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Ruthenium complexes supported by 2,6-bis(pyrazol-1-yl)pyridines

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Abstract

The synthesis and characterization of a series of ruthenium(II) complexes containing the planar tridentate ligands 2,6-bis(pyrazol-1-yl)pyridine (BPP) or 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (Me_4BPP) are described. The reaction of BPP with $RuCl_2(PPh_3)_3$ yields both the *cis* (**1a**) and *trans* (**1b**) isomers of $[RuCl(PPh_3)_2(BPP)]Cl$. Complexes of the general formula *trans*-$RuCl_2(L)(Me_4BPP)$ (L = PPh_3, **2**; C_2H_4, **3a**; CO, **3b**; MeCN, **3c**) are also reported, and were prepared from either $RuCl_2(PPh_3)_3$ and Me_4BPP (i.e. **2**), Et_3N reductions of $RuCl_3(Me_4BPP)$ in the presence of L (i.e. **2** and **3b**,**c**), or from $[RuCl_2(p\text{-cymene})]_2$, Me_4BPP and L (i.e. **3a**). The neutral vinylidene complex *cis*-$RuCl_2(=C=CHPh)(Me_4BPP)$ (**4**), was isolated from reactions of phenylacetylene with either **3a** or mixtures of $[RuCl_2(p\text{-cymene})]_2$ and Me_4BPP, while the cationic allenylidene complex $[RuCl(PPh_3)(=C=C=CPh_2)(Me_4BPP)][BF_4]$ (**5**), was prepared from **2**, $AgBF_4$ and 1,1-diphenyl-2-propyn-1-ol. Complexes **1**–**5** were characterized by multinuclear NMR and IR spectroscopy.

Keywords: Ruthenium; Vinylidene; Allenylidene; Tridentate nitrogen donor ligand

1. Introduction

Rational ligand design in organometallic chemistry and catalysis generally has been directed by a desire to enhance the reactivity, selectivity and/or thermal stability of homogeneous transition metal-based catalysts. In the wake of this desire, a multitude of new ligand systems have emerged, many of which have proven to exhibit exceptional properties with regard to catalysis. Undeniably, phosphorus-based ligands (and, to a lesser extent, the higher homologues) have played a crucial role in developing early synthetic applications involving transition metal catalysts; indeed, they have remained a dominant co-ligand in organometallic chemistry. However, in recent years, there has been increased interest in developing new classes of ligands bearing donor atoms other than phosphorus, particularly nitrogen donor ligands. This is partly in response to the susceptibility of common phosphine ancillary ligands to undergo degradation (e.g. P–C bond cleavage, oxidation to phosphine oxides, and *ortho*-metallation reactions) during catalysis, especially under thermal conditions. Furthermore, organometallic complexes bearing nitrogen donor ligands often exhibit high reactivities [1]. Synthetic applications involving transition metals containing tridentate nitrogen donor ligands have been well developed in recent years; some of the more notable classes include tris(pyrazolyl)borate ligands [2], 1,4,7-triazacyclononane ligands [3], and 2,6-bis(imino)pyridine [4], and the closely related 2,6-bis(oxazolinyl)pyridine [5], ligands. As well, some of these polydentate nitrogen donor ligands have found applications in the area of enzyme mimicry [6].

Transition metal complexes containing the class of planar tridentate nitrogen donor ligands 2,6-bis(pyrazol-1-yl)pyridines (Structure I) [7] have proven to be useful structural and redox mimics for analogous 2,2′:6′,2″-terpyridine complexes [8]. This ligand system is particularly more attractive than the terpyridine system because the steric and electronic properties can be readily and systematically altered by varying the substituents on the pyrazole rings. Several studies have shown that the structural, spectroscopic, magneto- and electrochemical properties of metal complexes bearing these ligands are sensitive towards substituent effects [9]. There have been

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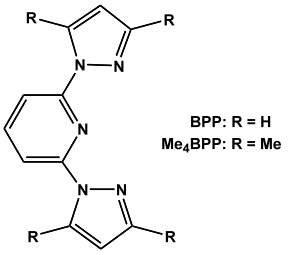
several reports regarding the redox properties of ruthenium complexes bearing this general class of ligand [8,10,11]. We wished to screen the coordination and organometallic chemistry of ruthenium complexes containing this ligand, especially since its sterics can be easily manipulated, and report the results herein.



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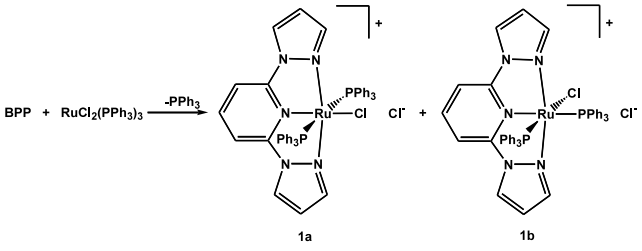
2. Results and discussion

2.1. Synthesis and characterization of cis- (1a) and trans- (1b) [RuCl(PPh3)2(BPP)]Cl (1), and trans-RuCl2(PPh3)(Me4BPP) (2)

When a 1:1 mixture of $RuCl_2(PPh_3)_3$ and BPP are boiled in CH_2Cl_2 for 3 h, the air-stable complex *trans*-[RuCl(PPh$_3$)$_2$(BPP)]Cl (**1a**), deposits as a pale yellow microcrystalline solid in fair (32%) isolated yield (Scheme 1). The PMe_3 analogue of **1a** has been prepared [11] by a much different route, while similar results were observed [12] for the reaction between $RuCl_2(PPh_3)_3$ and the structurally similar *mer*-tridentate ligand pybox [pybox = 2,6-bis(dihydrooxazolinyl)pyridine], which yielded *trans*-$[RuCl(PPh_3)_2(pybox)]^+$. The structure of **1a** is readily deduced via NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **1a** shows only a singlet at $\delta = 24.50$, which is consistent with two mutually *trans* phosphine ligands about the ruthenium center. This chemical shift is similar to that observed [12] for the cation *trans*-$[RuCl(PPh_3)_2(pybox)]^+$ ($\delta = 22.0$), as well as for the cation *trans*-$[RuCl(PPh_3)_2(terpy)]^+$ ($\delta = 20.1$), which also contains a planar *mer*-tridentate 2,6-disubstituted pyridine ligand (terpy = 2,2′:6′,2″-terpyridine) [13]. The overall C_{2v} symmetry of **1a** renders the 3- and 5-pyridyl hydrogens equivalent, as well as the 3 and 3″, 4 and 4″, and 5 and 5″ hydrogens of the pyrazolyl rings. Thus, in addition to the two pyridyl hydrogen signals ($\delta = 7.31$ for 3,5-H and $\delta = 7.63$ for 4-H) and three pyrazolyl hydrogen signals ($\delta = 8.26$ for 3,3″-H, $\delta = 6.60$ for 4,4″-H and $\delta = 8.71$ for 5,5″-H), the ^1H NMR spectrum of **1a** clearly shows a series of overlapping multiplets corresponding to, and integrating well for, the six phenyl groups of the two PPh_3 ligands ($\delta = 7.33$–7.19).



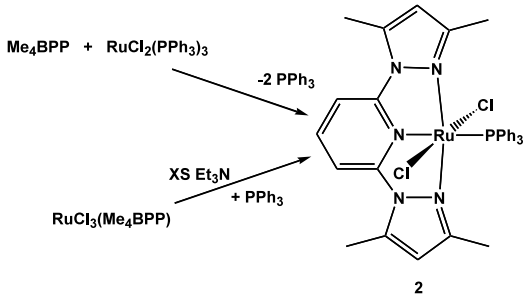
Scheme 1.

Further examination of the filtrate from the synthesis of **1a** via $^{31}P\{^1H\}$ NMR spectroscopy reveals the presence of the *cis* isomer, *cis*-[RuCl(PPh$_3$)$_2$(BPP)]Cl (**1b**) (Scheme 1), as the main (ca. 80%) component, with the balance consisting primarily of **1a** (ca. 15%) and free PPh_3. Separating pure **1b** from the mixture (i.e. via fractional crystallization or chromatography) was frustrated by the very low solubility of each complex, even in very polar solvents (i.e. DMSO). Similar structural elements are common to both **1a** and **1b**, as evidenced by solution NMR studies. Thus, two pyridyl ($\delta = 8.33$ and 8.05) and three pyrazolyl ($\delta = 9.19$, 8.25 and 6.76) hydrogen signals are observed in the ^1H NMR spectrum of **1b**, which shows that both halves of the *mer*-tridentate molecule are magnetically equivalent. The $^{31}P\{^1H\}$ NMR spectrum of complex **1b** is more diagnostic of its structure, and shows (in accord with the absence of C_2 symmetry) an AB doublet of doublets pattern centered at $\delta = 41.32$ ($^2J_{PP} = 28$ Hz), consistent with overall C_s symmetry of **1b** (i.e. a perpendicular mirror plane bisecting the BPP ligand through the pyridyl nitrogen and *para* carbon) brought about by the relative *cis* arrangement of the two PPh_3 ligands. Given the more sterically congested *cis* arrangement of the PPh_3 ligands in **1b** (vs. the *trans* arrangement in **1a**), we considered the possibility that **1b** is a kinetic product in the reaction of BPP with $RuCl_2(PPh_3)_2$, and that a *trans* disposition of phosphine ligands (i.e. **1a**) would be more thermodynamically preferred. Heating (80 °C) a DMSO solution of **1b** initially leads to a smooth increase in population of the *trans* isomer **1a**, and a concomitant decrease in **1b**, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. However, although **1b** is completely consumed within 24 h, several new complexes, along with free PPh_3, accompany the formation of **1a** during this time, and they could not be confidently characterized (the formation of ruthenium(II)–BPP–PPh_3 complexes containing DMSO should not be ruled out under these conditions, considering the polar nature and coordinating ability of this solvent).

As part of this work, we wished to examine and compare the steric effects of this ligand class, and this prompted us to investigate reactions involving alkyl substituted derivatives of 2,6-bis(pyrazol-1-yl)pyridine. Indeed, substituents may be readily incorporated onto

the pyrazole rings of the BPP framework [7]. Thus, when a benzene solution containing $RuCl_2(PPh_3)_3$ and the methyl substituted Me_4BPP ligand [Me_4BPP = 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine] in a 1:1 molar ratio is refluxed for 48 h, a color change from brown to deep red–orange is observed, and the complex *trans*-$RuCl_2(PPh_3)(Me_4BPP)$ (**2**), precipitates as an air-stable, red microcrystalline solid (Scheme 2). Complex **2** was found to be more soluble (vs. complexes **1**), particularly in halogenated solvents. Despite the lengthy reaction time, the yield via this method (38%) was moderate at best, therefore, alternative methods of preparing **2** were investigated. Interestingly, performing the same reaction in a higher boiling solvent (i.e. toluene) only produced intractable residues that did not contain **2**, based on $^{31}P\{^1H\}$ and ^1H NMR spectroscopic analyses. However, Et_3N reductions of ethanol slurries containing $RuCl_3(Me_4BPP)$ [10,11] and PPh_3 (1:1) at reflux temperatures yielded **2** (Scheme 2) in much better isolated yields (80% after recrystallization) and significantly shorter reaction times (5 h). We attempted to extend this latter procedure to include bulkier phosphines such as PCy_3 [i.e. *trans*-$RuCl_2(PCy_3)(Me_4BPP)$], however, under analogous conditions only insoluble black powders (presumably ruthenium metal) could be isolated. There has been some discussion [11] regarding the meridional steric crowding of 2,6-bis(pyrazol-1-yl) pyridine ligands bearing substituents in the 3,3″-positions of the pyrazole rings. Perhaps the comparatively larger PCy_3 phosphine, coupled with the sterics of the Me_4BPP ligand, inhibit the formation of *trans*-$RuCl_2(PCy_3)(Me_4BPP)$ under these conditions.

The proposed structure of **2** is based on its ^1H and $^{31}P\{^1H\}$ NMR spectra. In addition to two pyridyl hydrogen signals ($\delta = 7.04$ for the 3,5-H and $\delta = 7.37$ for 4-H), the ^1H NMR spectrum of **2** shows one pyrazolyl hydrogen ($\delta = 6.05$ for 4,4″-H) and two pyrazolyl methyl signals ($\delta = 2.83$ and 2.60 for 3,3″- and 5,5″-CH_3). While this data is consistent with overall C_{2v} symmetry, considering the meridionally coordinating geometry of the Me_4BPP ligand, the chloride ligands conceivably could adopt a *cis* geometry and yield similar



Scheme 2.

^1H NMR data. We, however, postulate a *trans* arrangement. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a singlet at $\delta = 49.51$, which is consistent with only one PPh_3 ligand coordinated to the ruthenium center. More importantly, this chemical shift lies in a range observed for several structurally similar ruthenium complexes of the general formula $RuCl_2(PR_3)(EN'E)$ (EN′E = *mer*-tridentate 2,6-disubstituted pyridine ligand, where E is either a nitrogen or phosphorus donor atom) in which the chloride ligands are *trans*, including *trans*-$RuCl_2[P(p\text{-}C_6H_4CH_3)](terpy)$ ($\delta = 41.6$) [13], *trans*-$RuCl_2(PPh_3)(pybox)$ ($\delta = 46.48$) [14] and *trans*-$RuCl_2(PPh_3)(PNP)$ [PNP = 2,6-bis(diphenylphosphinomethyl)pyridine] ($\delta = 42.0$) [15]. Furthermore, similarly formulated complexes in which the chloride ligands are *cis* display ^{31}P resonances that are shifted substantially upfield ($\Delta\delta \approx 10$–15 ppm) [13,14,16] compared with those observed for *trans* geometries. Within the context of this latter point, it seemed somewhat unusual that the PPh_3 ligand would preferentially occupy the more sterically congested meridional plane containing the Me_4BPP ligand (vs. the apical positions), considering the methyl substituents in the 3 and 3″-positions [for example [16], reactions of $RuCl_2(PPh_3)_3$ with tridentate 2,6-bis(imino)pyridine ligands bearing bulky substituents exclusively yield products analogous to **2** but with *cis* chlorides]. However, complex **2** does not isomerize to the corresponding *cis* isomer after heating (80 °C) in either $C_2D_4Cl_2$ or polar CD_3OD (60 °C) over 24 h (**2** is insoluble in toluene-d_8, even at 110 °C). These results contrast that observed [13] for the isomerization of *trans*-$RuCl_2(PPh_3)(terpy)$ to the *cis* isomer, which goes to completion under similar conditions, despite lacking any groups in the 6 and 6″-positions of the terpy ligand. A recent comparative X-ray crystallographic study [11] between analogous ruthenium complexes containing either 6,6″-substituted terpy ligands or 3,3″-substituted BPP ligands (both ligands bearing the same substituents) has shown that the 6,6″-substituted terpy complex imparts a greater steric impact on the fourth position in the meridional plane. Thus, a similar argument also may be made for **2** and *trans*-$RuCl_2(PPh_3)(terpy)$, where the dramatic difference in isomerization rates may simply rely on the fact that the terpy ligand greatly facilitates ligand (e.g. phosphine) dissociation in the meridional plane (vs. Me_4BPP) due to a greater steric hindrance, thus accelerating isomerization. This is supported [14] by the fact that *trans*-$RuCl_2(PPh_3)[(SS)\text{-}^i Pr\text{-}pybox]$ {(*SS*)-^{i}Pr-pybox = 2,6-bis[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine}, which bears bulky isopropyl groups on the 4′-position of the oxazoline ring, quantitatively rearranges to the *cis* isomer in refluxing acetone over 24 h, whereas *trans*-$RuCl_2(PPh_3)(pybox)$ (i.e. only hydrogens at the 4′-positions) does not under the same conditions.

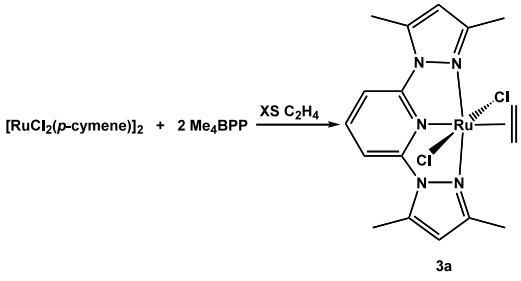
2.2. Synthesis and characterization of trans-$RuCl_2(L)(Me_4BPP)$ (3) ($L = C_2H_4$, 3a; CO, 3b; MeCN, 3c)

Several other *trans*-$RuCl_2(L)(Me_4BPP)$ derivatives also could be prepared, all of which are isostructural with complex **2**. Following a procedure reported by Nishiyama et al. [17], a 1:2 mixture of $[RuCl_2(p\text{-cymene})]_2$ and Me_4BPP refluxed under an ethylene atmosphere cleanly provides the orange–brown ethylene complex *trans*-$RuCl_2(\eta^2\text{-}C_2H_4)(Me_4BPP)$ (**3a**), in moderate yield (64%) after work-up (Scheme 3). Complex **3a** is stable in the solid state, even under reduced pressure for weeks, and solutions of **3a** show no decomposition over 24 h when left exposed to atmospheric elements. The C_{2v}-symmetric structure of **3a** is easily deduced via NMR spectroscopy. The ^1H NMR spectrum reveals details indicating structural similarities with **2**, in particular the presence of a {*trans*-$RuCl_2(Me_4BPP)$} fragment (i.e. two pyridyl hydrogen signals, one pyrazolyl hydrogen signal and two pyrazolyl methyl signals, all of which are consistent with a plane of symmetry bisecting the planar Me_4BPP ligand through the *para*-carbon and nitrogen of the 2,6-pyridine bridge). The coordinated ethylene ligand of **3a** appears as a sharp singlet at $\delta = 3.11$ (similar to that reported for several other ruthenium–ethylene complexes bearing *mer*-tridentate nitrogen donor ligands) [16,18–20] indicating either the ethylene ligand in solution is fluxional (i.e. freely rotating about the ruthenium centroid–ethylene axis at room temperature on the NMR time scale) or is rigidly coplanar with either of the two mirror planes present in the {*trans*-$RuCl_2(Me_4BPP)$} fragment of **3a**. X-ray crystallographic analysis of structurally related *trans*-$RuCl_2(\eta^2\text{-}C_2H_4)$(pybox) [20], and *cis*-$[RuCl(\eta^2\text{-}C_2H_4)_2$\{2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine\}$][BAr'_4]$ [18] has revealed that the C_2H_4 molecule coordinated *trans* to the 2,6-pyridine bridge lies parallel to the N–Ru–N plane. Considering the similarities between these *mer*-tridentate ligands and Me_4BPP, a similar (preferred) conformation of the ethylene ligand in **3a** could be expected. We attempted to isolate a coordinatively unsaturated 16-electron *trans*-$RuCl_2(Me_4BPP)$ complex from refluxed benzene mixtures of $[RuCl_2(p\text{-cymene})]_2$ and Me_4BPP (1:2) (i.e. in the absence of any ligand L), but were unsuccessful (i.e. only reactants were isolated after work-up).

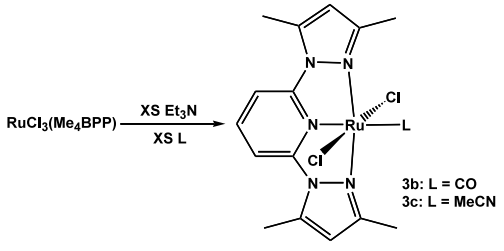
Extending this general procedure for the preparation of **3a** to include other ligands L (L = CO or MeCN) proved difficult, yielding mixtures of products even with slight modifications to the reaction conditions. However, using a similar approach (Scheme 4) for the preparation of complex **2**, stirring methanol suspensions of $RuCl_3(Me_4BPP)$ in the presence of excess Et_3N and reagent L (L = CO or MeCN), the complexes *trans*-$RuCl_2(CO)(Me_4BPP)$ (**3b**), or *trans*-$RuCl_2(NCMe)(Me_4BPP)$ (**3c**), could be prepared in good to excellent yields (78 and 90%, respectively). NMR spectroscopic data clearly indicate that **3a**–**c** are isostructural (see Section 4). Interestingly, the ν_{CO} stretch in the IR spectrum of **3b** appears at 1938 cm^{-1}, which is slightly lower than that observed ($\nu_{CO} = 1948\ cm^{-1}$) [21] for the structurally analogous *mer*,*trans*-$RuCl_2(CO)(NN'N)$ {NN'N = 2,6-[bis(dimethylamino)methyl]pyridine}. This would seem to suggest that the Lewis basicity of the Me_4BPP ligand is comparable to the NN'N ligand, despite containing 'softer' pyrazolyl donors (compared with 'harder' dimethylamino donors). Perhaps the methyl groups in the 3,3″ and 5,5″-positions on the pyrazole rings of the Me_4BPP ligand influence its basicity. Indeed, electrochemical and spectroscopic studies [10] performed on ruthenium(II)–Me_4BPP complexes containing β-diketonate ligands suggest that the electron density of the ruthenium center is strongly influenced by the electron donating nature of the pyrazole substituents on the BPP framework.

2.3. Vinylidene complexes containing Me_4BPP: synthesis and characterization of cis-$[RuCl_2(=C=CHPh)(Me_4BPP)]$ (4)

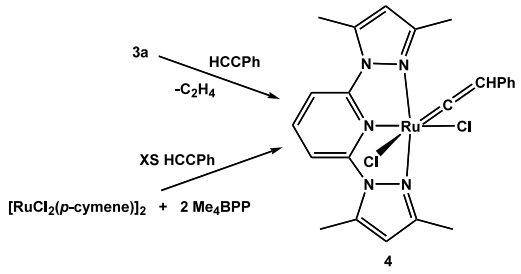
Substitution of the ethylene ligand in **3a** was found to occur quite readily (Scheme 5). Thus, refluxing a benzene mixture of **3a** in the presence of a slight (i.e. 1.2-fold) excess of phenylacetylene over 24 h cleanly yields the air-stable dark brown vinylidene complex *cis*-$[RuCl_2(=C=CHPh)(Me_4BPP)]$ (**4**), in moderate isolated yield (67%). Performing similar reactions with *tert*-



Scheme 3.



Scheme 4.



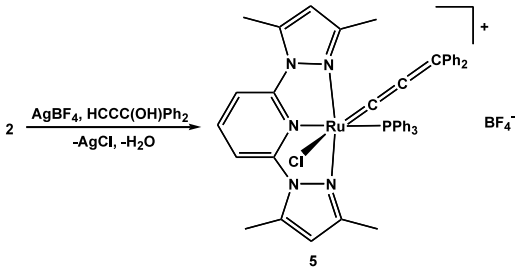
Scheme 5.

butylacetylene or trimethylsilylacetylene, in benzene or toluene, led either to decomposition to unidentified products or the quantitative isolation of **3a**. Alternatively, and more conveniently, **4** also may be prepared (Scheme 5) in comparable yields (67%) directly from $[RuCl_2(p\text{-cymene})]_2$, Me_4BPP and a comparatively large excess of phenylacetylene (1:2:5, respectively) in refluxing benzene over 24 h. The reaction proceeds at a much slower rate via this method (i.e. several days are required for completion) when only stoichiometric or even a slight (1.2 M) excess amount of phenylacetylene is used. Unfortunately, this alternate approach also failed for bulkier alkynes (i.e. *tert*-butylacetylene); clearly, steric demands of the larger alkynes and the coordinated Me_4BPP ligand must inhibit tautomerization by the ruthenium center to the corresponding vinylidene in these reactions. There are few precedents in the literature describing the isomerization of terminal alkynes to the corresponding vinylidene by ruthenium(II) complexes containing tridentate nitrogen donor ligands [19,22], and even fewer examples in which the complex does not bear a phosphine ligand.

The structure of **4** is easily deduced via ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and IR spectroscopy. Along with signals attributed to the coordinated Me_4BPP ligand, the $^{13}C\{^1H\}$ NMR spectrum of **4** reveals resonances that clearly indicate tautomerization of phenylacetylene has occurred, the most diagnostic of which are C_α ($\delta = 356.1$) and C_β ($\delta = 111.3$) of the vinylidene ligand [23]. The ^1H NMR spectrum of **4** at room temperature is consistent with a mirror plane bisecting the coordinated Me_4BPP ligand through the *para*-carbon and nitrogen of the 2,6-pyridine bridge, and containing the *cis*-chloride ligands [i.e. one signal each for the pyridyl 3,5-H ($\delta = 7.60$), pyrazolyl 4,4″-H ($\delta = 6.25$), and pyrazolyl 3,3″- and 5,5″-methyl groups ($\delta = 2.76$ and 2.73) are observed]. No changes were observed when the spectrum was acquired at −80 °C. Thus, the presence of this mirror plane would seem to suggest that the vinylidene ligand rapidly rotates about the Ru–C bond on the NMR time scale at temperatures above −80 °C (theoretical and variable temperature NMR spectroscopic studies of d^6 ruthenium–vinylidene complexes have revealed that the barrier to rotation about the ruthenium–carbon double bond is small, on the order of several kcal mol^{-1}) [24]. The far-infrared spectrum of **4** shows two intense absorptions at 315 and 223 cm^{-1}, consistent with a relative *cis* arrangement of chloride ligands about the ruthenium center [25]. Similar spectroscopic results were observed for the structurally similar and crystallographically characterized complex *cis*-$RuCl_2$(=C=CHPh)(NN′N) [19] in which the chloride ligands are *cis* disposed. Clearly, in the synthesis of **4** from **3a**, the apical *trans*-chlorides rearrange to *cis* in the product. One could argue that positioning the vinylidene in the apical position minimizes any steric interactions between the C_β substituents on the vinylidene and the more congested meridional plane. Equally arguable, electronics may also contribute to this rearrangement.

2.4. Allenylidene complexes containing Me_4BPP: synthesis and characterization of $[RuCl(PPh_3)(=C=C=CPh_2)(Me_4BPP)][BF_4]$ (5)

Intrigued by the synthesis of the neutral vinylidene **4**, we tried to extend this general procedure to include higher cumulenes, in particular allenylidenes, by using propargyl alcohols as convenient precursors. The majority of reported allenylidene complexes are cationic [26], and examples of neutral allenylidene complexes remain comparatively rare. Unfortunately, despite modifying the conditions over several runs, reactions of **3a** with, for example, 1,1-diphenyl-2-propyn-1-ol, did not produce the anticipated allenylidene $RuCl_2$(=C=C=CPh_2)(Me_4BPP) (i.e. the allenylidene analogue of **4**), nor did reactions of this alkyne with mixtures of $[RuCl_2(p\text{-cymene})]_2$ and Me_4BPP. Presumably sterics are responsible for the lack of reactivity in these reactions. However, refluxing CH_2Cl_2 solutions of **2** and $AgBF_4$ (1:1) in the presence of a slight excess of 1,1-diphenyl-2-propyn-1-ol yields (76%) the deep, dark red cationic allenylidene complex [RuCl(PPh_3)(=C=C=CPh_2)(Me_4BPP)][BF_4] (**5**), after work-up (Scheme 6). As expected, the $^{31}P\{^1H\}$ NMR spectrum of **5** shows a singlet resonance; more importantly, the chemical shift ($\delta = 41.96$) of this signal is consistent with that observed for complexes reported in this, and other [13–15] work, in which the PPh_3 ligand is *trans* to the 2,6-pyridine bridge of the Me_4BPP ligand (vide supra). The $^{13}C\{^1H\}$



Scheme 6.

NMR spectrum of **5** clearly shows the presence of an allenylidene ligand, with the typical downfield resonance of C_α appearing as a doublet ($^2J_{PC} = 20$ Hz) at $\delta = 313.5$; C_β and C_γ of the allenylidene ligand appear as singlets at $\delta = 212.2$ and 157.7, respectively. The IR spectrum of **5** supports the $^{13}C\{^1H\}$ NMR data and shows a strong absorption for the allenylidene ligand at, $\nu_{(C=C=C)} = 1922$ cm^{-1}, a region characteristic of such ligands [26]. Complex **5** is frustratingly soluble, even in solvents of low polarity (e.g. hexanes and Et_2O), and despite numerous attempts, including changing the counteranion (e.g. PF_6^-), we were unable to grow X-ray quality single crystals for a structure determination.

3. Conclusions

Several key points emerge from this work. There appears to be a subtle balance between steric and electronic effects of the BPP ligands examined as part of this work. Thus, halide dissociation occurs in reactions of $RuCl_2(PPh_3)_3$ with BPP (e.g. cationic diphosphine **1a**) presumably because of the increased electron density at the metal center (brought about by the coordination of BPP) which would subsequently weaken the bond between the metal and the π-donor chloride ligand. However, when the sterics of the BPP ligand are increased (i.e. Me_4BPP), phosphine dissociation prevails (e.g. neutral monophosphine **2**), despite the Me_4BPP ligand being a better Lewis base versus BPP. Although we were unable to isolate the 16-electron complex $RuCl_2(Me_4BPP)$, the presence of a labile C_2H_4 ligand in complex **3a** makes it a convenient source for this coordinatively unsaturated complex, which can serve as a precursor for the synthesis of other $RuCl_2(L)(Me_4BPP)$ complexes (e.g. the vinylidene complex **4**). The most intriguing results presented in this work center around the ability of the {Ru(Me_4BPP)} fragment to isomerize terminal alkynes, including propargyl alcohols, to the corresponding vinylidenes (e.g. **4**) and allenylidenes (e.g. **5**). Ruthenium(II)–cumulene complexes containing tridentate nitrogen donor ligands are known to be effective catalysts in a variety of applications, particularly C–C coupling reactions [27]. Thus, complexes **4** and **5** may exhibit novel reactivities in this regard; studies in our group are currently underway.

4. Experimental

All experiments and manipulations were conducted under an inert atmosphere of prepurified N_2 using standard Schlenk and syringe techniques. Bulk solvents used in large-scale preparations were rigorously dried and distilled from appropriate drying agents immediately prior to use: CH_2Cl_2 (CaH_2); C_6H_6, Et_2O and hexanes (sodium/benzophenone); MeCN, MeOH and EtOH (activated 4 Å sieves). NMR solvents used in solution structure elucidations were dried with appropriate drying agents, vacuum distilled, freeze–pump–thaw degassed three times, and stored in bulbs with Teflon taps: $CDCl_3$ (anhydrous $CaCl_2$); CD_3CN, CD_3OD and DMSO-d_6 (activated 4 Å sieves); CD_2Cl_2 and $C_2D_4Cl_2$ (CaH_2); toluene-d_8 (Na metal). NMR spectra (^1H, ^{13}C and ^{31}P) were obtained on a Varian Unity INOVA 500 MHz spectrometer, with chemical shifts (in ppm) referenced to residual protio solvent peaks (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P). IR spectra were recorded using a Bruker IFS-66 FT IR spectrophotometer as Nujol mulls between either NaCl or polyethylene plates. Elemental analyses were performed on a CEC 240XA analyzer by the Lakehead University Center for Analytical Services. The ligands [7] BPP and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (Me_4BPP), and the complexes $RuCl_2(PPh_3)_3$ [28a], $[RuCl_2(p\text{-cymene})]_2$ [28b] and $RuCl_3(Me_4BPP)$ [10b,11a] were prepared according to the methods cited previously.

4.1. Synthesis of cis- (**1a**) and trans- (**1b**) [RuCl(PPh$_3$)$_2$(BPP)]Cl (**1**)

A brown CH_2Cl_2 (15 ml) solution of $RuCl_2(PPh_3)_3$ (0.500 g, 0.521 mmol) and BPP (0.110 g, 0.521 mmol) was refluxed for 3 h, during which time *trans*-[RuCl(PPh_3)$_2$(BPP)]Cl (**1a**), deposited as a pale yellow solid. The solid was collected using a glass filter frit and washed with several volumes of Et_2O (3 × 10 ml) before drying under reduced pressure. Yield: 0.153 g (32%). *Anal.* Calc. for $C_{44}H_{39}Cl_2N_5P_2Ru$: C, 58.21; H, 4.33; N, 7.72. Found: C, 58.54; H, 4.26; N, 7.15%. ^1H NMR (499.9 MHz, DMSO-d_6, 22 °C): 8.71 (d, 2H, $^3J_{HH} = 3$ Hz, C^5H of Pz), 8.25 (d, 2H, $^3J_{HH} = 3$ Hz, C^3H of Pz), 7.63 (t, 1H, $^3J_{HH} = 8$ Hz, C^4H of Py), 7.31 (d, 2H, $^3J_{HH} = 8$ Hz, C^3H of Py), 7.33–7.19 (m, 30H, Ph), 6.60 (dd, 2H, $^3J_{HH} = 3$ Hz, C^4H of Pz). $^{31}P\{^1H\}$ NMR (202.3 MHz, DMSO-d_6, 22 °C): 24.50 (s, PPh_3). Removal of the volatiles from the filtrate under reduced pressure followed by several Et_2O washes (3 × 20 ml) yielded a yellow–orange solid which contained *cis*-[RuCl(PPh_3)$_2$(BPP)]Cl (**1b**) (ca. 80%), along with small quantities of **1a** (ca. 15%) and free PPh_3, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. Despite numerous attempts and methods, complex **1b** could not be isolated as a pure product. NMR data for **1b** follows. ^1H NMR (499.9 MHz, DMSO-d_6, 22 °C): 9.19 (d, 2H, $^3J_{HH} = 3$ Hz, C^5H of Pz), 8.33 (t, 1H, $^3J_{HH} = 8$ Hz, C^4H of Py), 8.25 (d, 2H, $^3J_{HH} = 3$ Hz, C^3H of Pz), 8.05 (d, 2H, $^3J_{HH} = 8$ Hz, C^3H of Py), 7.32–7.19 (m, Ph), 6.76 (dd, 2H, $^3J_{HH} = 3$ Hz, C^4H of Pz). $^{31}P\{^1H\}$ NMR (202.3

MHz, DMSO-d_6, 22 °C): $\delta(P_A) = 43.85$ (d, $^2J_{PP} = 28$ Hz, PPh_3), $\delta(P_B) = 38.78$ (d, $^2J_{PP} = 28$ Hz, PPh_3).

4.2. Synthesis of *trans*-$RuCl_2(PPh_3)(Me_4BPP)$ (**2**)

4.2.1. Method A

A Schlenk tube containing $RuCl_2(PPh_3)_3$ (0.200 g, 0.209 mmol) and Me_4BPP (0.0559 g, 0.209 mmol) was treated with C_6H_6 (15 ml), and the mixture was refluxed. After 48 h, a red microcrystalline solid had deposited. Once the mixture had cooled to room temperature (r.t.), the solid was filtered off, washed with Et_2O (2 × 10 ml) and dried under reduced pressure. Yield: 0.0711 g (38%). *Anal.* Calc. for $C_{33}H_{32}Cl_2N_5PRu$: C, 56.49; H, 4.61; N, 9.98. Found: C, 55.20; H, 4.33; N, 9.30%. ^{1}H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.37 (t, 1H, $^3J_{HH} = 10$ Hz, C^4H of Py), 7.30 (m, 6H, Ph), 7.21 (m, 3H, Ph), 7.10 (m, 6H, Ph), 7.04 (d, 2H, $^3J_{HH} = 10$ Hz, $C^{3,5}H$ of Py), 6.05 (s, 2H, $C^{4,4''}H$ of Pz), 2.83 (s, 6H, CH_3 of Pz), 2.60 (s, 6H, CH_3 of Pz). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 157.7, 153.0 (s, $C^{2,6}$ of Py and $C^{5,5''}$ of Pz), 142.8 (C^4 of Py), 133.7 (d, $^1J_{PC} = 42$ Hz, C^1 of Ph in PPh_3), 133.2 (d, $^2J_{PC} = 10$ Hz, $C^{2,6}$ of Ph in PPh_3), 128.9 ($C^{3,3''}$ of Pz), 128.3 (s, C^4 of Ph in PPh_3), 127.5 (d, $^3J_{PC} = 9$ Hz, $C^{3,5}$ of Ph in PPh_3), 113.4, 104.7 (s, $C^{4,4''}$ of Pz and $C^{3,5}$ of Py), 15.12, 14.43 (s, 2 × CH_3 of Pz). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): 49.51 (s, PPh_3).

4.2.2. Method B

An ethanol (10 ml) slurry of $RuCl_3(Me_4BPP)$ (0.200 g, 0.421 mmol) and PPh_3 (0.110 g, 0.421 mmol) was treated with excess Et_3N (1 ml) via syringe. After 5 h at reflux, the deep dark red–orange solution was allowed to cool to r.t. before removing the volatiles under reduced pressure. The dark red–orange solid that remained was extracted into CH_2Cl_2 (25 ml) and filtered through Celite. The volume of the filtrate was reduced to approximately 10 ml under reduced pressure and excess hexanes (30 ml) were carefully layered and allowed to slowly diffuse into the CH_2Cl_2 solution. Over 24 h, red crystals were obtained. The crystals were filtered off, washed well with Et_2O (2 × 10 ml) and dried under reduced pressure. Yield: 0.237 g (80%). The NMR data were analogous to the product obtained by Method A, above.

4.3. Synthesis of *trans*-$RuCl_2(\eta^2\text{-}C_2H_4)(Me_4BPP)$ (**3a**)

The ligand Me_4BPP (0.0872 g, 0.326 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.100 g, 0.163 mmol) were dissolved in CH_2Cl_2 (15 ml). The solution was heated to reflux while a slow, steady stream of ethylene was passed through the mixture. After 6 h at reflux, the solution had turned orange–brown. The flow of ethylene was stopped and the mixture was allowed to cool to r.t. Next, excess hexanes (40 ml) were added, precipitating out an orange–brown solid. The solid was collected on a glass frit and washed with Et_2O (2 × 10 ml) before drying under reduced pressure. Yield: 0.0980 g (64%). *Anal.* Calc. for $C_{17}H_{21}Cl_2N_5Ru$: C, 43.68; H, 4.54; N, 14.99. Found: C, 42.39; H, 4.21; N, 14.41%. ^{1}H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.72 (t, 1H, $^3J_{HH} = 8.5$ Hz, C^4H of Py), 7.46 (d, 2H, $^3J_{HH} = 8.5$ Hz, $C^{3,5}H$ of Py), 6.33 (s, 2H, $C^{4,4''}H$ of Pz), 3.11 (s, 4H, C_2H_4), 2.84 (s, 6H, CH_3 of Pz), 2.80 (s, 6H, CH_3 of Pz). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 157.2, 152.7 (s, $C^{2,6}$ of Py and $C^{5,5''}$ of Pz), 143.2 (C^4 of Py), 135.7 ($C^{3,3''}$ of Pz), 113.8, 105.6 (s, $C^{4,4''}$ of Pz and $C^{3,5}$ of Py), 68.71 (s, C_2H_4), 15.33, 14.12 (s, 2 × CH_3 of Pz).

4.4. Synthesis of *trans*-$RuCl_2(CO)(Me_4BPP)$ (**3b**)

A methanol (10 ml) suspension of $RuCl_3(Me_4BPP)$ (0.103 g, 0.217 mmol) was saturated with CO by passing a slow stream of the gas through the mixture for 5 min. Excess Et_3N (0.5 ml) was added via syringe and the mixture was allowed to stir under CO. After 30 min, the flow of CO was stopped and the deep, dark brown mixture was reduced to dryness under reduced pressure. The dark brown solid that remained was extracted into CH_2Cl_2 (25 ml) and filtered through Celite. The volatiles were removed from the filtrate under reduced pressure to yield an orange–brown solid, which was washed with Et_2O (2 × 20 ml) before drying under reduced pressure. Yield: 0.0788 g (78%). *Anal.* Calc. for $C_{16}H_{17}Cl_2N_5ORu$: C, 41.12; H, 3.87; N, 14.99. Found: C, 41.07; H, 5.59; N, 12.18%. IR (Nujol): $\nu_{(CO)} = 1938$ (s) cm^{-1}. ^{1}H NMR (499.9 MHz, $CDCl_3$, 22 °C): 8.32 (t, 1H, $^3J_{HH} = 8$ Hz, C^4H of Py), 7.85 (d, 2H, $^3J_{HH} = 8$ Hz, $C^{3,5}H$ of Py), 6.25 (s, 2H, $C^{4,4''}H$ of Pz), 2.93 (s, 6H, CH_3 of Pz), 2.65 (s, 6H, CH_3 of Pz). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 205.1 (s, CO), 157.7, 149.7 (s, $C^{2,6}$ of Py and $C^{5,5''}$ of Pz), 144.4 (C^4 of Py), 142.5 ($C^{3,3''}$ of Pz), 112.5, 107.2 (s, $C^{4,4''}$ of Pz and $C^{3,5}$ of Py), 15.25, 15.11 (s, 2 × CH_3 of Pz).

4.5. Synthesis of *trans*-$RuCl_2(NCMe)(Me_4BPP)$ (**3c**)

The complex $RuCl_3(Me_4BPP)$ (0.100 g, 0.211 mmol) was suspended in MeOH (10 ml). Excess MeCN (1 ml) followed by excess Et_3N (0.5 ml) were added via syringe and the solution immediately turned deep, dark yellow–brown. The solution was stirred at r.t. for 30 min and then the volatiles were removed under reduced pressure. The dark brown residue was extracted into CH_2Cl_2 (15 ml) and filtered through Celite. The solvent was removed from the filtrate and the remaining brown solid was washed with Et_2O (2 × 10 ml) before drying under reduced pressure. Yield: 0.0912 g (90%). *Anal.* Calc. for $C_{17}H_{20}Cl_2N_6Ru$: C, 42.5; H, 4.20; N, 15.00. Found: C, 43.06; H, 6.75; N, 14.05%. ^{1}H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.69 (t, 1H, $^3J_{HH} = 8$ Hz, C^4H of

Py), 7.58 (d, 2H, $^3J_{HH} = 8$ Hz, $C^{3,5}H$ of Py), 6.22 (s, 2H, $C^{4,4''}H$ of Pz), 2.87 (s, 6H, CH_3 of Pz), 2.77 (s, 6H, CH_3 of Pz), 2.73 (s, 3H, CH_3CN). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 155.7, 154.3 (s, $C^{2,6}$ of Py and $C^{5,5''}$ of Pz), 143.6 (C^4 of Py), 134.6 ($C^{3,3''}$ of Pz), 125.8 (s, CH_3CN), 112.2, 105.5 (s, $C^{4,4''}$ of Pz and $C^{3,5}$ of Py), 15.11, 14.02 (s, $2 \times CH_3$ of Pz), 5.191 (s, CH_3CN).

4.6. Synthesis of cis-[$RuCl_2$(=C=CHPh)(Me_4BPP)] (4)

4.6.1. Method A

Complex **3a** (0.100 g, 0.214 mmol) in C_6H_6 (10 ml) was treated with a slight (1.2 molar) excess of phenylacetylene (29 μl, 0.257 mmol), and the mixture was refluxed for 24 h. During this time, the color of the solution gradually turned deep, dark brown. Next, the solution was allowed to cool to r.t. and then the volatiles were removed under reduced pressure. The remaining dark brown solid was washed with Et_2O (2 × 10 ml) and then dried under reduced pressure. Yield: 0.0777 g (67%). *Anal.* Calc. for $C_{23}H_{23}Cl_2N_5Ru$: C, 51.01; H, 4.29; N, 12.94. Found: C, 50.95; H, 4.13; N, 12.33%. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 8.12 (t, 1H, $^3J_{HH} =$ 8 Hz, C^4H of Py), 7.60 (d, 2H, $^3J_{HH} = 8$ Hz, $C^{3,5}H$ of Py), 7.05 (m, 2H, Ph), 6.88 (m, 1H, Ph), 6.74 (m, 2H, Ph), 6.25 (s, 2H, $C^{4,4''}H$ of Pz), 4.62 (s, 1H, Ru = C = CHPh), 2.76 (s, 6H, CH_3 of Pz), 2.73 (s, 6H, CH_3 of Pz). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 356.1 (s, Ru=C= CHPh), 158.7, 150.5 (s, $C^{2,6}$ of Py and $C^{5,5''}$ of Pz), 144.0 (C^4 of Py), 142.3 ($C^{3,3''}$ of Pz), 141.4 (s, Ph), 129.0 (s, Ph), 128.6 (s, Ph), 125.2 (s, Ph), 113.6, 107.2 (s, $C^{4,4''}$ of Pz and $C^{3,5}$ of Py), 111.3 (s, Ru=C=CHPh), 15.43, 14.50 (s, $2 \times CH_3$ of Pz).

4.6.2. Method B

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (0.100 g, 0.163 mmol) and Me_4BPP (0.0872 g, 0.326 mmol) in C_6H_6 (15 ml) was treated with excess phenylacetylene (179 μl, 1.63 mmol) via syringe. After refluxing for 24 h, a deep, dark brown mixture was obtained. The mixture was allowed to cool to r.t. and then the volatiles were stripped off under reduced pressure. The deep dark brown solid that remained was washed with Et_2O (2 × 10 ml) before drying under reduced pressure. Yield: 0.117 g (67%). The ^1H NMR spectrum ($CDCl_3$) of the product obtained by this method was identical to that obtained by Method A, above.

4.7. Synthesis of [$RuCl(PPh_3)$(=C=C=CPh_2)(Me_4BPP)][BF_4] (5)

Complex **2** (0.120 g, 0.171 mmol), $AgBF_4$ (0.0333 g, 0.171 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.0427 g, 0.205 mmol) were combined and dissolved in CH_2Cl_2 (10 ml). After refluxing the mixture for 24 h, a deep dark red solution was obtained, along with a white precipitate. The mixture was allowed to cool to r.t. and then it was filtered through Celite. The volatiles were removed from the dark red filtrate under reduced pressure, and the dark red solid that remained was washed with small portions of Et_2O (2 × 5 ml) before drying under reduced pressure. Yield: 0.123 g (76%). *Anal.* Calc. for $C_{48}H_{42}BClF_4N_5PRu$: C, 61.12; H, 4.50; N, 7.43. Found: C, 60.52; H, 5.25; N, 6.65%. IR (Nujol): $\nu_{(C=C=C)} = 1922$ (s) cm^{-1}. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 8.32 (t, 1H, $^3J_{HH} = 8$ Hz, C^4H of Py), 7.96 (d, 2H, $^3J_{HH} = 8$ Hz, $C^{3,5}H$ of Py), 7.97–7.01 (m, 25H, Ph), 6.17 (s, 2H, $C^{4,4''}H$ of Pz), 2.83 (s, 6H, CH_3 of Pz), 2.11 (s, 6H, CH_3 of Pz). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 313.5 (d, $^2J_{PC} = 20$ Hz, Ru=C=C=CPh_2), 212.2 (s, Ru=C=C= CPh_2), 159.5, 146.5 (s, $C^{2,6}$ of Py and $C^{5,5''}$ of Pz), 157.7 (s, Ru=C=C=CPh_2), 145.6 (C^4 of Py), 144.5 (s, Ph), 144.3 (s, Ph), 143.7 ($C^{3,3''}$ of Pz), 132.6 (d, $^2J_{PC} = 10$ Hz, $C^{2,6}$ of Ph in PPh_3), 131.0 (s, Ph), 129.3 (s, Ph), 128.5 (d, $^3J_{PC} = 9.4$ Hz, $C^{3,5}$ of Ph in PPh_3), 128.3 (s, C^4 of Ph in PPh_3), 127.8 (s, Ph), 126.0 (s, Ph), 113.9, 108.6 (s, $C^{4,4''}$ of Pz and $C^{3,5}$ of Py), 15.77, 15.21 (s, $2 \times CH_3$ of Pz). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): 41.96 (s, PPh_3).

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