in CH_2Cl_2 (4 mL). Next, 1-hexyne (71 μL, 0.618 mmol) was added to

the solution via syringe, and the mixture was allowed to stir for 24 hours. The resulting clear orange solution was evaporated to dryness under reduced pressure, and the orange-red solid that remained was washed with diethyl ether (2 H 15 mL).Yield: 0.0420 g (56%). Recrystallization from CH_2Cl_2/hexanes and washing with diethyl ether yielded analytically pure samples. Anal. Calcd. for $C_{78}H_{75}BN_2P_2Ru•0.5CH_2Cl_2$: C, 75.0; H, 6.10; N, 2.23. Found: C, 75.5; H, 5.97; N, 2.56. ^{1}H NMR (500 MHz, 22EC, $CDCl_3$): 7.64-6.19 (overlapping m, 46 H, Ph of -PPh_2, PPh_3 and BPh_3, C^5*H*-C^8*H*, C$^{3'}$*H*, C$^{5'}$*H*), 5.82 (d, $^1J_{HH}$ = 8 Hz, C$^{2'}$*H*, C$^{6'}$*H*), 5.57 (m, 1 H, C$_\beta$*H*), 5.05 (d, 1 H, $^2J_{HH}$ = 15 Hz, -C*H*$_A$H$_B$-), 4.68 (d, 1 H, $^2J_{HH}$ = 15 Hz, -CH$_A$*H*$_B$-), 2.34 (br m, 1 H, *n*-Bu), 2.04 (br m, 1 H, *n*-Bu), 1.58 (br m, 4 H, *n*-Bu), 1.27 (s, 15 H, Cp*), 0.96 (t, 3 H, $^3J_{HH}$ = 7 Hz, *n*-Bu). ^{13}C{^{1}H} NMR (125 MHz, 22EC, $CDCl_3$): 166.2 (q, $^1J_{BC}$ = 48 Hz, *C*$^{4'}$), 163.4 (q, $^1J_{BC}$ = 49 Hz, *ipso C* of B-Ph), 154.2 (d, $^1J_{PC}$ = 19 Hz, *C*^{2}), 153.3 (dd, $^2J_{PC}$ = 22 Hz, $^2J_{PC}$ = 19 Hz, *C*$_\alpha$), 136.6-123.5 (Ph, *C*$^{1'}$-*C*$^{3'}$, *C*$^{5'}$, *C*$^{6'}$, *C*^{4} and *C*^{9}), 121.9 (s, *C*^{6}, *C*^{7}), 121.6 (s, *C*$_\beta$), 118.4 (s, *C*^{5}), 114.9 (s, *C*^{8}), 94.8 (s, *C*$_5$Me$_5$), 53.1 (s, -*C*H$_2$-), 34.9 (s, *n* -Bu), 33.9 (s, *n*-Bu), 22.7 (s, *n*-Bu), 14.3 (s, *n*-Bu), 9.84 (s, -*C*H$_3$ of Cp*). ^{31}P{^{1}H} NMR (202 MHz, 22EC, $CDCl_3$): 66.5 (d, $^2J_{PP}$ = 33 Hz, *P*Ph_3), 52.5 (d, $^2J_{PP}$ = 33 Hz, -*P*Ph_2). ^{11}B{^{1}H} NMR (160 MHz, 22EC, $CDCl_3$): -6.8 ppm (s).

X-ray Crystallography. A clear, yellow rod-like specimen of **2**•$2CH_2Cl_2$•$(CH_3CH_2)_2O$, with approximate dimensions 0.06 mm x 0.13 mm x 0.19 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Apex2 diffractometer using MoKα radiation. Data were collected on a Bruker Apex2 SMART CCD system with MoKα radiation at -100°C. Consecutive 0.5 degree omega scans were used to ensure complete coverage, and the total exposure time was 2.96 hours. The frames were integrated with the Bruker SAINT software package (Apex2 2013.10.1) using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 59803 reflections to a

maximum θ angle of 28.33° (0.75 Å resolution), of which 16002 were independent (average redundancy 3.737, completeness = 99.6%, R(int) = 5.98%, $R\sigma$ = 8.90%) and 12036 (75.22%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.9751(8) Å, b = 18.6007(8) Å, c = 20.4062(9) Å, and volume = 6443.2(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 7046 reflections above 20 σ(I) with 4.553° < 2θ < 39.05°. Data were corrected for absorption effects using the numerical method (SADABS). The ratio of minimum to maximum apparent transmission was 0.914. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9093 and 0.9864. The structure was solved and refined using the Bruker SHELXTL 2013 Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit $C_{73}H_{69}BCl_4N_2OP_2Ru$. The final anisotropic full-matrix least-squares refinement on F^2 with 743 variables converged at R_1 = 5.81% for the observed data, and wR_2 = 15.64% for all data. The goodness-of-fit was 1.037. The largest peak in the final difference electron density synthesis was 1.084 $e^-/Å^3$ and the largest hole was -0.803 $e^-/Å^3$, with an RMS deviation of 0.100 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.346 g/cm^3 and F(000), 2704 e^-. The main molecule showed no disorder, but three disordered solvent molecules were refined: two molecules of CH_2Cl_2 (0.61(1) and 0.510(6)) and one molecule of diethyl ether (0.763(7)).

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Appendix. Supplementary material

CCDC 979032 contains the supplementary crystallographic data for **2**•$2CH_2Cl_2$•$(CH_3CH_2)_2O$. This data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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33. Although we did not pursue the full assignment of complexes **6**-**9** as either *E* or *Z* using solution methods, a partial X-ray structure determination of complex **8** not only confirmed that ring-opening had occurred to form the five-membered ring vinylidene insertion product, but also that the connectivity about the double bond was *E*. Unfortunately, extensive solvent disorder prevented the complete solution of the structure.

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Caption for Figure 1:

Figure 1. Molecular structure of complex **2** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru(1)-P(1), 2.342(2); Ru(1)-P(2), 2.316(2); Ru(1)-N(1), 2.164(4); Ru(1)-C(1), 2.233(7); Ru(1)-C(2), 2.217(7); Ru(1)-C(3), 2.178(8); Ru(1)-C(4), 2.167(8); Ru(1)-C(5), 2.193(6); P(1)-C(6), 1.824(6); P(1)-C(6)-N(1), 104.4(4); P(1)-C(6)-N(2), 142.0(4); N(1)-Ru(1)-P(1), 67.6(1); P(2)-Ru(1)-N(1), 90.9(1); P(2)-Ru(1)-P(1), 97.89(5).

Captions for Schemes 1-6:

Scheme 1. Synthesis of ligand **1**.

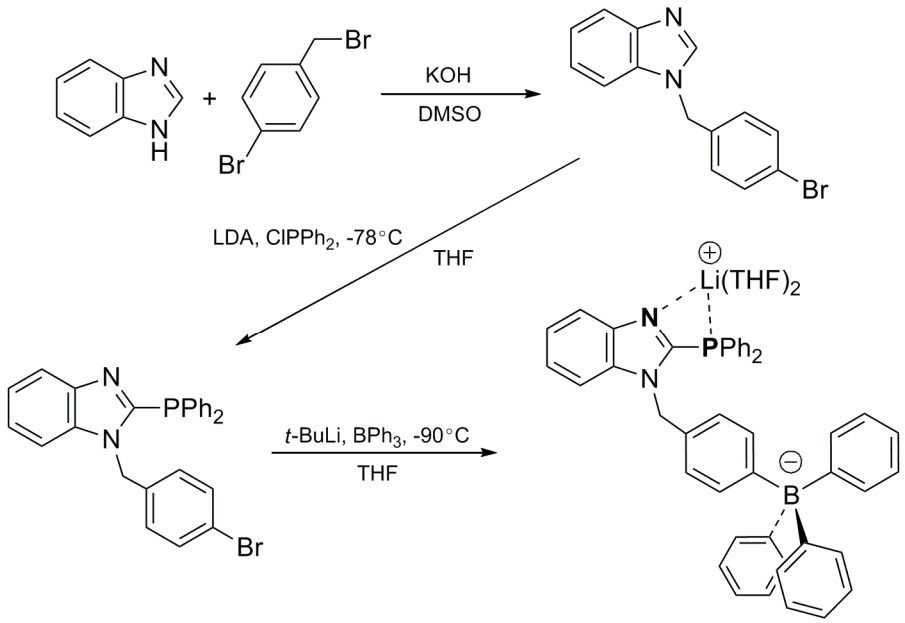
Scheme 2. Synthesis of complexes **2** and **3**.

Scheme 3. Hemilabile behaviour of ligand **1**.

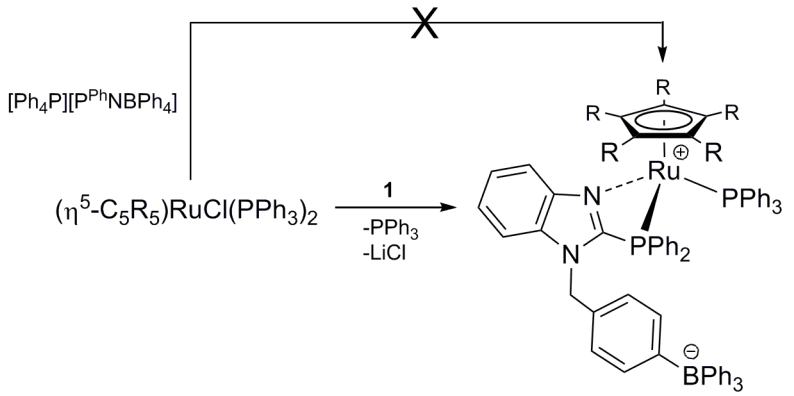
Scheme 4. Synthesis of the *E*- and *Z*-isomers of complex **6**.

Scheme 5. Possible mechanism for the synthesis of complexes **6**-**9**.

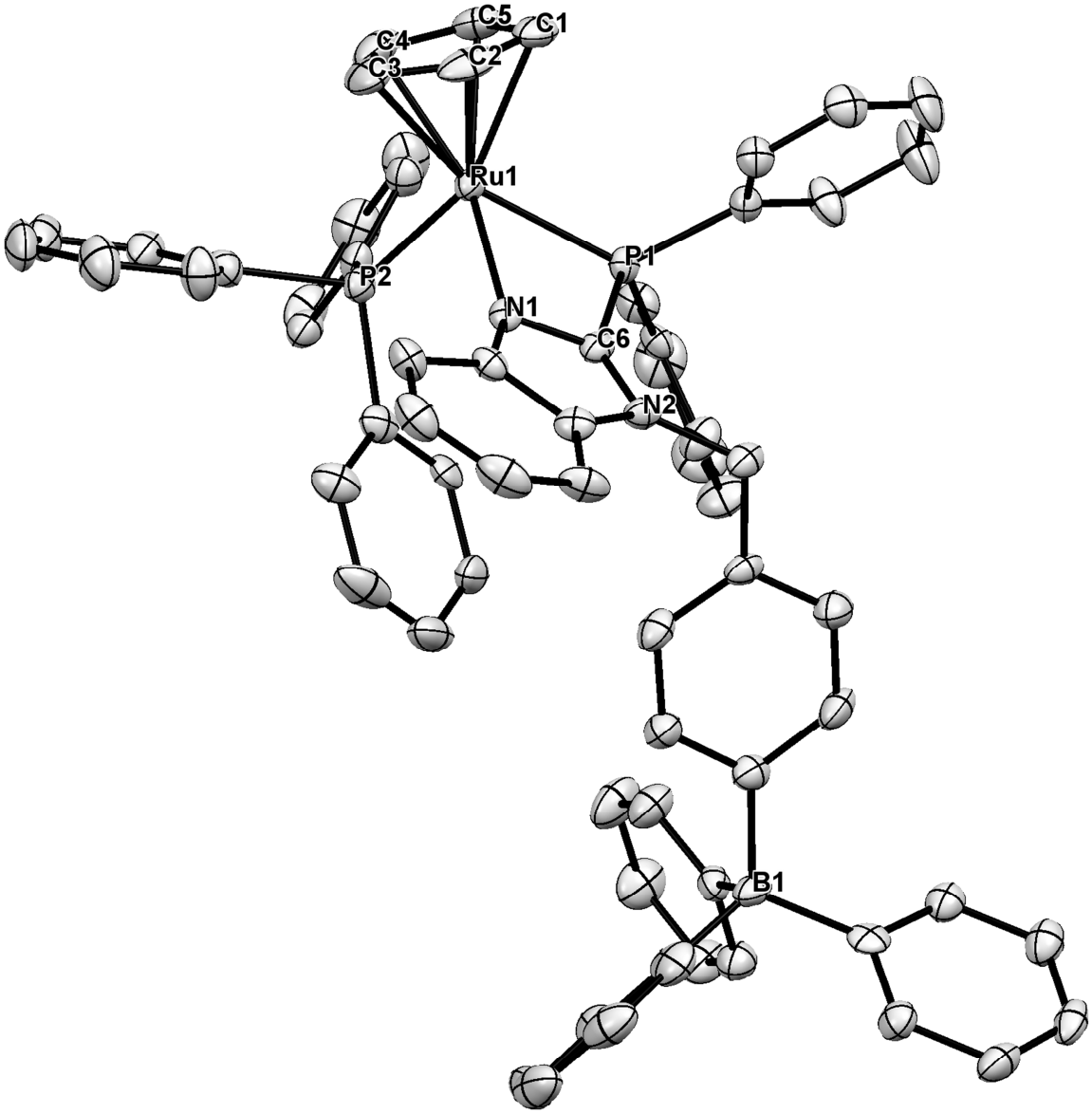
Scheme 6. Alternate synthetic route to complex **8**.

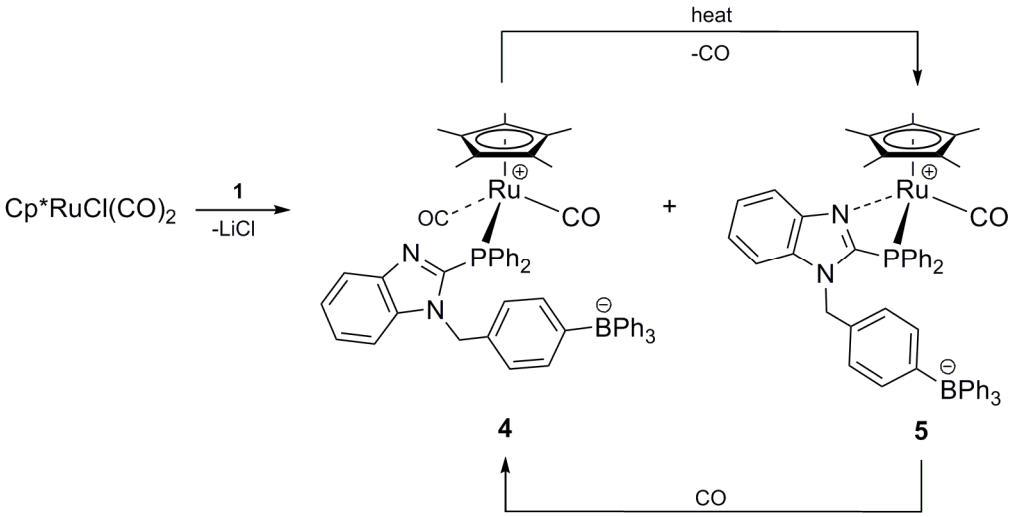


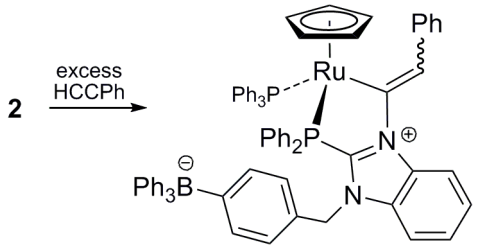
1



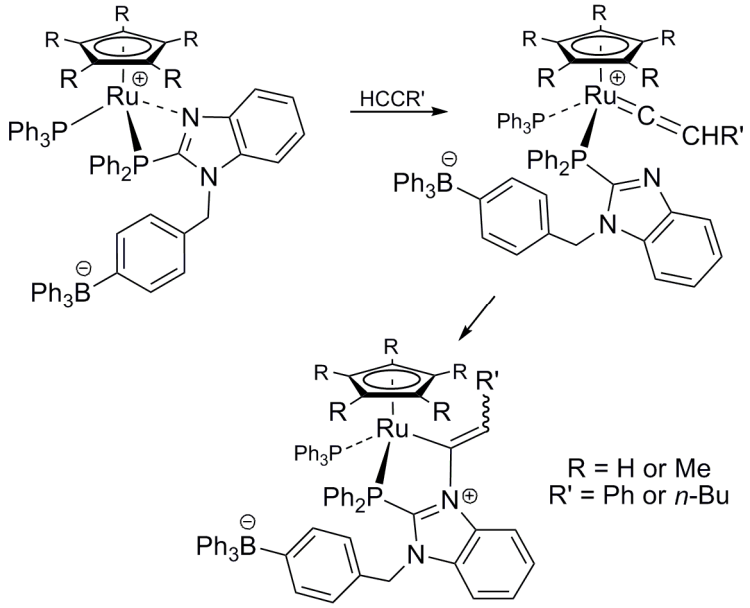
R = H (**2**) or Me (**3**)

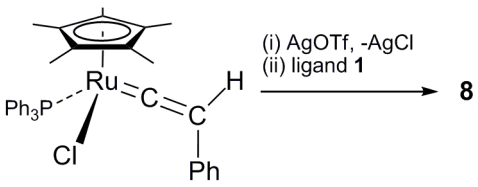

C5
C1
C4
C2
C3
Ru1
P1
P2
N1
C6
N2
B1

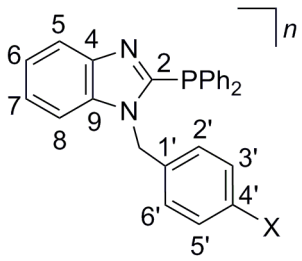




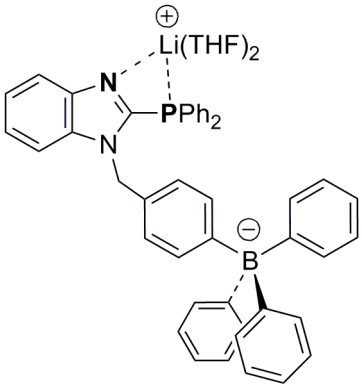
E/*Z*-**6**







X = Br, *n* = 0
X = BPh_3, *n* = 1-



1

Structure I

Highlights:

- A [P,N]-hybrid ligand is made anionic by functionalizing with a tetraphenylborate substituent
- Zwitterionic ruthenium piano-stool complexes have been prepared with this anionic hybrid ligand
- Hemilability under mild conditions was observed
- Vinylidene ligands insert into the ruthenium-nitrogen bond of the κ^2-P,N ligand