Proton-responsive pyridine-based ligands: Synthesis, coordination chemistry and catalysis

de Boer, S.Y.

Citation for published version (APA):
Chapter 2

Pd(II) and Rh(I) Complexes Featuring a Reactive Bidentate PN-Ligand for N-H Bond Activation Processes

Abstract The first examples of reactivity at the backbone of a bidentate PN-ligand L1 relevant to N-H activation are described, leading to novel Pd(II) and Rh(I) amido complexes. Deprotonation of the PN-ligand backbone led to dearomatization of the pyridyl ring structure. The intermediates could be efficiently stabilized with neutral co-ligands or solvent molecules. Successful selective N-H bond cleavage of several amines resulted in facile formation of mononuclear metal-amido species that have been crystallographically characterized. Application of these bidentate complexes in the hydroamination of aminoalkenes is hampered by coordination of the substrate trans to the phosphorus atom of the ligand.

*Part of this work has been published: S. Y. de Boer, Y. Gloaguen, J. N. H. Reek, M. Lutz and J. I. van der Vlugt*, Dalton Trans. 2012, 41, 11276-11283.
2.1 Introduction

Bidentate compounds that contain both phosphorus and nitrogen donors have been extensively investigated as ligand auxiliaries in a variety of important catalytic transformations.\(^1\) Additional interest in such ligands with these hard-soft combinations comes from their potential hemilabile behavior and a plethora of structural and reactivity reports underlines their early popularity and importance.\(^2\) One of the best-known phosphorus-nitrogen-based bidentate ligands is 2-(diphenylphosphino)pyridine (Scheme 1, left), which closely resembles the widely used triphenylphosphine. Although applied as both chelating and bridging ligand, the high rigidity and small bite angle of this ligand limit its applicability for many catalytic reactions.\(^3\) The addition of an extra methylene spacer in the backbone of the ligand increases the flexibility and this 2-(diphenylphosphinomethyl)pyridine (Scheme 1, right) has been intensively investigated over the past 50 years and has proven to be an efficient ligand in numerous oligomerization and polymerization reactions.\(^4,5\)

![Scheme 1. 2-(diphenylphosphino)pyridine and 2-(diphenylphosphinomethyl)pyridine.](image)

Although the tridentate ligands based on lutidine, discussed in Chapter 1, have been studied quite extensively in the last decade for their potentially cooperative character, the related bidentate analogs like 2-(diphenylphosphinomethyl)pyridine have been largely overlooked. Furthermore, only very few reports on alkyl-substituted PN ligands have appeared.\(^6\) A paper published by van der Vlugt et al. shows the first example of a bidentate NP\(^{tBu}\) scaffold that exhibits cooperativity through dearomatization behavior when coordinated to Cu(I). Facile C-H bond activation was shown for phenylacetylene and this dimeric [CuBr(NP\(^{tBu}\))]\(_2\) catalyst has shown to be an active cooperative catalyst for the [2+3] polar cycloaddition of acetylenes and azides, for which the proposed catalytic cycle is shown in Figure 1. Next to the activation of C-H bonds, functionalization of small molecules such as carbon dioxide, dihydrogen, dinitrogen, or ammonia has gained great interest over the past years.\(^7\) These molecules have strong covalent bonds that need to be broken in order to convert them in catalytic processes. Transition metal complexes can react with small molecules through insertion into an X-H bond, via oxidative addition. In this way, catalysis with H\(_2\), C-H, O-H, and N-H bonds (hydrogenation and hydroformylation, hydroarylation, hydroxylation and hydroamination, respectively) becomes accessible, which may lead to new routes for industrially interesting chemicals. Especially the activation of N-H bonds by transition metals (and main group compounds) is of huge interest these days, because it could lead to the development of new catalytic routes to functionalize e.g. alkenes with amines.\(^8\)
Connected to this research area is the potential use of ammonia as an interesting substrate for homogeneous catalysis. Ammonia, the most fundamental amine, is a very versatile building block for fine chemicals, polymers, and pharmaceuticals and therefore of great interest for both academic and industrial research. The activation of N-H bonds of ammonia is, however, very challenging. The use of ammonia is still very limited in homogeneously catalyzed processes and, to the best of our knowledge, none of these systems involve the actual metal-based rupture of the N-H bond. Many metal-mediated processes with ammonia generate a complex where the amine is simply coordinated, and thus a Werner-type complex. Because the nitrogen atom binds via its lone pair and not via a $\sigma$-bond, the N-H bond splitting of ammonia is significantly suppressed and this represents one of the inherent limitations of this interesting and widely available building block. The activation of substituted amines is less difficult, as the N-H bond is more acidic due to the electron-withdrawing substituents. The development of complexes that may engage in efficient N-H activation and functionalization processes is therefore very relevant. One potential pathway for selective and productive N-H bond activation proceeds via a cooperative ligand-metal mechanism, and this may provide a viable strategy to generate metal-amido species in a controlled manner and facilitate intramolecular reactivity. Palladium amido species have recently been studied extensively to understand C-N bond formation via reductive elimination, but facile and general preparative methods to obtain these species are still relatively scarce. Rh-amido species have been reported in combination with unactivated olefins to generate imines, the group of Turculet has shown the activation of N-H bonds by Rh(PSiP) complexes to form amido hydrido compounds and the group of Oro has shown the formation of rhodium amido complexes through N-H activation of ammonia. However, to the best of our knowledge no Pd-amido or Rh-amido species have been prepared to date using a reactive or cooperative ligand approach.

As stated above, N-H bond activation may lead to the development of new catalytic routes where alkenes are functionalized with amines. Intramolecular hydroamination of...
Path a, which occurs via activation of the olefin, involves a nucleophilic attack of the amine onto the coordinated olefin, assisted by the pyrazolato ligand that accepts the amine proton. Subsequent proton transfer from the pyrazolato in A leads to Ir-C bond cleavage and release of the product. Path b proceeds via initial activation of the N-H bond across the Ir-pyrazolato. The next step entails coordination of the olefin to the metal center, which requires additional processes such as Cp* ring slippage in this particular example, as the metal is coordinatively saturated. Although less plausible for this complex, this pathway should certainly not be rejected for other cooperative systems. Nonetheless, the cooperative bifunctional ligand in these complexes is deemed of essential importance in such hydroamination reactions. We therefore decided to explore metal-ligand bifunctional reactivity with late transition metals, with the focus on a bidentate PN-ligand, which can be considered as derived from the tridentate pincer PNP ligands that display cooperative behavior by deprotonation. It was hypothesized that the bidentate nature of the targeted PN system might allow for more structural versatility as well as steric accessibility and enhanced reactivity of the transition metal with incoming exogenous substrates such as amines. This chapter contains our results on cooperative N-H activation by Pd and Rh complexes with a bidentate PN analogue of these
lutidine-derived PNP ligands. Although extensively studied in the last decade,4,5 the potential cooperative character of these PN ligands and their application in specific bond activation processes has hardly been exploited to date, nor have such ligands been applied in hydroaddition reactions.

2.2 Results and Discussion

2.2.1 Synthesis of bidentate PN ligands

Ligand L1, 2-(di-tert-butylphosphino)methyl-6-methyl-pyridine, was prepared following a modified literature procedure starting from 2,6-lutidine. In a one-pot two-step reaction, one of the methyl-groups of 2,6-lutidine is mono-lithiated, followed by phosphorylation with ClP(tBu)2 (Scheme 2, left). Ligand L1 was obtained as a white solid in an overall yield of 70% and the corresponding 31P NMR spectrum showed a singlet at δ 34.9 (CsD6). The unreacted flanking methyl-group acts as both a spectroscopic handle as well as a steric and electronic factor upon coordination to transition metals. Besides this pyridine-based ligand, we attempted to use pyrazine as nitrogen donor, as dearomatization of the pyrazine ring should give notable differences in the electronic structure compared to the parent pyridine system. It was also reasoned that the dearomatization of the pyrazine ring is easier than that of the pyridine ring and this could be an advantage for further reactivity. The synthesis of ligand L2, which should not be different from ligand L1, unfortunately did not lead to the desired product (Scheme 2, left). However, recently the group of Milstein published the synthesis of such pyrazine-derived PNP ligands using a slightly different approach, starting from 2,6-bis(chloromethyl)pyrazine and di-tert-butylphosphine.21

As a comparison to ligand L1 and 2-(diphenylphosphinomethyl)pyridine which lacks the flanking Me-group, the synthesis of ligand L3, with the phosphorus atom bearing two phenyl rings, was attempted (Scheme 2, left). The synthesis, which was carried out in the same manner as L1, did not only yield the desired product L3, but also a species bearing two geminal phosphorus atoms on the same arm (Scheme 2, right, L3'). Although L3’ is a very interesting ligand itself for coordination chemistry, as shown by others22,23 and by preliminary data from our laboratory, this chapter will only feature coordination and reactivity studies with ligand L1.

Scheme 2. Synthesis of ligands L1-3, according to a literature procedure (left) and the undesired byproduct in the synthesis of ligand L3 (right).
2.2.2 Formation of Pd(II) and Rh(I) species with L1

Reaction of bidentate PN ligand L1 with PdCl(Me)(cod) (cod = 1,5-cyclooctadiene) yielded a yellow solid that was fully characterized as Pd(Me)(Cl)(L1), complex 1 (Scheme 3, left). Single crystals suitable for X-ray structure determination were obtained via slow diffusion of hexane into a concentrated solution of dichloromethane, of which the molecular structure is depicted in Figure 3.

Scheme 3: Synthesis of complex 1 and 2 from Pd(Me)(Cl)(cod) and [Rh(CO)2(μ-Cl)]2, respectively.

Figure 3. ORTEP plot (50% probability displacement ellipsoids) of complex 1, Pd(Me)(Cl)(L1). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles and torsion angles (°): Pd1-P1 2.2216(5); Pd1-N1 2.2474(16); Pd1–Cl1 2.3906(5); Pd1–C16 2.0679(18); P1–C7 1.834(2); C6–C7 1.497(3); P1–Pd1–N1 82.80(4); P1–Pd1–C16 170.637(19); P1–Pd1–C16 93.22(6); N1–Pd1–C16 173.19(7); P1–C7–C6–N1 26.3(2); Pd1–P1–C7–C6–38.34(15); Pd1–N1–C6–C7 1.5(2).

The palladium atom displays a slightly distorted square planar geometry, with angles P1-Pd1-N1 and P1-Pd1-C1 of 82.80(4) and 170.637(19)°, respectively. The Pd1-P1 (2.2216(5) Å), Pd1-N1 (2.2474(16) Å) and Pd1-C16 (2.0679(18) Å) bond lengths are all within the expected ranges. The methyl ligand is located cis to the phosphine donor (in agreement with the doublet observed in the 1H NMR spectrum at δ 1.04 (2JPH = 1.6 Hz)) and the pyridine is coordinated to the palladium center, as also confirmed by IR spectroscopy, showing bands at 1572 and 1600 cm\(^{-1}\).

Also coordination of L1 with [Rh(CO)2(μ-Cl)]2 occurs in a straightforward manner, yielding a bright yellow powder that was fully characterized as RhCl(CO)(L1), complex 2 (Scheme 3, right). One of the CO ligands dissociates from the rhodium center to accommodate coordination of ligand L1 in a bidentate fashion. This species displays a doublet at δ 106.0
ppm in the $^{31}$P NMR spectrum with a coupling constant of $^{1}J_{RhP} = 162.9$ Hz, and the IR spectrum contains bands at 1957 cm$^{-1}$ (CO stretch) and 1601 and 1567 cm$^{-1}$ (pyridyl stretch). The molecular ion peak of $m/z$ 417.0498 ($m/z$ calc. 417.0496) was observed by mass spectrometry (FAB). This is consistent with previously reported RhCl(CO)(PN) structures with other ligand constructs.$^{26}$

Next, we set out to prepare $[\text{Rh}(L_1)_2]\text{BF}_4$, as similar complexes with picolyl-based PN ligands have been reported earlier by the groups of Pignolet and Breit.$^{26,27}$ These homoleptic cationic complexes have been used in the catalytic decarbonylation of benzaldehyde and the anti-Markovnikov addition of carboxylic acids to terminal alkynes. However, in both papers, no claims were made about the role of the (potentially) cooperative ligand in their proposed mechanisms. In theory, both PN ligands could be deprotonated, which offers two reactive sites in one complex and this could be an advantage in the activation of substrates. The synthesis of $[\text{Rh}(L_1)_2]\text{BF}_4$ started with the generation of $[\text{Rh}(\text{THF})_2(\text{coe})_2]\text{BF}_4$ in situ from $[\text{Rh}(\mu-\text{Cl})(\text{coe})_2]_2$ and AgBF$_4$ in THF. Addition of two equivalents of L$_1$ to $[\text{Rh}(\text{THF})_2(\text{coe})_2]\text{BF}_4$ in THF resulted in a mixture of two species in a 1:1 ratio after work-up (a third unidentified species – doublet at $\delta$ 80.6 in $^{31}$P NMR spectroscopy – is removed in the work-up procedure (Figure 4)).

Figure 4. $^{31}$P NMR spectrum of the initial attempt to synthesize $[\text{Rh}(L_1)_2]\text{BF}_4$, which gave a mixture of complexes 3 and 4.

Selective phosphorus-decoupling NMR experiments revealed that the doublet at 95.7 ppm corresponds to a highly symmetric species in the $^1$H NMR spectrum, with only one signal for the flanking methyl, the tert-butyl and the methylene protons. The signal at 59.8 ppm shows signs of second-order coupling. Mass spectrometry only showed a signal for cationic $[\text{Rh}(L_1)_2]^+$, but it seems unlikely that this mixture is simply a combination of cis and trans isomers, as this is in disagreement with the complex NMR signals. Slow diffusion of pentane into a CH$_2$Cl$_2$ solution of this mixture resulted in two types of crystalline material, i.e. red and
colorless solids. The latter crystals proved suitable for X-ray structure determination, of which the molecular structure is shown in Figure 5.

Figure 5. ORTEP plot (50% probability displacement ellipsoids) of complex 3, [Rh(L1)2](BF₄)₂. Hydrogen atoms have been omitted for clarity, except for those of the methylene group. Left – front view; right – side view. Selected bond lengths (Å), angles and torsion angles (°): Rh1–Rh2 2.9271(2); Rh1–N2 2.1943(15); Rh2–N1 2.1874(15); Rh1–P1 2.3835(5); Rh2–P2 2.3707(5); Rh1–F4 2.883; Rh2–F7 2.784; Rh1–Rh2–P 88.74(1); Rh2–Rh1–P 88.01(1); Rh1–Rh2–N1 95.08(4); Rh2–Rh1–N2 92.85(4); P1–Rh1–Rh2–P 147.16; N1–Rh2–Rh1–N2 128.55; P1–Rh1–Rh2–N1 -40.07; P2–Rh2–Rh1–N2 -44.22.

To our surprise, an unusual binuclear complex is observed, wherein both PN-ligands act as bridging ligand. Furthermore, the two rhodium atoms can only display slightly distorted square planar geometries when a Rh-Rh bond as well as weak interactions with fluorine atoms of the two BF₄ counterions (one per Rh) are taken into consideration. The Rh-Rh distance of 2.9271(2) Å also supports the existence of a true rhodium-rhodium bond. Complex 3 corresponds to the two signals around 60 ppm in the ³¹P NMR spectrum. ³¹P NMR measurements recorded at different magnetic fields (121, 162, and 202 MHz) showed that the signal indeed has a very large coupling of ¹J_RhP = 635 Hz, with both phosphorus atoms being marginally different. Similar systems have been described with bond lengths and angles within the expected ranges.²⁻²⁸ We attributed the formation of complex 3 to concentration effects, as the dimer should be formed easily at higher concentration. This interesting bimetallic complex might show very fascinating reactivity once both ligands are deprotonated with the metal-metal bond still intact. Therefore, we set out to selectively synthesize this complex as we were not able to separate it from the other species. Unfortunately, regardless of applied reaction conditions or the use of different batches of the Rhprecursor, reproduction of the formation of complex 3 proved unsuccessful and we therefore focused on the characterization of the [Rh(L1)2]BF₄ complex.

When the same reaction between [Rh(µ-Cl)(coe)₂]₂ and AgBF₄ with subsequent addition of two equivalents of L1 was carried out in acetone, with intermediacy of the known cationic solvent-species [Rh(acetone)₂(coe)₂]BF₄, a single species (complex 4) was obtained as an orange red solid, showing a doublet (¹J_RhP = 171.5 Hz) at 95.7 ppm in the ³¹P NMR spectrum.
Mass spectrometry showed a signal corresponding with the initially targeted cationic [Rh(L1)_2]^+ species. X-ray structure determination of red-colored single crystals obtained via slow diffusion of pentane into a concentrated solution of dichloromethane confirmed the presence of the homoleptic cis compound, of which the molecular structure is depicted in Figure 6.

![Figure 6. ORTEP plot (50% probability displacement ellipsoids) of complex 4, [Rh(L1)_2]BF_4. BF_4 anion has been omitted for clarity. Hydrogen atoms have been omitted for clarity, except for those of the methylene group. Left – front view; right – side view. Selected bond lengths (Å) and angles (°): Rh1-P1 2.2635(12); Rh1-P1' 2.2635(12); Rh1-N1 2.1419(35); Rh1-N1' 2.1419(35); N1-Rh1-P1 80.82(11); N1'-Rh1-P1' 80.82(11); N1-Rh1-N1' 89.86(21); P1-Rh1-P1' 114.30(6); N1-Rh1-P1' 158.07(12); P1-Rh1-N1' 158.07(11).](image)

The rhodium atom displays a highly distorted square planar geometry, likely due to steric hindrance of the Me- and 'Bu-groups, but does however show C_2 symmetry. Moreover, all bond lengths and angles are all within the expected ranges for similar complexes.\textsuperscript{27}

2.2.3 Ligand backbone reactivity of complexes 1 and 2

In analogy to reported Pd chemistry with the structurally related 2,6-bis(di-tert-butylphosphino)methylpyridine (PNP) ligand, the addition of a strong base to complex 1 is expected to result in deprotonation of the methylene spacer of the ligand backbone. Upon addition of one equivalent of KOtBu to palladium complex 1, a clean reaction at the ligand methylene CH_2-spacer indeed occurred, generating a homogeneous red solution (Scheme 4). The relative instability of this intermediate compared to starting complex 1 precluded its full characterization. However, in situ measured spectroscopic data (δ(^31P) 66.7 ppm and δ(^1H) 3.12 ppm (d, 3J_{PH} = 8.8 Hz) for –CH spacer) provide support for dearomatization of the ligand backbone, in agreement with reported data for related PNP-based systems,\textsuperscript{29,30} with likely formation of a solvent-stabilized Pd(Me)(L1*)-species 1'THF (Scheme 4). The addition of HCl to this in situ formed species 1'THF resulted in the re protonation of the ligand and coordination of the chloride to the palladium center, regaining complex 1.
Scheme 4. Preparative route from Pd(Me)(Cl)(L1*)-complex 1 to the in situ formed species 1'THF and 1'py and stabilized deprotonated species 5a-b.

The Pd species that was formed upon dearomatization of the ligand backbone could be stabilized by neutral co-ligands such as PMe₃ and PPh₃, which yielded dark-red solutions. The ³¹P NMR spectrum of complex 5a (Figure 7, left, with PMe₃) showed two doublets at δ 68.8 and -23.2 for the PtBu₂ and PMe₃ donors, respectively, both with a ²Jₚ₂ₚ coupling constant of 439 Hz, indicative of mutual trans disposition. The ¹H NMR spectrum showed a doublet (²Jₚₕ = 7.6 Hz) at δ 3.37 for the –CH spacer and a doublet of doublets (³Jₚ₁ₕ = 9.6 Hz; ³Jₚ₂ₕ = 3.6 Hz) at δ 0.56 for the Me ligand at the Pd center (Figure 7, right). The formation of complex 5a as Pd(Me)(L1*)(PMe₃) was also confirmed by FAB-MS spectrometry, showing the molecular ion peak at m/z 448.1522 (m/z calc. 448.1522).

Figure 7. (left) ³¹P NMR spectrum of complex 5a, two doublets at δ 68.8 (PtBu₂) and -23.2 (PMe₃), both with a coupling constant ²Jₚ₂ₚ of 439 Hz, indicative of mutual trans disposition. (right) ¹H NMR spectrum of complex 5a, a doublet of doublets (³Jₚ₁ₕ = 9.6 Hz; ³Jₚ₂ₕ = 3.6 Hz) at δ 0.56 for the Me-ligand at the Pd center.

The analogous complex 5b (with PPh₃) provided similar NMR spectra, indicating that the triphenylphosphine also coordinates in a trans position of the phosphine group. In the ³¹P NMR spectrum, two doublets were observed at 72.9 and 18.3 ppm for the PtBu₂ and PPh₃, respectively, with a coupling constant ²Jₚ₂ₚ of 399 Hz. This coupling constant is significantly smaller than for complex 5a, which indicates that for trimethylphosphine there is a stronger interaction through the P-Pd-P bond than for PPh₃. While all these reactions were carried out in THF, the solvent-stabilized deprotonated species 1'THF was not stable enough to be analyzed after isolation. However, when the deprotonation of complex 1 was carried out in pure pyridine, complex 1'py was stable enough to measure ¹H and ³¹P NMR spectra. A sharp singlet
was observed in the $^{31}$P NMR spectrum at $\delta$ 69.5 ppm and in $^1$H NMR a signal was found for the $-\text{CH}$-spacer in $\alpha$-position. Although more stable than species $1'_{\text{THF}}$, complex $1'_{\text{py}}$ was still not stable enough to measure $^{13}$C NMR spectroscopy or to conduct mass spectrometry.

Rhodium complex 2 shows the same reactivity in backbone dearomatization as complex 1. When a stoichiometric amount of base was added to the rhodium complex, a bright red solution was obtained (Scheme 5). When carried out in THF, no attempts were made to isolate the deprotonated species, in contrast to the reaction done in pyridine. Like Pd species $1'_{\text{py}}$, this solvent-stabilized species $2'_{\text{py}}$ had a sufficient long lifetime to obtain relevant NMR spectroscopic data. The pyridine ligand is not coordinated very strongly to the metal center, as multiple species were observed. The major species, however, is complex $2'_{\text{py}}$, and an upfield shift was observed in the $^{31}$P NMR spectrum. The expected reversible reactivity is shown by the addition of an equimolar amount of HCl to the in situ generated deprotonated species.

![Scheme 5. Preparative route from RhCO(Cl)(L1)-complex 2 to the in situ formed species 2$'_{\text{THF}}$ and 2$'_{\text{py}}$ and stabilized deprotonated species 6a-b.](image)

Stabilization of the deprotonated complex with phosphine donors again gave better insights into the identity of such species. Triphenylphosphine rapidly coordinated to the rhodium center, forming complex 6b. In the $^{31}$P NMR spectrum two doublets of doublets were found at 97.1 and 26.6 ppm for the $^{13}$Bu$_2$ and PPh$_3$, respectively, with coupling constants of $^2J_{PP}$ = 285 Hz and $^1J_{RhP}$ = 128 Hz. Whereas PMe$_3$ coordination to the deprotonated palladium complex was rather straightforward, this proved not to be the case for the rhodium analogue. The result of this reaction showed a mixture of four products, which could unfortunately not be separated, yet could be identified as the following compounds (Figure 7). Both compounds 6a and 6a$'$ give rise to a doublet of doublet in $^{31}$P NMR spectroscopy with large coupling constants, indicative of mutual trans disposition. Free ligand L1 is formed due to the formation of complex 6a$''$, with the PN ligand substituted by the competitive and apparently more strongly coordinating PMe$_3$. Changing the order of addition (i.e. first phosphine, then base) also did not lead to the clean formation of the desired product 6a, as formation of the latter three products was already observed after addition of PMe$_3$ to complex 2. Especially the last two compounds show that the trimethylphosphine binds stronger to the rhodium center than ligand L1. Ligand L1 binds less strongly to the rhodium center, compared to palladium, and although not stable when isolated, both the deprotonated palladium and rhodium compounds show reactivity at the ligand backbone and can be reprotonated upon addition of an acidic substrate.
Figure 7. $^{31}$P NMR spectrum of the reaction of 2'THF and PMe$_3$, which provided 6a and the undesired byproducts 6a', 6a'', and L1.

2.2.4 Reactivity of complex 4

For cationic homoleptic complex 4, we envisioned that the addition of base would lead to the formation of the neutral species 4', with one of the ligand backbones deprotonated (Scheme 6). One equivalent of KO'Bu did not give full conversion, according to $^{31}$P NMR spectroscopy (*vide infra*), but upon addition of a second equivalent of KO'Bu, the mixture turns black instantly. Upon reaction with the first equivalent of base, the phosphorus atoms are not equivalent anymore, as a very complex signal is shown in the $^{31}$P NMR spectrum (Figure 8). However, the $^1$H NMR spectrum clearly displays that both pyridine rings are still aromatic, as the usual downfield shift upon dearomatization is not observed.

Scheme 6. Deprotonation of complex 4 does not lead to the neutral species 4'.

Complex 4 is not completely square planar, and deprotonation likely inflicts a sterically undesirable flattening of one of the ligand fragments. Rather than abstracting a proton, the tert-butoxide might interact with or even coordinate to the metal center to generate a species with inequivalent phosphorus donors.
We reasoned that the formation of an octahedral Rh(III) species might favor the deprotonation of one of the ligand backbones, therefore one equivalent of iodine was added to complex 4 (Scheme 7). The $^{31}$P NMR spectrum of the reaction mixture showed a doublet ($^{1}J_{RhP} = 136$ Hz) at 159.5 ppm, corresponding to complex 7, and a singlet at 71.5 ppm, which belongs to an undesired phosphonium compound. The most likely structure for 7 is a cationic octahedral Rh(III) complex. Deprotonation of complex 7 with one equivalent of base however did not give the desired neutral species 7' (Scheme 7). Given the bulky side-groups of the ligand, it is likely that deprotonation with the concomitant geometric rearrangement of the ligand around the rhodium center is inhibited.

![Scheme 7](image)

**Scheme 7.** Oxidation of Rh(I) (4) to Rh(III) (7), which does not undergo deprotonation upon treatment with KO'Bu.

### 2.2.4 Activation of amine N-H bonds

Deprotonation of ligand L1 was shown to be reversible by addition of hydrochloric acid (*vide supra*). Other acidic substrates, such as amines, are considered to also facilitate this ligand-rearomatization. Addition of one molar equivalent of H$_2$NTf (trifluoromethanesulfonamide) to either the deprotonated complex 1'tHF or the isolated PMe$_3$-derivative 5a led to an immediate color change from red to yellow-brown (Scheme 8). The $^{31}$P NMR spectrum of the resultant brown solid 8a displayed one singlet at δ 75.2, and all expected signals in the $^1$H NMR spectrum. A doublet ($^2J_{PH} = 10.0$ Hz) at δ 3.80 is apparent in the $^1$H NMR spectrum for the reprotonated -CH$_2$-spacer of the ligand backbone and a singlet for the NH moiety at δ 3.15. Two signals indicative of formation of the amido-species were distinctly observed by FAB-MS, at m/z 505.0529 [M–Me] and 372.1089 [M–NHTf]. The IR spectrum displayed two bands at ν 1600 and 1564 cm$^{-1}$, suggestive of rearomatization of the pyridine moiety.
Scheme 8. Addition of trifluoromethanesulfonamide to either complex 1′_{THF} or 5a gives full conversion to Pd-amido species 8a.

Single crystals of complex 8a, suitable for X-ray structure determination, were grown by slow diffusion of pentane into a concentrated CH₂Cl₂ solution (Figure 9, left). The molecular structure reveals a slightly distorted square planar geometry around the palladium atom, with angles P-Pd-N1 and P-Pd-N2 of 82.28(9) and 170.03(10)°, respectively. There are marginal changes for complex 8a compared to complex 1 with respect to the Pd1-P1 (2.2232(10) Å) and Pd1-C16 (2.042(4) Å) bond lengths, but the Pd1-N1 (2.24749(16) Å) bond is significantly shorter. The Pd1-N2 bond length of 2.108(3) Å is typical for a palladium-sulfonamido bond. Substitution of the halide co-ligand has occurred with retention of configuration around the palladium center, as the amide is coordinated trans to the phosphine donor. The aromaticity of the heterocycle is restored (C7) and the C6–C7 bond length of 1.500(6) Å is in the normal range for a C-C single bond. The solid state structure of this complex reveals intermolecular hydrogen bonding of two sulfonamide units to generate a dimeric conformation (Figure 9, right).

*Figure 9.* (left) ORTEP plot (50% probability displacement ellipsoids) of complex 8a, hydrogen atoms have been omitted for clarity, except for those at C7 and N2. Selected bond lengths (Å), angles and torsion angles (°): Pd1-P1 2.2232(10); Pd1-N1 2.191(3); Pd1–N2 2.108(3); Pd1–C16 2.042(4); P1–C7 1.850(4); C6–C7 1.500(6); N2-Si 1.540(4); P1–Pd1–N1 82.28(9); P1–Pd1–N2 170.03(10); N1-Pd1-C16 175.92(15); P1–C7–C6–N1 -18.4(5); Pd1–P1–C7–C6 35.7(3); Pd1–N1–C6–C7 -10.9(4). (right) Dimeric H-bonded structure of complex 7a, with Pd---Pd [1-x, 1-y, 1-z] of 8.4216(6) Å.
In addition to trifluoromethanesulfonamide, several other primary amines were examined as well in combination with both complexes 1 and 2 (Scheme 9). Palladium complexes 8b and 8c (with p-toluenesulfonamide (NHTs) and 2,3,4,5,6-pentafluoroaniline (HNArF₅), respectively) could be prepared in a similar fashion, as indicated by the various analytical data. For both complexes, mass spectrometry showed indicative fragments of the complex, i.e. [M-CH₃]+ and [M-NHR]+ for both complexes 8a and 8b. Also rhodium complexes 9a and 9b were cleanly obtained with characteristic NMR signatures. Mass spectrometry again did not reveal the molecular ion peak, but the significant fragmentation of the activated complexes (both [M-CO]+ and [M-NHR]+).

![Scheme 9. Activation of different amines, forming complexes 8a-d / 9a-d.](image)

Complexes 1 and 2 were also exposed to ammonia gas. A setup was prepared in which the solvent-stabilized deprotonated species 1’THF or 2’THF was generated in situ and 1 atm of ammonia was subsequently bubbled through the solution for 45 minutes. When using rhodium complex 2’THF, an immediate color change was observed upon addition of the ammonia stream, but unfortunately the ³¹P NMR spectrum showed the formation of a mixture of products. The desired product 9d may be found but this could not be conclusively supported. For palladium complex 8d it is clear from both ¹H and ³¹P NMR spectra that, although not pure, the Werner-type coordination complex was obtained rather than the activated species. This suggests pre-coordination of the substrate to the metal center, which could result in efficient N-H bond activation and subsequent proton transfer, as pre-coordination of amines on transition metals often results in increased acidity of N-H bonds. In the ³¹P NMR spectrum a small shift of 0.7 ppm was observed from the in situ generated deprotonated species (δ = 66.7) to the NH₃ coordinated complex (δ = 67.4). An additional experiment was carried out in a J-Young NMR tube wherein species 1’THF was exposed to 4 bars of ammonia pressure. Both the ¹H and ³¹P NMR spectrum indicate that a very small amount of activated species 8d was formed, but the equilibrium lies far to the left-hand side of equation [1]. This suggests that the potential substrate scope for subsequent (catalytic) transformations involving N-H activation using a bifunctional mechanism may be extended to non-activated amines as well.
Next to amine N-H activation we have also probed the activation of acetylenic C-H bonds with cooperative complexes 1 and 2. Applying the same procedure regarding the in situ formation of the deprotonated complex and subsequent addition of substrate led to the formation of complexes 10 and 11 (Scheme 10). The activation of the acetylene is slower than for the amines, as the color change was only observed over the course of several minutes. From the $^{31}$P NMR spectrum of 10 it can be concluded that the acetylide, which is trans to the phosphorus donor, is not only a $\sigma$-donor like the activated amides but also a $\pi$-acceptor, as a shift of 13 ppm upfield was observed for complex 10 compared to complex 1. In the $^1$H NMR spectrum a doublet was present for the reconstituted CH$_2$-arm of the backbone. Also, the IR spectrum displayed two bands at $\nu$ 1592 and 1571 cm$^{-1}$, suggestive of rearomatization of the pyridine moiety, and a band at 2086 cm$^{-1}$ for the C-C triple bond that is coordinated to the metal center. The $^{13}$C NMR spectrum also shows the two signals for the C-C triple bond coordinated to the metal at the expected chemical shifts. These combined spectroscopic and spectrometric data indicate that the acetylene is indeed activated and not side-on coordinated as a $\pi$-base. Although the rhodium analogue 11 was not obtained purely, spectroscopic data ($^{31}$P: $\delta = 93.1$ (d, $^1$J$_{RhP} = 111.2$ Hz), $^1$H: $\delta = 3.63$ (d, $^2$J$_{PH} = 7.8$ Hz, 2H, CH$_2$-backbone)) verify its partial formation via this route.

Scheme 10. Formation of acetylide complexes 10 and 11 from precursors 1 and 2.

### 2.2.5 Coordination studies relevant for hydroamination reactivity

Either initial amine or alkene activation via coordination to the metal center is required for cyclization of an aminoalkene via metal-mediated hydroamination. We have probed both possibilities by means of the addition of an equimolar amount of a model aminoalkene substrate to the pre-activated Pd and Rh complexes 1$^{\text{THF}}$ and 2$^{\text{THF}}$. In the case of the Pd-species 1$^{\text{THF}}$ the red solution slowly turned back to yellow over the course of 15 minutes, indicating activation of the N-H bond of the amine fragment of the aminoalkene (Scheme 11, left). $^1$H NMR spectroscopy clearly showed a clean, yet slightly broadened spectrum for complex 12, reminiscent of the analogous PdNHTf complex 8a. $^{31}$P NMR spectroscopy shows a signal with a chemical shift of $\delta$ 74.6, which is also comparable to complex 8a. A solution of
complex 12 in THF was heated to 75 °C inside a pressure tube to induce cyclization of the aminealkene, but unfortunately no reaction occurred.

Scheme 11. Formation of complexes 12 and 13; (left) activation of the aminealkene on complex 1, (right) coordination of the alkene-end to the palladium center.

Coordination of the alkene moiety to palladium was induced by reaction of complex 1 with AgSbF₆ and subsequent addition of the aminealkene (13, Scheme 11, right). A small downfield shift was observed in the ³¹P NMR spectrum at 83.1 ppm and the ¹H NMR spectrum indicated coordination of the aminealkene to the palladium center. During the ¹H NMR experiment, isomerization of the aminealkene double bond occurred, as evident from the ¹H NMR spectrum (13', Scheme 12). However, no change in the ³¹P NMR spectrum had occurred, implying the double bond was similarly coordinated to the palladium center. For the hydroamination reaction, starting from the isomerized internal alkene is in theory possible, but very difficult to accomplish in reality.

Scheme 12. Isomerization of the double bond of the aminealkene.

2.2.6 Hydroamination of aminealkenes

The catalytic intramolecular hydroamination of several amine-functionalized aminealkenes was investigated in the presence of complexes 1 and 2. All aminealkenes are derivatives of 2,2-diphenyl-4-pentenylamine, including triflic-, tosyl- and urea-functionalized amines (Scheme 13).

Scheme 13. The catalytic hydroamination was investigated for four aminealkenes: 2,2-diphenyl-4-pentylamine and three derivatives.
Catalytic reactions were performed in toluene at different temperatures in the presence of one equivalent of silver tetrafluoroborate (AgBF$_4$) with respect to the metal species. Yields were determined by $^1$H NMR spectroscopy, see Table 1. Products a and b would correlate to the anti-Markovnikov and Markovnikov products, respectively, while iso is formed via double bond isomerization of the terminal alkene into the internal derivative.

**Table 1. The results of the catalytic intramolecular hydroamination reaction for different aminoalkenes catalyzed by complexes 1 and 2.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH$_2$</td>
<td>1</td>
<td>rt</td>
<td>17</td>
<td>SM</td>
</tr>
<tr>
<td>2</td>
<td>NHTf</td>
<td>1</td>
<td>rt</td>
<td>18</td>
<td>SM</td>
</tr>
<tr>
<td>3</td>
<td>NH$_2$</td>
<td>1</td>
<td>50</td>
<td>18</td>
<td>11% iso</td>
</tr>
<tr>
<td>4</td>
<td>NHTf</td>
<td>1</td>
<td>50</td>
<td>16</td>
<td>2% iso</td>
</tr>
<tr>
<td>5</td>
<td>Urea</td>
<td>1</td>
<td>50</td>
<td>19</td>
<td>6% iso</td>
</tr>
<tr>
<td>6</td>
<td>NHTs</td>
<td>1</td>
<td>80</td>
<td>18</td>
<td>100% iso</td>
</tr>
<tr>
<td>7</td>
<td>NH$_2$</td>
<td>1*</td>
<td>50</td>
<td>6</td>
<td>10% iso</td>
</tr>
<tr>
<td>8</td>
<td>Urea</td>
<td>2</td>
<td>50</td>
<td>20</td>
<td>SM</td>
</tr>
</tbody>
</table>

* 1 equiv. of KOtBu (to complex 1) was used instead of AgBF$_4$.

Entries 1 and 2 of Table 1 show that when the hydroamination is performed at room temperature, no reaction takes place for both the primary as well as the triflic-functionalized amine. When the reaction was carried out at 50 °C, partial isomerization of the alkene bond occurred for both the primary amine, the triflic-functionalized amine and the urea-derivative (entries 3 - 5), similar as observed for the stoichiometric reaction with complex 13’. When the catalysis was carried out at 80 °C, the isomerization product is cleanly generated (entry 6). Entry 7 shows that the addition of one equivalent of base rather than AgBF$_4$ does not positively affect the outcome of the catalysis, as only isomerization was observed together with unreacted substrate. Hence, it can be concluded that the C-N bond formation mechanism most likely does not go via N-H bond activation, but rather via alkene coordination and subsequent attack of the amine. Lastly, in entry 8 the hydroamination of the urea-containing substrate was carried out by rhodium complex 2, but unfortunately only starting material was observed. As comparable [PdPNP]BF$_4$ complexes are known to catalyze the hydroamination of aminoalkenes in high yields, it is somewhat surprising that complex 1 does not give similar results. A possible explanation is the fact that when the cationic PNP-pincer complex is formed, the position trans to the nitrogen atom of the pyridine becomes vacant. Upon formation of our cationic complexes from 1 and 2 however, the position trans to the phosphorus atom becomes vacant. Here, a completely different environment and electronic influence is created upon coordination of the alkene prior to the cyclization, leading to isomerization or no activity at all.
Beside the intramolecular hydroamination, also intermolecular hydroamination was attempted by performing experiments with complexes $8a$ and $9a$ in the presence of styrene in a pressure tube (Scheme 14). Unfortunately, only complex decomposition was observed with no formation of any product, which again might be attributed to the amide being coordinated trans to phosphorus vs. nitrogen, or the fact that the alkene has to coordinate rather than the amine (isolated cases of late transition metal amido complexes reacting with C=C bonds are known).\textsuperscript{32,33}

![Scheme 14. Envisioned intermolecular hydroamination between the secondary tosyl amine and styrene.]

\[ 8a: \text{Pd-Me} \quad \text{or} \quad 9a: \text{Rh-CO} \]

### 2.3 Conclusions

In summary, we have shown the improved synthesis of the (electron-rich) di-tert-butylphosphinopyridine framework $L_1$ and its coordination as a reactive bidentate PN-ligand to Pd(CH$_3$)(Cl)(cod), [Rh(CO)$_2$(μ-Cl)]$_2$, and [Rh(acetone)$_2$(coe)$_2$]BF$_4$. Where complex 4 did not show the desired reactivity, deprotonation of complexes 1 and 2 with a strong base provided ligand-activated complexes 1$^{THF}$ and 2$^{THF}$ which could be efficiently stabilized by various additional phosphine ligands or solvent molecules. Using a dearomatization-reprotonation strategy, the selective activation of N-H bonds resulted in the formation of Pd(II) or Rh(I) metal-amido species. The substrate scope of these complexes in N-H bond activation is limited to acidic amines, as ammonia showed only minor activation. However, this does suggest pre-coordination of the substrate to the metal center, resulting in activation of the N-H bond and subsequent proton transfer to the ligand backbone, indicating a metal-ligand bifunctional pathway for this mechanism of N-H bond activation.\textsuperscript{11} Unfortunately, intra- and intermolecular hydroamination reactions with these complexes were unsuccessful, suggesting that coordination of the substrate trans to the phosphorus atom of the ligand is not a productive intermediate to acquire the desired reactivity. Therefore, different ligand systems will be investigated towards the intramolecular hydroamination in Chapters 4 and 5.

### 2.4 Experimental Section

#### General procedures

Solvents were either distilled over suitable drying agents or dried using an MBraun SPS (Solvent Purification System). All experiments were carried out under an inert-gas atmosphere using standard Schlenk techniques. The chemicals used were commercially available and used without further purification, unless described otherwise. The $^1$H, $^1$H($^{31}$P), $^3$P($^1$H) and $^{13}$C($^1$H) NMR spectra were recorded
at room temperature on a Bruker AV400 (at 400, 162, and 100 MHz, respectively) and on a Bruker DRX500 (at 500, 202, and 126 MHz, respectively) and calibrated to the residual proton and carbon signals of the solvent.34 High resolution mass spectra were recorded on a JEOL AccuTOF GC v 4g, JMS-T100GCV mass spectrometer (FD), on a JEOL AccuTOF LC, JMS-T100LP mass spectrometer (CSI) and on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as a matrix. IR spectra were recorded with a Bruker Alpha-p FT-IR spectrometer operated in the ATR mode. Pd(CH₃)(Cl)(1,5-cod) was synthesized according to a literature procedure.35,36

**Syntheses and characterization**

**L₁, 2-((di-tert-butylphosphino)methyl)-6-methylpyridine.** Modification of a literature procedure.³ Freshly distilled 2,6-lutidine (3.0 mL, 25.8 mmol) was dissolved in diethyl ether (35 mL) and then cooled to 0 °C, whereafter n-butyllithium (2.5M solution in hexanes) (10.4 mL, 26.0 mmol) was added dropwise. The yellow-orange solution was stirred for 1 hour at 0 °C and then cooled to −78 °C. Subsequently, di-tert-butylchlorophosphine (5.0 mL, 26.0 mmol) was added and the mixture was stirred for an additional hour at −78 °C. After this, the yellow reaction mixture was allowed to warm up to room temperature and stirred for 18 hours to give an orange suspension. The suspension was quenched with degassed water (40 mL) and extracted with diethyl ether (3 × 30 mL). The ether fractions were combined and dried over Na₂SO₄. Evaporation of the solvent gave a yellow-white oil. The remaining di-tert-butylchlorophosphine was removed via flash chromatography over basic alumina (10:1 hexane/ether), yielding the product as a white solid (4.59 g, 70.2%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.37 (d, Jᵢ = 8 Hz, 1H, pyH), 7.20 (t, Jᵢ = 7.6 Hz, 1H, pyH), 6.68 (d, Jᵢ = 7.2 Hz, 1H, pyH), 3.21 (d, Jᵢ = 2.4 Hz, 2H, CH₃), 2.54 (s, 3H, CH₃), 1.23 (d, Jᵢ = 10.8 Hz, 18H, tBu-H). ³¹P NMR (162 MHz, CDCl₃, ppm): δ 34.9 (s). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 161.7 (d, Jᵢ = 14.4 Hz, pyC), 157.2 (d, pyC), 135.6 (d, pyCH), 120.6 (d, Jᵢ = 9.6 Hz, pyCH), 119.3 (d, pyCH), 32.0 (d, Jᵢ = 25.3 Hz, CH₃), 31.5 (d, Jᵢ = 23.8 Hz, tBu-C), 29.5 (d, Jᵢ = 13.7 Hz, tBu-CH₃), 24.3 (d, CH₃). HRMS (FAB) (C₈H₁₈NP): m/z calcd, 252.1881; found, 252.1884. IR (ATR, cm⁻¹): 1592 (m), 1577 (m).

**Complex 1, Pd(Me)(Cl)(L₁).** Adaptation of a literature procedure.³ L₁ (180.5 mg, 0.72 mmol) and Pd(Me)(Cl)(1,5-cod) (190.4 mg, 0.72 mmol) were dissolved in dichloromethane (5 mL) and the mixture was stirred at room temperature for 18h. Then, the light-yellow solution was concentrated to approximately 0.5 mL and diethyl ether (10 mL) was added under vigorously stirring. The precipitate was collected by cannula-filtration and washed with diethyl ether (3 × 5 mL). The product was obtained as an off-white powder (277.8 mg, 94.8%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.56 (t, Jᵢ = 8 Hz, 1H, pyH), 7.17 (d, Jᵢ = 8 Hz, 1H, pyH), 7.09 (d, Jᵢ = 7.6 Hz, 1H, pyH), 3.51 (d, Jᵢ = 10 Hz, 2H, CH₃), 3.16 (s, 3H, CH₃), 1.33 (d, Jᵢ = 14 Hz, 18H, tBu-H), 1.04 (d, Jᵢ = 1.6 Hz, 3H, Pd-Me). ³¹P NMR (162 MHz, CDCl₃, ppm): δ 72.8 (s). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 162.5 (s, pyC), 158.2 (d, pyC), 137.8 (s, pyCH), 123.9 (s, pyCH), 119.9 (d, Jᵢ = 7.5 Hz, pyCH), 35.6 (d, Jᵢ = 16.6 Hz, tBu-C), 35.2 (d, Jᵢ = 20.2 Hz, CH₃), 29.4 (d, Jᵢ = 4 Hz, tBu-CH₃), 27.5 (s, CH₃), 8.6 (s, Pd-Me). HR-MS (FAB) (C₁₆H₂₆CINPPd): m/z calcd, 407.0761, 372.1079 [M–Cl]; found, 372.1076 [M–Cl]. IR (ATR, cm⁻¹): 1600 (m), 1572 (m).

**Complex 2, RhCl(CO)(L₁).** L₁ (262.9 mg, 1.05 mmol) and [Rh(CO)₂(μ-Cl)]₂ were dissolved in dichloromethane (10 mL) and the mixture was stirred at room temperature for 2h. Then, the yellow solution was concentrated to approximately 1 mL and diethyl ether (15 mL) was added under vigorously stirring. The precipitate was collected by cannula-filtration and dried in vacuo. The product was obtained as a yellow powder (216.4 mg, 99.2%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.64 (t, Jᵢ = 7.7 Hz, 1H), 7.28 (d, Jᵢ = 7.7 Hz, 1H), 7.14 (d, Jᵢ = 7.7 Hz, 1H), 3.69 (d, Jᵢ = 9.5 Hz, 2H), 3.13 (s, 3H), 1.33 (d, Jᵢ = 14.1 Hz, 18H). ³¹P NMR (162
Complex 3, [Rh(L1)BF₄]. A mixture of [Rh(coe)(μ-Cl)]₂ (85.7 mg, 0.119 mmol) and AgBF₄ (46.5 mg, 0.239 mmol) was charged in a Schlenk wrapped with aluminum foil. 5 mL THF was added and the mixture was stirred for 30 minutes. The filtered solution was added to L1 (120.0 mg, 0.479 mmol) and the solution was stirred for 2 hours before all volatiles were removed in vacuo. The product is obtained as an orange red solid. As this reaction resulted in a mixture and the two species could not be separated, this product was not isolated. ¹H NMR (400 MHz, CD₂Cl₂, ppm) δ 7.94 (t, J = 7.8 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 5.5 Hz, 2H), 3.79 (s, 2H), 2.85 (s, 3H), 1.40 (d, J = 14.8 Hz, 18H). ³¹P NMR (162 MHz, CD₂Cl₂, ppm) δ 61.8 (m), 57.9 (m). ¹³C NMR spectroscopy could not be carried out.

Complex 4, [Rh(L1)-BF₄]. A mixture of [Rh(coe)(μ-Cl)]₂ (29.5 mg, 0.041 mmol) and AgBF₄ (16.0 mg, 0.082 mmol) was charged in a schlenk wrapped with aluminum foil. 2 mL acetone was added and the mixture was stirred for 30 minutes. The filtered solution was added to L1 (41.3 mg, 0.164 mmol) and the solution was stirred for 2 hours before all volatiles were removed in vacuo. The product is obtained as an orange red solid. ¹H NMR (500 MHz, CD₂Cl₂, ppm) δ 7.71 (t, J₁H = 7.7 Hz, 1H), 7.01 (d, J₂H = 7.7 Hz, 1H), 4.13 (dd, J₁H₂H = 15.9, 3.8 Hz, 1H), 3.72 - 3.46 (m, 1H), 1.68 (d, J₁H = 12.3 Hz, 9H), 1.00 (d, J₂H = 12.9 Hz, 9H). ³¹P NMR (202 MHz, CD₂Cl₂, ppm) δ 95.7 (d, J = 171.3 Hz). ¹³C NMR (126 MHz, CD₂Cl₂, ppm) δ 160.93 (d, J = 5.1 Hz), 137.98 , 123.47 , 120.20 (t, J = 4.3 Hz), 38.20 - 37.77 (m), 35.41 (d, J = 1.7 Hz), 34.62 (td, J = 9.0, 4.1 Hz), 30.09 (dt, J = 27.5, 2.7 Hz), 24.62. HR-MS (CSI) (C₃₀H₂₅N₂P₂Rh): m/z calc'd, 605.26607; found, 605.26634. IR (ATR, cm⁻¹): 1602 (m), 1564 (m).

Complex 1'THF, Pd(Me)(L1*) (THF). Complex 1 (14.6 mg, 0.036 mmol) and KO'Bu (4.0 mg, 0.036 mmol) were dissolved in 0.6 mL deuterated THF in a NMR tube and the red solution was shaken thoroughly. NMR was measured. ¹H NMR (400 MHz, THF-d₈) δ 6.17 (t, J = 7.5 Hz, 1H), 5.74 (d, J = 8.6 Hz, 1H), 5.06 (d, J = 6.5 Hz, 1H), 2.77 (s, 1H), 2.59 (s, 3H), 1.26 (d, J = 12.4 Hz, 18H), 0.24 (s, 3H). ³¹P NMR (162 MHz, THF-d₈) δ 66.7.

Complex 1'py, Pd(Me)(L1*) (py). To a solution of complex 1 (25.0 mg, 0.061 mmol) in 2 mL pyridine was added KO'Bu (1M solution in THF) (61 μL, 0.061 mmol) at room temperature. The mixture became bright red immediately and was stirred for thirty minutes. All volatiles were removed in vacuo and the product was obtained as a red solid. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.70 (d, J₁H = 5.2 Hz, 2H), 7.79 (t, J₂H = 7.7 Hz, 1H), 7.40 (d, J₃H = 6.5 Hz, 2H), 6.40 (t, J₄H = 7.7 Hz, 1H), 6.05 (d, J₅H = 8.8 Hz, 1H), 5.16 (d, J₆H = 6.6 Hz, 1H), 3.00 (d, J₇H = 2.5 Hz, 1H), 1.36 (d, J₈H = 13.5 Hz, 18H), 1.36 (s, 3H), 0.23 (s, 3H). ³¹P NMR (162 MHz, CD₂Cl₂, ppm): δ 69.5 (s). Due to the rather short lifetime of this complex, mass spectrometry and ¹³C NMR spectroscopy could not be carried out.
Complex 2$^*$py, Rh(CO)(L1$^*$)py. To a solution of complex 2 (15.6 mg, 0.037 mmol) in 5 mL pyridine was added KHMS (0.5M solution in toluene) (0.075 mL, 0.037 mmol) at room temperature and the mixture, which became maroon immediately, was stirred for thirty minutes. Then, all volatiles were evaporated in vacuo. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.66 (s, 2H), 7.75 (s, 1H), 7.35 (s, 2H), 6.31 (t, J = 7.6 Hz, 1H), 5.96 (d, J = 8.7 Hz, 1H), 5.07 (d, J = 6.4 Hz, 1H), 3.14 (d, J = 3.0 Hz, 1H), 1.39 (d, J = 13.6 Hz, 22H). $^3$P NMR (162 MHz, CD$_2$Cl$_2$) δ 94.84 (d, J = 147.8 Hz). Due to the short lifetime of this complex, mass spectrometry and $^{13}$C NMR spectroscopy could not be carried out.

Complex 5a, Pd(Me)(L1$^*$)(PMe$_3$). To a suspension of complex 1 (47.3 mg, 0.116 mmol) in THF was added KOBu (1M solution in THF) (0.12 mL, 0.116 mmol) at room temperature and the mixture, which became red immediately, was stirred for five minutes. Then, trimethylphosphine (1M solution in toluene) (0.12 mL, 0.116 mmol) was added and the color of the solution changed to dark-red. The reaction was left stirring for 2h before the solvent was removed in vacuo. The product was obtained as a red powder. $^1$H NMR (400 MHz, CD$_2$D$_2$, ppm): δ 6.60 (ddd, J$_{H}$ = 8.8 Hz, J$_{H}$ = 6.4 Hz, J$_{HH}$ = 2.4 Hz, 1H, pyH), 6.26 (d, J$_{H}$ = 8.8 Hz, 1H, pyH), 5.56 (d, J$_{H}$ = 6.4 Hz, 1H, pyH), 3.37 (d, J$_{H}$ = 7.6 Hz, 1H, CH), 2.09 (s, 3H, CH$_3$), 1.42 (d, J$_{HH}$ = 13.2 Hz, 18H, tBu-H), 0.77 (d, J$_{HH}$ = 8.0 Hz, 9H, P(CH$_3$)$_3$), 0.56 (dd, J$_{P}$ = 3.6 Hz, J$_{PH}$ = 9.6, 3H, Ph-PH$_3$). $^3$P NMR (162 MHz, CD$_2$D$_2$, ppm): δ 68.8 (d, J$_{PP}$ = 439 Hz, P$_2$), -23.2 (d, J$_{PP}$ = 439 Hz, P$_2$). $^{13}$C NMR (100 MHz, CD$_2$D$_2$, ppm): δ 172.8 (d, J$_{CC}$ = 23.2 Hz, 1C, pyC), 154.2 (s, 1C, pyC), 132.9 (s, 1C, pyCH), 111.9 (d, J$_{PC}$ = 19.3 Hz, 1C, pyCH), 102.4 (s, 1C, pyCH)$_3$, 36.7 (d, J$_{PC}$ = 22.7 Hz, 2C, tBu-C), 32.3 (s, 1C, CH), 29.4 (d, J$_{PC}$ = 6.7 Hz, 2C, tBu-CH$_3$), 27.5 (s, 1C, CH$_3$), 13.6 (d, J$_{PC}$ = 26.8 Hz, 3C, P(CH$_3$)$_3$), -13.3 (d, J$_{PC}$ = 12.1 Hz, 1C, Pd-CH$_3$). HR-MS (FAB) (C$_6$H$_{29}$ClNPPd): m/z calcd, 448.1522; found, 448.1522.

Complex 5b, Pd(Me)(L1$^*$)(PPh$_3$). To a suspension of complex 1 (20.2 mg, 0.049 mmol) in THF (2 mL) was added KOBu (1M solution in THF) (49 μL, 0.049 mmol) at room temperature and the mixture was stirred for 15 minutes before all volatiles were removed in vacuo. The product was obtained as a red powder. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.51 (m, 15H), 6.36 (t, J = 7.6 Hz, 1H), 5.94 (d, J = 8.6 Hz, 1H), 4.97 (d, J = 0.5 Hz, 1H), 3.10 (s, 1H), 1.65 (s, 3H), 1.31 (d, J = 13.0 Hz, 18H), 0.33 (s, 3H). $^3$P NMR (162 MHz, CD$_2$Cl$_2$) δ 72.9 (d, J = 399 Hz), 18.3 (d, J = 399 Hz). Due to the short lifetime of this complex, mass spectrometry and $^{13}$C NMR spectroscopy could not be carried out.

Complex 6b, Rh(CO)(L1$^*$)(PPh$_3$). To a suspension of complex 2 (21.1 mg, 0.051 mmol) in THF (2 mL) was added KOBu (1M solution in THF) (51 μL, 0.051 mmol) at room temperature and the obtained red solution was stirred for 5 minutes. Then, triphenylphosphine (12.8 mg, 0.049 mmol) was added and the mixture was stirred for 15 minutes before all volatiles were removed in vacuo. The product was obtained as a red powder. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.81 – 7.30 (m, 15H), 6.25 (s, 1H), 5.85 (d, J = 8.7 Hz, 1H), 4.85 (m, 1H), 3.17 (s, 2H), 1.70 (s, 3H), 1.32 (d, J$_{PH}$ = 13.6 Hz, 18H). $^3$P NMR (162 MHz, CD$_2$Cl$_2$) δ 97.1 (dd, J$_{PP}$ = 285.3, 128.4 Hz), 26.6 (dd, J$_{PP}$ = 285.3, 128.5 Hz). Due to the short lifetime of this complex, mass spectrometry and $^{13}$C NMR spectroscopy could not be carried out.
Complex 7, [Rh(L1)2L]BF₄. Complex 4 (17.6 mg, 0.025 mmol) and iodine (6.5 mg, 0.025 mmol) were dissolved in deuterated dichloromethane (0.5 mL) in an NMR tube. The color of the mixture turned to black immediately. ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.73 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 3.42 (d, J = 12.3 Hz, 2H), 3.10 (s, 3H), 1.59 (d, J = 16.7 Hz, 18H). ³¹P NMR (162 MHz, CDCl₃, ppm) δ 159.5 (d, J = 136.2 Hz).

Complex 8a, Pd(Me)(NHTf)(L1). To a suspension of complex 1 (63.8 mg, 0.16 mmol) in THF (15 mL) was added KO·Bu (1M solution in THF) (0.16 mL, 0.16 mmol) at room temperature and the mixture, which became dark red immediately, was stirred for five minutes. Then, trifluoromethanesulfonamide (23.3 mg, 0.16 mmol) was added and the color of the mixture changed to yellowish brown. The reaction was left stirring for 2h before the solvent was removed in vacuo. After addition of toluene (10 mL), the solution was filtered and evaporated. The product was obtained as a sand-brown powder (30.0 mg, 36.8%). ¹H NMR (400 MHz, (CD₃)₂CO, ppm): δ 7.75 (t, J = 7.6 Hz, 1H, pyH), 7.44 (d, J = 7.6 Hz, 1H, pyH), 7.23 (d, J = 7.6 Hz, 1H, pyH), 3.80 (d, J = 9.2 Hz, 2H, CH₂), 2.99 (s, 3H, CH₃), 2.23 (s, 1H, NH), 1.34 (d, J = 13.6 Hz, 18H, tBu-H). ¹³C NMR (100 MHz, (CD₃)₂CO, ppm): δ 161.2 (s, 1C, pyC), 159.1 (s, 1C, pyC), 138.1 (s, 1C, pyC), 123.4 (s, 1C, pyC), 122.3 (q, J = 290.6 Hz, 1C, CF₃), 120.5 (d, J = 9.6 Hz, 1C, pyCH). HR-MS (FAB) (C₁₀H₁₂O₂P): m/z calc'd, 520.0753; found, 505.0524 [M–NHTf], 372.1072 [M–Cl]; IR (ATR, cm⁻¹): 1600 (m), 1564 (m).

Complex 8b, Pd(Me)(NHTs)(L1). This product is synthesized in a similar fashion as complex 3, using complex 1 (69.4 mg, 0.17 mmol), KO·Bu (1M solution in THF) (0.17 mL, 0.17 mmol) and tosyl amine (29.2 mg, 0.17 mmol), and was obtained as a sand-brown powder (78.3 mg, 84.8%). ¹H NMR (400 MHz, (CD₃)₂CO, ppm): δ 7.72 (t, J = 7.6 Hz, 1H, pyH), 7.62 (d, J = 8 Hz, 2H, TsH), 7.41 (d, J = 9.2 Hz, 1H, pyH), 7.17 (d, J = 7.2 Hz, 1H, pyH), 7.10 (d, J = 8 Hz, 2H, TsH), 3.69 (d, J = 9.6 Hz, 2H, CH₂), 3.11 (s, 3H, CH₃), 2.31 (s, 3H, TsCH₃), 2.23 (s, 1H, NH), 1.21 (d, J = 13.2 Hz, 18H, tBu-H). ¹³C NMR (162 MHz, (CD₃)₂CO, ppm): δ 73.5 (s). HR-MS (FAB) (C₁₂H₂₄F₂O₂PPdS): m/z calc'd, 542.1348, 527.1113 [M–Me], 372.1072 [M–NHTs]; found, 527.1121 [M–Me], 372.1075 [M–NHTs]. IR (ATR, cm⁻¹): 1601 (m), 1576 (m).

Complex 8c, Pd(Me)(NHArF₅)(L1). To a suspension of complex 1 (44.4 mg, 0.109 mmol) in THF was added KO·Bu (1M solution in THF) (0.11 mL, 0.109 mmol) at room temperature and the mixture, which became red immediately, was stirred for five minutes. Then, pentafluoroaniline (H₂NF₅) (20 mg, 0.109 mmol) and the reaction was left stirring for 0.5h before the solvent was removed in vacuo. The product was obtained as an orange powder. ¹H NMR (400 MHz, C₆D₆, ppm): δ 6.74 (t, J = 7.6 Hz, 1H, pyH), 6.32 (d, J = 7.6 Hz, 1H, pyH), 6.28 (d, J = 7.6 Hz, 1H, pyH), 3.04 (br s, 1H, NH), 2.84 (s, 3H, CH₃), 2.77 (d, J = 9.6 Hz, 2H, CH₂), 0.97 (d, J = 3.2 Hz, 3H, Pd-CH₃), 0.89 (d, J = 13.2 Hz, 18H, tBu-H). ¹³C NMR (100 MHz, C₆D₆, ppm): δ 161.8 (s, 1C, pyC), 158.9 (s, 1C, pyC), 140.4 (s, 2C, aniline-CF), 139.6 (s, 2C, aniline-CF), 138.0 (s, 1C, aniline-CF), 137.2 (s, 1C, aniline-C), 136.9 (s, 1C, pyCH), 123.2 (s, 1C, pyCH), 119.5 (d, J = 7.4 Hz, 1C, pyCH), 34.2 (d, J = 18.4 Hz, 1C, CH₃), 33.9 (d, J = 15.7 Hz, 2C, tBu-C), 28.7 (d, J = 4.4 Hz, 6C, tBu-CH₃), 24.9 (s, 1C, CH₃), -9.1 (s, 1C, Pd-CH₃). ¹⁹F NMR (282 MHz, C₆D₆, ppm): δ -166.8 (m), -169.7 (m), -190.2 (m). HR-MS (FAB)
Complex 8d, Pd(Me)(NH$_3$)(L$_1$)$^+$ – Pd(Me)(NH$_2$)(L$_1$). In a J-Young NMR tube complex 1 (14.6 mg, 0.039 mmol) and KO' Bu (4.01 mg, 0.039 mmol) were dissolved in 0.7 mL THF-d$_8$ and the tube was shaken thoroughly until a red solution was obtained. The tube was pressurized with 4 bar of ammonia and the mixture was measured over time and at different temperatures. NH$_3$: $^1$H NMR (500 MHz, THF-d$_8$, ppm) $\delta$ 6.29 (ddd, $J$ = 8.6, 6.5, 2.1 Hz, 1H), 5.95 (d, $J$ = 8.6 Hz, 1H), 5.21 (d, $J$ = 6.4 Hz, 1H), 2.91 (d, $J$ = 2.1 Hz, 1H), 2.02 (s, 3H), 1.32 (d, $J$ = 13.1 Hz, 18H), 0.43 (d, $J$ = 3.3 Hz, 3H), 0.18 (d, $J$ = 1.1 Hz, 3H). $^3$P NMR (202 MHz, THF-d$_8$, ppm): $\delta$ 66.7 (s). NH$_2$: $^1$H NMR (500 MHz, THF-d$_8$, ppm) $\delta$ 8.45 (d, $J$ = 7.7 Hz, 1H), 7.26 (t, $J$ = 7.6 Hz, 1H), 6.88 (d, $J$ = 7.4 Hz, 1H), 3.55 (d, $J$ = 9.5 Hz, 2H), 2.43 (s, 3H), 1.30 (d, $J$ = 13.1 Hz, 18H), 0.88 (s, 3H), -0.63 (s, 2H). $^3$P NMR (202 MHz, THF-d$_8$, ppm) $\delta$ 70.1.

Complex 9a, Rh(CO)(L$_1$)NHTf. To a solution of complex 2 (21.7 mg, 0.052 mmol) in 5 mL THF was added KHMDI (0.5M solution in toluene) (0.1 mL, 0.052 mmol) at room temperature and the mixture, which instantaneously became maroon-colored, was stirred for five minutes. Then, trifluoromethanesulfonamide (7.8 mg, 0.052 mmol) was added and the color of the solution became light orange. The reaction was left stirring for 2h before the all volatiles were evaporated in vacuo. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 7.69 (t, $J$ = 7.7 Hz, 1H), 7.31 (d, $J$ = 7.7 Hz, 1H), 7.18 (d, $J$ = 7.7 Hz, 1H), 3.69 (d, $J$ = 9.4 Hz, 2H), 2.96 (s, 3H), 2.16 (s, 1H), 1.32 (d, $J$ = 14.1 Hz, 18H). $^3$P NMR (162 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 105.9 (d, $J$$_{HP}$ = 150.7 Hz). HR-MS (FD+) (C$_{24}$H$_{30}$F$_3$N$_3$O$_3$PRhS): m/z calcld, 530.04871; found, 520.05380 [M–CO], 382.08070 [M–NHTf]; IR (ATR, cm$^{-1}$): 1970 (s), 1602 (m), 1567 (m).

Complex 9b, Rh(CO)(L$_1$)NHTs. To a solution of complex 2 (29.2 mg, 0.07 mmol) in 5 mL THF was added KHMDI (0.5M solution in toluene) (0.14 mL, 0.07 mmol) at room temperature and the mixture, which turned to a maroon color instantaneously, was stirred for five minutes. p-Toluenesulfonamide (12.0 mg, 0.07 mmol) was added and the color of the solution became brown. The reaction was left stirring for one hour before all volatiles were evaporated in vacuo. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 7.82 (d, $J$ = 7.8 Hz, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.65 (t, $J$ = 7.7 Hz, 1H), 7.38 (d, $J$ = 8.0 Hz, 1H), 7.27 (d, $J$ = 7.4 Hz, 1H), 7.23 − 7.12 (m, 2H), 4.86 (s, 1H), 3.59 (d, $J$ = 9.0 Hz, 2H), 3.00 (s, 3H), 2.38 (s, 3H), 1.23 (d, $J$ = 13.8 Hz, 18H). $^3$P NMR (162 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 104.3 (d, $J$$_{HP}$ = 142.6 Hz). HR-MS (FD+) (C$_{24}$H$_{30}$N$_3$O$_3$PRhS): m/z calcld, 552.10828, 524.11336 [M–CO], 382.08070 [M–NHTs]; found, 524.11645 [M–CO], 382.09092 [M–NHTs]. IR (ATR, cm$^{-1}$): 1963 (s), 1601 (m), 1568 (m).

Complex 10, Pd(Me)(CCPh)(L$_1$). To a suspension of complex 1 (12.7 mg, 0.031 mmol) in THF was added KO' Bu (1M solution in THF) (31 $\mu$L, 0.031 mmol) at room temperature and the mixture, which became red immediately, was stirred for five minutes. Then, phenylacetylene (3.4 $\mu$L, 0.031 mmol) and the reaction was left stirring for 0.5h before the solvent was removed in vacuo. The product was obtained as an orange powder. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.61 (t, $J$ = 7.7 Hz, 1H), 7.41 − 7.04 (m, 7H), 3.50 (d, $J$$_{HP}$ = 8.0 Hz, 2H), 3.27 (s, 3H), 1.32 (d, $J$ = 13.0 Hz, 18H), 0.96 (d, $J$ = 6.5 Hz, 3H). $^3$P NMR (162 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 60.3 (s). $^3$C NMR (126 MHz, CD$_2$Cl$_2$, ppm) $\delta$ 162.1 (s, pyC), 158.6 (s, pyC), 137.9 (s, pyC), 131.4 (s, PhCH), 128.2 (s, PhCH), 127.5 (s, PhCH), 124.1 (s, PhC), 123.7 (pyCH), 120.2 (d, $J$ = 7.6 Hz,
pyCH), 85.8 (s, Pd-C=CH), 79.40 (s, C=C-Ph), 35.48 (d, J = 16.9 Hz, tBu-C), 35.11 (d, J = 20.8 Hz, CH2), 29.16 (d, J = 4.0 Hz, tBu-CH3), 27.06 (s, CH3), -9.47 (s, Pd-Me). HR-MS (FD+) (C24H34NPPd): m/z calcd, 473.1473; found, 473.1565. IR (ATR, cm⁻¹): 2086 (m), 1592 (m), 1571 (m).

**Complex 11, Pd(Me)(CCPh)(L1).** To a solution of complex 2 (10.5 mg, 0.025 mmol) in THF was added KHMDS (0.5M solution in toluene) (50 µL, 0.025 mmol) at room temperature and the mixture, which became red immediately, was stirred for five minutes. Then, phenylacetylene (2.8 µL, 0.025 mmol) and the color of the solution changed slowly to brown. The reaction was left stirring for 0.5h before the solvent was removed in vacuo. The product was obtained as an brown solid.

**Complex 12, Pd(Me)(L1)NRTf.** To a solution of complex 1 (15.0 mg, 0.037 mmol) in 2 mL THF was added KOtBu (1M solution in THF) (3.7 µL, 0.037 mmol) at room temperature and the mixture, which became red immediately, was stirred for five minutes. The aminoalkene (13.6 mg, 0.037 mmol) was added and over a period of 15 minutes, the color of the solution turned back to yellow. The reaction was left stirring for 30 more minutes and then all volatiles were evaporated in vacuo. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (t, Jₕ = 7.5 Hz, 1H), 7.42 - 6.95 (m, 12H), 5.73 - 5.42 (m, 1H), 4.92 (m, 2H), 3.82 (s, 3H), 3.50 (d, JₚH = 10.3 Hz, 2H), 3.07 (s, 3H), 2.95 (s, 3H), 1.30 (d, JₚH = 14.1 Hz, 18H), 0.90 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ 74.6. IR (ATR, cm⁻¹): 1601 (m), 1574 (m).

**Complex 13, [Pd(Me)(L1)alkene]SbF₆.** A suspension of complex 1 (19.0 mg, 0.047 mmol) and AgSbF₆ (16.0 mg, 0.047 mmol) in 2 mL THF was stirred for 15 minutes in the dark before the aminoalkene (17.4 mg, 0.047 mmol) was added. The suspension was stirred for another hour and filtered. The solution was evaporated and a light yellow solid was obtained.

**Complex 13', [Pd(Me)(L1)alkene]SbF₆.** ¹H NMR (400 MHz, CDCl₃) δ 7.79 (t, Jₕ = 7.7 Hz, 1H), 7.45 - 7.20 (m, 12H), 6.14 (d, Jₕ = 15.7, 1H), 5.32 (m, 1H), 4.83 (s, 1H), 4.10 (d, Jₕ = 5.5 Hz, 2H), 3.67 (d, Jₕ = 11 Hz, 2H), 2.66 (s, 3H), 1.83 (dd, J = 6.4, 1.7 Hz, 3H), 1.38 (d, Jₕ = 15.1 Hz, 18H), 0.75 (s, 3H). ³¹P NMR (162 MHz, CDCl₃, ppm): δ 83.1 (s). ¹³C NMR (126 MHz, CDCl₃) δ 159.35 (s), 158.02 (s), 143.43 (s), 133.93 (s), 128.59 (s), 128.20 (s), 127.07 (s), 124.38 (s), 121.32 (d, J_C = 8.4 Hz), 119.7 (q, J_C = 321.7 Hz), 53.16 (s), 51.53 (s), 36.27 (d, J_C = 20.7 Hz), 35.01 (d, J_C = 24.1 Hz), 28.95 (d, J_C = 3.4 Hz), 25.39 (s), 18.04 (s), -6.86 (d, J_C = 2.2 Hz). HR-MS (FD+) (C₃₈H₇₃F₃N₅O₂PdS): m/z calcd, 741.2095; found, 741.33186.

**Hydroamination experiments**

Typically, either complex 1 or 2 (0.012 mmol) and AgBF₄ (0.012 mmol) were dissolved in THF (2 mL) and stirred for 10 minutes. The aminoalkene (0.12 mmol) was added to the mixture and the reaction was
stirred at room temperature unless stated otherwise. Reaction times varied from 16 to 20 hours. The product composition was determined by NMR analysis.

X-ray crystallography

X-ray intensities were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K. Intensity data were integrated with the Saint software. Absorption correction and scaling was performed with SADABS or TWINABS. The structures were solved with Direct Methods using the program SHELXS-97 and refined with SHELXL-97 against F² of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions. Geometry calculations and checking for higher symmetry was performed with the PLATON program.

Details for complex 1. C₆H₅ClNPPd, Fw = 408.22, yellow block, 0.26 x 0.18 x 0.08 mm³, monoclinic, P2₁/n (no. 14), a = 10.0545(3), b = 15.8268(5), c = 11.3903(4) Å, β = 91.6010(10)°, V = 1811.84(10) Å³, Z = 4, Dc = 1.497 g/cm³, μ = 1.26 mm⁻¹. 49119 Reflections were measured up to (sin θ/λ)max = 0.65 Å⁻¹. 4161 Reflections were unique (Rint = 0.022), of which 3706 were observed [I > 2σ(I)]. 189 Parameters were refined with no restraints. Minor disorder between chlorine and methyl has been ignored. R1/wR2 [I > 2σ(I)]: 0.0206 / 0.0475. R1/wR2 [all refl.]: 0.0263 / 0.0508. S = 1.108. Residual electron density between -0.35 and 0.48 e/Å³. CCDC 861127.

Details for complex 2. C₆H₅F₂N₂O₂PPdS, Fw = 520.86, brown plate, 0.50 x 0.40 x 0.15 mm³, triclinic, P1 (no. 2), a = 9.8419(3), b = 10.8652(3), c = 11.6779(4) Å, α = 109.9870(15), β = 99.6665(15), γ = 101.8868(15)°, V = 1109.16(6) Å³, Z = 2, Dc = 1.560 g/cm³, μ = 1.04 mm⁻¹. The crystal was cracked into two fragments related by a rotation of 7.1° about an arbitrary axis. This was taken into account during the integration, which resulted in a file in HKLF5 format. 36399 Reflections were measured up to (sin θ/λ)max = 0.65 Å⁻¹. 5033 Reflections were unique (Rint = 0.050), of which 4207 were observed [I > 2σ(I)]. 257 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0432 / 0.1061. R1/wR2 [all refl.]: 0.0579 / 0.1148. S = 1.067. Residual electron density between -1.03 and 1.74 e/Å³. CCDC 861128.

2.5 References

Chapter 2


[38] Sheldrick, G. M. *SADABS and TWINABS: Area-Detector Absorption Correction*, Universität Göttingen, Germany, 1999.

