Fundamental reactivity of the Metal-Carbon bond in cyclometalated PNC-complexes

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2 | Facile Synthesis and Versatile Reactivity of an Unusual Cyclo-
metalated Rh\(^{1}\) Pincer Complex

2.1 Introduction

Cyclometalated complexes\(^{1}\) are proposed to be intermediates in C-H functionalization reactions of aromatic substrates, mediated by directing group ligation to a range of transition metals.\(^{2-5}\) Reactivity studies have indicated that the M-C bond in cyclometalated metal-aryl complexes can interact with a variety of reagents. Pyridine can be used as directing group to induce selective ortho-metallation of phenyl groups. The use of phenylpyridine, and close analogues thereof, as substrate has been explored extensively in catalytic C-H functionalization reactions with late row transition metals, amongst which Rh\(^{11}\) catalysts.\(^{6-9}\) Isolated high oxidation state Rh\(^{11}\) complexes featuring a cyclometalated phenylpyridine ligand or substrate scaffold are well-documented.\(^{10-13}\) In contrast, besides the ‘classic’ orthometalated ECE pincer complexes,\(^{14}\) well-characterized examples of low oxidation state Rh\(^{1}\) cyclometalated complexes are rare (Figure 2.1).\(^{15-17}\) As a consequence, the potential reactivity of the metalacyclic Rh\(^{1}\)-C bond and the scope for follow-up chemistry is unexplored.

![Figure 2.1: Overview of known cyclometalated Rh\(^{1}\) complexes.](image)

Agostic metal-(C-H) interactions can stabilize coordinatively unsaturated, low-valent and electron-deficient metals by donating some of the electron density of the C-H bond to the metal forming a three-center two-electron (3c-2e) bond.\(^{18,19}\) Additionally, sufficient π-back donation of d-orbitals of low valent transition metals into the σ*-orbitals of agostic C-H bonds embedded in a chelating ligand scaffold should enable facile C-H activation. Agostic interactions can stabilize 16-electron species\(^{20}\) and are hemilabile in nature, which could be beneficial for catalysis with crowded metal-centers.\(^{21}\) As such,
chelating ligands that easily switch between binding modes with either weak (agostic) or strong (cyclometalated) metal-ligand interactions by simple protonation and deprotonation are highly interesting.

The reactivity of cyclometalated metal-carbon bonds with acidic substrates has been discussed for a number of metals (Rh\textsuperscript{III}, Ir\textsuperscript{III}, Pt\textsuperscript{II}, Au\textsuperscript{III}, Pd\textsuperscript{II}, Ru\textsuperscript{II}, Ni\textsuperscript{II}, Lu\textsuperscript{III})\textsuperscript{32} and reversible cyclometalation has been postulated as a possible ligand-mediated mechanism in catalysis, primarily based on theoretical calculations.\textsuperscript{37-40} However, we are unaware of any strategies to exploit both hemilabile agostic interactions and reversible cyclometalation as part of a reactive ligand concept in coordination chemistry (see Scheme 2.1).\textsuperscript{21}

![Scheme 2.1: General concept for novel PN(C) ligand design and potential bond activation reactivity available through reversible cyclometalation.](image)

Obviously, the concept requires ligand architectures that permit the agostic C-H bond to dissociate from the (low-valent) transition metal when needed. This scenario contrasts with reported examples wherein the agostic C-H bond interaction is enforced by geometric constraints imposed by other ligand donors, such as the phenyl-based P(CH)P (P(CH)P = 2,6-bis(phosphinomethyl)benzene) pincer system reported by Milstein, wherein a Rh\textsuperscript{I}(C\textsubscript{Ph}-H) bond was detected as an intermediate toward oxidative addition of the C-H bond.\textsuperscript{41-44} Examples of structurally characterized complexes with an agostic C\textsubscript{aromatic}-H bond bound to Rh\textsuperscript{I} wherein the arene is not supported by flanking donors but is itself a flanking group have not been described to date, to our best knowledge.\textsuperscript{1}

In this chapter we describe our initial investigations on the use of agostic interactions and reversible M-C\textsubscript{Ar} cyclometalation in the design of new flexidentate ligands. We chose to work on a Rh\textsuperscript{I} platform, because of the availability of vacant sites on the metal and expected facile oxidation to Rh\textsuperscript{III} upon reaction with a substrate. To assess whether such a ligand concept could be established for Rh\textsuperscript{I} complexes, the fundamental reactivity of the PN(C)-Rh\textsuperscript{I} complex is systematically explored to gain understanding of the metal-carbon fragment. The main question that is addressed is the potential for and mechanism of C-H activation of the PN(C)-ligand at Rh\textsuperscript{I}. The reversibility of the cyclometalation is demonstrated by the reactivity of the resulting Rh-C bond with acids.

\textsuperscript{1}Examples do exist for Rh\textsuperscript{III} and Ru\textsuperscript{II}.\textsuperscript{45,46}
and carbon-based electrophiles. Moreover, the novel structure of the PN(C)-ligand allows us to uncover whether a Rh\textsuperscript{i} complex with an M-(C-H) interaction can also be isolated for less conformationally restrictive geometries.

2.2 Results and Discussion

2.2.1 Bidentate versus tridentate coordination of PN(C) ligand to a Rh\textsuperscript{i} species

Addition of ligand \textsuperscript{1}H to 0.5 molar equiv of [Rh(\mu-Cl)(CO)\textsubscript{2}]\textsubscript{2} yielded a yellow solid, which displays a doublet in the \textsuperscript{31}P NMR spectrum at $\delta = 104$ ppm ($J_{\text{Rh-P}} = 160$ Hz) Scheme 2.2. X-ray crystal structure determination of single crystals, grown from THF-pentane, confirmed the square planar geometry expected for this complex \textsuperscript{2}, formulated as RhCl(CO)(\kappa^2-P,N-1\textsuperscript{H}), as depicted in Figure 2.2. The most striking feature of the molecular structure is the flanking phenyl ring that strongly points out of the Rh-coordination plane (Rh1-N1-C5-C15 19.32(18)$^\circ$), in order to accommodate the Cl-ligand, which also results in a somewhat acute P1-Rh1-Cl1 angle of 162.983(15)$^\circ$.

![Scheme 2.2: Synthesis of Rh\textsuperscript{i} complexes 2 and 3 that display facile reversible metalation.](image)

Figure 2.2: ORTEP (ellipsoids set at 50 % probability) for complex 2 (front and side view). Selected bond lengths [Å] and angles [$^\circ$]: Rh1-P1 2.2243(4); Rh1-N1 2.1546(12); Rh1-Cl1 2.4128(4); Rh1-C21 1.8039(16); P1-Rh1-N1 81.95(3); P1-Rh1-Cl1 162.983(15); P1-Rh1-C21 94.07(5); N1-Rh1-Cl1 93.75(3); torsion angle N1-C5-C15-C16 38.6(2).
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Figure 2.3: ORTEP (ellipsoids set at 50% probability) for complex 3 (front and side view). Selected bond lengths [Å] and angles [°]: Rh1-P1 2.3054(3); Rh1-N1 2.0751(11); Rh1-C1 2.0427(14); Rh1-C21 1.8144(16); P1-Rh1-N1 82.87(3); P1-Rh1-C1 162.47(4); P1-Rh1-C21 99.92(4); N1-Rh1-C1 80.26(5); torsion angle C1-C6-C7-N1 -0.79(17).

Notably, reaction of $^{1H}$ with Rh(acac)(CO)$_2$ (acac = acetylacetonate) results in a the red complex 3 with very different spectroscopic features compared to 2. $^{31}$P NMR spectroscopy proved particularly insightful to probe the chemistry occurring at the Rh-center for the various reactions described herein (Figure 2.4). The $^{31}$P NMR spectrum shows a doublet at $\delta$ 76 ppm with a significantly smaller coupling constant ($J_{\text{Rh-P}} = 101$ Hz) than observed for 2, which indicates the presence of a strong $\sigma$-donor trans to the phosphine. Furthermore, the $^{13}$C spectrum contains a doublet of doublets at $\delta$ 177 ppm ($J_{\text{Rh-C}} = 82$ Hz, $J_{\text{C-P}} = 37$ Hz). Formation of free Hacac was confirmed by $^1$H NMR spectroscopy. These observations suggest efficient and selective C-H activation of the phenyl side-arm of $^{1H}$. The resulting ($\kappa^3$-P,N,C)-coordination mode of the ligand in this unusual Rh$^1$ cyclometalated complex was unambiguously confirmed by X-ray structure determination (Figure 2.3). The cyclometalated ligand structure bears considerable strain, with $\angle$P1-Rh1-C1 at 162.47(4)° and $\angle$N1-Rh1-C1 at 80.26(5)°. The Rh-N and Rh-C bond lengths are similar as found in Rh$^I$(pyridylyphenyl) and Rh$^I$(CO)(PCP). 47-50
2.2.2 Influence of the base on the mechanism of cyclometalation

The mechanism of acetate-assisted C-H activation has been studied by DFT calculations. Especially for PdII catalysts it is well-understood that the mechanism for electrophilic activation proceeds through a six-membered transition state wherein the non-coordinated acetate oxygen of the κ1-O ligated acetate deprotonates the C-H bond. In the relevant transition state, the C-H bond forms an agostic complex rather than a Wheland/arenium intermediate. The same mechanism is operational with RhIII and Ir. Based on this precedent, we speculate that a similar mechanism is plausible for RhI with acetate as external base and with internal bases (e.g. acac).

For this specific case, where the ligand may be expected to be chemically noninocent in analogy to reported Rh-chemistry with a structurally related PNP ligand (PNP = 2,6-di(phosphinomethyl)lutidine), we propose that the use of a strong base results in a different mechanism for C-H activation. Addition of KOTBu to 2 at -78 °C is proposed to initially result in deprotonation of the methylene unit of the ligand backbone, generating 2' (Scheme 2.3). Besides a distinct darkening of the solution upon dearamatization of the pyridine fragment, deuteration experiments are indicative for methylene reactivity. The addition of a DCl solution in toluene right after the addition of KOTBu at -78 °C results in selective deuteration at the -CH2(P) position (Figure 2.5). However, this dearamatized species rapidly converts to 3 by proton transfer from the ortho-phenyl position to the CH backbone, even at -78 °C, preventing unambiguous spectroscopic identification of this transient species. This type of mechanism is also proposed for Csp3-H activation of the backbone of a PNN ligand at RuII, but in this case the dearamatized species was stable enough to be detected at -35°C.

PMe3 was added as co-ligand to stabilize the putative species 2', which gave complex 2'-PMe3 (Scheme 2.3). Although follow-up C-H activation to give 3 was impeded...
Scheme 2.3: Deprotonation of the reactive side-arm present in 2 concomitant with pyridine dearomatization and subsequent intramolecular C-H activation of the phenyl arm to generate 3, in the absence and presence of PMe$_3$ as stabilizing co-ligand.

Figure 2.5: NMR spectra after the reprotonation with DCl of dearomatized species 2'. Lower: $^1$H NMR spectrum. Upper: $^2$H NMR showing selective deuterium incorporation at the CH$_2$(P)-arm (signal at 3.8 ppm).

In order to understand the observed reaction sequence of initial deprotonation at the -CH$_2$(P) arm followed by C-H activation of the phenyl ring and intramolecular proton transfer, we resorted to DFT calculations. The direct proton transfer from hydride species 2" has a relatively high lying transition state TS$_{2''}$ → 3 of 29.5 kcal mol$^{-1}$
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Therefore, the mechanism most likely involves proton-shuttling via tBuOH, generated by protonation of KtBu, which gives a very low barrier of only approximately 1 kcal mol\(^{-1}\) (TS\(_{2''-tBuOH} \rightarrow 3\)).

Figure 2.6: DFT (BP86, def2-TZVP, disp3) calculated free energy profile (\(\Delta G_{298K}\) in kcal mol\(^{-1}\)) of two possible mechanisms for proton transfer from the ortho-phenyl position to the dearomatized backbone. Methyl groups instead of tert-butyl groups on the phosphine are used in these calculations.

2.2.3 Reactivity of the cyclometalated Rh\(^{1}\) complex with acid: Formation of a Rh\(^{1}\)-complex with a Rh-(C\(_{Ph}\)-H) interaction

Upon addition of ethereal HBF\(_{4}\) to a red solution of species 3 in diethyl ether (Scheme 2.4), instantaneous precipitation of a yellow solid was observed. Redissolution of the yellow solid in CD\(_2\)Cl\(_2\) yielded a doublet at \(\delta\) 121 ppm (\(\Delta\delta\) 45.1 ppm vs. 3) in the \(^{31}\)P spectrum, with a coupling constant \(^1J_Rh-P\) of 202 Hz (\(\Delta J\) 101 Hz vs. 3, see Figure 2.4). These data indicate the coordination of a weak \(\sigma\)-donor or presence of a ‘vacant site’ at Rh\(^{1}\) trans to phosphorus. Yellow single crystals suitable for single crystal X-ray structure determination were obtained from CH\(_2\)Cl\(_2\)-pentane and the resulting
structure of complex 4 (Figure 2.7) shows a distinct Rh($\eta^2$-C-H) interaction, with a Rh1-C11 bond length of 2.3750(12) Å. The H11 proton was located in the difference Fourier map and refined freely. The Rh1-H11 bond length of 2.192(19) Å is significantly shorter than the sum of the contact radii (3.45 Å) and falls in the range observed for agostic interactions.\textsuperscript{18,19} The C-H bond is located outside of the aromatic plane by 15° (dihedral angle C9-C10-C11-H11). This distortion was also observed for [(PCHP)Rh(CO)](BF$_4$)$_2$,\textsuperscript{41,42} for which the Rh-(C-H) interaction was identified as agostic by DFT calculations. Furthermore, the X-ray structure does not indicate any distortion in the aromaticity of the phenyl ring, excluding an arenium (Wheland-type) structure in which the positive charge of the metal is transferred to the phenyl-group.

In solution, agostic interactions may result in an upfield shift up to about 4 ppm in the $^1$H NMR spectrum for the respective proton. Another characteristic property of an agostic interaction is a decreased value for $^1$J$_{CH}$ due to the decreased electron density in the C-H bond. In case of 4, the phenyl group has symmetric signals for the phenyl-group in $^1$H NMR spectroscopy indicating fast rotation around the C$_{Ph}$-C$_{Py}$ bond. Cooling the solution down to -90°C did not slow the rotation down to a point where the agostic interaction is static.\textsuperscript{62} The signal for the two ortho-CH carbons does show an upfield shift to 117 ppm in the $^{13}$C NMR spectrum compared to complex 2, but the $^1$J$_{CH}$ of the ortho-C-H bonds is 152 Hz, only approximately 10 Hz less than the other aromatic C-H bonds. Values between 50 and 100 Hz are usually found for agostic interactions.\textsuperscript{18,19} Hence, the resulting interaction, if any, between Rh and the phenyl ortho-C-H protons is deemed to be much weaker in solution than in the solid state.

DFT calculations clearly confirm an interaction between the C25-H35 bond of the phenyl group with rhodium (for labelling see Figure 2.9). This interaction was analysed at both the BP86/def2-TZVP and the B3LYP/def2-TZVP level, with and without dispersion corrections in both cases. The relevant bond orders and bond distances for all methods used are listed in Table 2.1 and Table 2.2 in the experimental section. The agostic interaction is stronger in the BP86 calculations than in the B3LYP calculations. The use of dispersion corrections leads to a somewhat stronger Rh-C bond and a somewhat weaker Rh-H bond in the agostic interaction, and an overall slightly weaker interaction.
Figure 2.8: Aromatic region of $^1$H NMR (500 MHz, CD$_2$Cl$_2$) spectra of complex 4 in a variable temperature experiment ranging from 25 °C to -90 °C). Spectra are stacked under an angle of 5°. The signal at 7.78 ppm belongs to the two ortho protons that interact with the Rh center.

The bonding situation is perhaps best described as a combination of a pure agostic interaction and a Wheland-type interaction, dominated by the agostic contribution but shifting slightly in the direction of Wheland-type interaction when using dispersion corrections. This effect is observed both for the BP86 and the B3LYP functional. As the bond lengths found in the X-ray structure are best represented by the B3LYP-disp3 calculations, we compare the values obtained with this method with the ones found in literature.

The B3LYP-disp3 calculations for complex 4 reveal a Wiberg bond order (BO) of 0.241 between Rh and C and 0.098 between Rh and H. The bond order for the C-H bond is significantly lower than for the other C-H bonds (0.797 vs. 0.954), indicating weakening of this bond. These results are comparable with the bond order found in [(PCHP)Rh(CO)](BF$_4$), although the interaction in 4 is slightly weaker than in this PCP complex. Furthermore, the three-center bond order between Rh-(C-H) is 0.041, indicating that the agostic interaction in 4 is rather weak (a three-center BO of 0.10 was found for an agostic Pd complex).
2.2.4 Methylation of the cyclometalated Rh\textsuperscript{I} complex: Involvement of a Rh\textsuperscript{III} intermediate

Reactivity of a Rh-phenyl fragment with methyl iodide to induce selective methylation of the aryl ring has been reported for a (PCP)Rh\textsuperscript{I}(CO) complex, but this reaction proved to be very sluggish, taking two weeks to complete, or it required exogenous coordination of CO. In contrast, species \(\text{3}\) reacts very rapidly (< 5 minutes) with MeI at r.t. to form a single well-defined species [Scheme 2.5]. Complex \(\text{5}\) resembles compound \(\text{2}\) in its composition and NMR features. In line with this, addition of base to \(\text{5}\) results in smooth regeneration of a rhodacyclic species based on \(\text{31P}\) NMR spectroscopy, with an almost identical chemical shift (\(\delta \) 74 ppm) and coupling constant \(J_{\text{Rh-P}}\) of 100 Hz as observed for cyclometalated complex \(\text{3}\). \(\text{1H}\) NMR spectroscopy and FD-MS support the formulation of complex \(\text{5}\) as Rh(CO)(I)(κ\textsuperscript{2}-PN-1\textsuperscript{Me})\, with \(1\text{Me}\) being the ortho-tolyl variant of ligand \(1\). The pathway for formation of this complex is proposed to involve metal-centered oxidative addition of methyl iodide to give Rh\textsuperscript{III}(CO)(I)(Me)(I) \(\text{A}\) as intermediate, which subsequently undergoes C-C reductive elimination [Scheme 2.5]. This pathway was supported by variable temperature NMR spectroscopic investigations. The suggested Rh\textsuperscript{III} species could be detected as the major species at -20 °C, with a doublet at 52 ppm \(J_{\text{Rh-P}}\) of 66 Hz in the \(\text{31P}\) NMR spectrum and the methyl ligand appearing as a doublet of doublets at 0.73 ppm \(J_{\text{Rh-P}}\) of 5.0 Hz, \(J_{\text{Rh-H}}\) of 2.4 Hz in the \(\text{1H}\) NMR spectrum.

To establish a more stable Rh\textsuperscript{III} derivative bearing ligand \(1\) as cyclometalated entity for comparison, complex \(\text{3}\) was reacted with I\(_2\), resulting in a clean and facile formation of a deep-red species that exhibited an upfield-shifted \(\text{31P}\) NMR signal at \(\delta\) 45 ppm \((\Delta\delta 31\text{ ppm compared to }\text{3})\) and a coupling constant \(J_{\text{Rh-P}}\) of 69 Hz. IR spectroscopy showed
a distinctly shifted CO-band at $\nu_{\text{CO}} 2049$ cm$^{-1}$. These observations strongly support the presence of a Rh$^{\text{III}}$ center. X-ray diffraction confirmed the formulation as neutral Rh$^{\text{III}}$(CO)(I)$_2$(tBu). The molecular structure of complex 6 displays a distorted octahedral Rh$^{\text{III}}$ center, with the two iodido ligands in the axial positions, which suggests a similar S$_{\text{N}}$2-type mechanism as for e.g. Mel addition to electron-rich metal-centers. The I1-Rh1-I2 angle is rather acute at 161.345(12)$^\circ$ as a result of steric interference with the bulky tBu-groups of the phosphine arm. The Rh1-P1 bond length is significantly elongated compared to 3 ($\Delta d = 0.18$ Å). Heating this species to reflux in toluene did not result in reductive elimination, according to $^{31}$P NMR spectroscopic analysis. Notably, Rh$^{\text{III}}$ complex 6 does not react with HBF$_4$, which suggests that the Rh-C can not directly be protonated by the acid and that initial protonation of the metal is required before Rh-C bond cleavage. Furthermore, preliminary results suggest that dearomatization of complex 6 by deprotonation of the CH$_2$P arm with a strong base, such as e.g. KOtBu, is possible. However, the product seems to be unstable and unreactive to protic reagents and therefore, this type of reactivity was not further investigated.

Figure 2.10: ORTEP (ellipsoids set at 50% probability) for complex 6 (front and side view). Selected bond lengths [Å] and angles [$^\circ$]: Rh1-P1 2.4853(9); Rh1-N1 2.054(3); Rh1-C1 2.054(3); Rh1-C21 1.875(4); Rh1-I2 2.7115(3); P1-Rh1-N1 81.20(8); P1-Rh1-C1 160.95(10); P1-Rh1-C21 99.18(10); N1-Rh1-C1 80.26(5); I1-Rh1-I2 161.345(12).
To test whether the observed methylation of the phenyl group with MeI requires the tridentate ligand coordination or is intrinsic reactivity displayed by Rh(I)(phenylpyridine) complexes, a control experiment was performed with [{Rh(μ-Cl)(CO)\(_2\)}\(_2\)] and phenylpyridine (2 equiv.) in THF in the presence of NaOAc or NEt\(_3\). Addition of MeI to the \textit{in situ} formed complex under similar conditions as for complex 3 did not result in well-defined \textit{ortho}-methylation. Besides, no reaction was observed upon mixing phenylpyridine with Rh(acac)(CO)\(_2\) and phenylpyridine indicating that already cyclometalation requires the bidentate coordination of the P^N moiety. Furthermore, it is known that addition of Mel to a non-cyclometalated [{RhCl(CO)\(_2\)}\(_2\)]/phenylpyridine mixture leads to the formation of acyl species \textit{via} insertion of the methyl group into the Rh-CO bond.

Considering the ease of C-C bond formation from intermediate A and complex 6, we wondered if C-C reductive elimination could also be established with more challenging coupling partners, such as C\(_{\text{Ar}}\)-CF\(_3\) coupling. The effective installation of a CF\(_3\) group on an aryl ring gained much attention in recent years because fluoroorganic compounds find numerous applications in pharmaceuticals, agrochemicals and polymers due to their unique properties, such as enhanced lipophilicity and membrane permeability, elevated electronegativity and oxidation resistance. Despite their relevance, most fluoroorganic molecules are not naturally occurring and have to be synthesized. Many procedures nowadays rely on Cu, Ag and Pd catalyzed reactions, but these processes are considered difficult and are far from optimal yet. One of the reasons for this is the formation of strong M-CF\(_3\) bonds that are reluctant to reductive undergo elimination.

The only catalytic trifluoromethylation reaction mediated by Rh is reported for \(\alpha\)-\(\beta\)-unsaturated ketones. Catalytic aromatic trifluoromethylation is, to the best of our knowledge, not reported for Rh. Examples of isolated Ar-Rh-CF\(_3\) complexes are rare and such species are normally synthesized by oxidative addition of a PC(CF\(_3\))P ligand to Rh\(_I\). Actually, Rh-CF\(_3\) complexes in general are uncommon and are mostly only reported for Rh\(_I\).

[5-(trifluoromethyl)dibenzothiophenium]OTf, Umemoto reagent, is a common source of a CF\(_3^+\) fragment for electrophilic perfluoroalkylations. Being an electrophile, it resembles the reactivity of Mel and should react in a similar fashion with complex 3. Moreover, Sanford \textit{et al.} already showed that this reagent can be used for the selective 2e\(^-\) oxidation of Pd and Ni complexes. In our case, too, [5-(trifluoromethyl)dibenzothiophenium](OTf) readily reacts with complex 3 in MeCN to produce a doublet of quartets in \(^{31}\)P NMR (δ 65 ppm, \(^1\)J\(_{\text{Rh-P}}\) = 63 Hz, \(^3\)J\(_{\text{P-F}}\) = 8 Hz) and a doublet of doublets in \(^{19}\)F NMR (δ -5.6 ppm, \(^2\)J\(_{\text{Rh-F}}\) = 19 Hz, \(^3\)J\(_{\text{P-F}}\) = 8 Hz) (Scheme 2.6). The chemical shift and multiplicity in \(^{19}\)F NMR are also consistent for a Rh\(_{\text{III}}\)-CF\(_3\) complex, as well as the \(\nu\)\(\text{CO}\) (2095 cm\(^{-1}\)) observed by IR spectroscopy. This species is unstable in solution and converts cleanly to another species within 3 days in MeCN, interfering with attempts to obtain single crystalline material. The new complex shows similar signals in \(^{31}\)P NMR (δ 55 ppm, \(^1\)J\(_{\text{Rh-P}}\) = 69 Hz, \(^3\)J\(_{\text{P-F}}\) = 20 Hz) and \(^{19}\)F NMR (δ -7.1 ppm, \(^2\)J\(_{\text{Rh-F}}\) = 11 Hz, \(^3\)J\(_{\text{P-F}}\) = 19 Hz), but with an increased \(J_{\text{P-F}}\) coupling constant. Furthermore, a lower frequency for the CO ligand is
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found ($\nu_{CO} = 2077 \text{ cm}^{-1}$). These features indicate that the product still contains a Rh$^{III}$ center and that only the geometry around the metal is changed. When the reaction is carried out in the less polar and non-coordinating solvent CH$_2$Cl$_2$ the product at 55 ppm is immediately formed and could be crystallized by layering the solution with pentane. The crystal structure of complex 7 [Figure 2.11] shows that indeed a Rh$^{III}$ complex is formed with a CF$_3$ group bound to Rh. The complex has an octahedral geometry with the triflate anion coordinating and furthermore, the CF$_3$ group occupies the fourth equatorial position next to the CNP ligand. This proves that the CO relocates to the axial position trans to OTf and explains the difference in $\nu_{CO}$ and $J_{Rh-P}$ values found for the two Rh$^{III}$ complexes.

Scheme 2.6: Synthesis of Rh$^{III}$ complex 7 by reaction of complex 3 with [5-(trifluoromethyl)dibenzothiophenium]OTf, presumably via intermediate B.

Figure 2.11: ORTEP (ellipsoids set at 50% probability) for complex 7. Selected bond lengths [Å] and angles [°]: Rh1-P1 2.472(2); Rh1-C22 2.043(4); Rh1-C1 2.077(6); Rh1-N1 2.102(4); Rh1-C21 1.832(5); P1-Rh1-N1 80.9(1); N1-Rh1-C1 80.0(2); P1-Rh1-C1 160.3(1); P1-Rh1-C21 97.4(2); C1-Rh1-C22 98.0(2).

Unfortunately, complex 7 is stable and does not undergo reductive elimination to form a C-CF$_3$ bond, even at elevated temperatures. When [5-(trifluoromethyl)dibenzothiophenium][BF$_4$] is reacted with 3 in CH$_2$Cl$_2$, to prevent the formation of stable octahedral complexes, decomposition is observed. The only promising results were obtained in toluene, as, next to the same doublet of quartes at $\delta$ 55 ppm, a doublet at $\delta$ 105 ppm ($J_{Rh-P}$ 157 Hz) is observed in $^{31}$P NMR. Both the chemical shift and the $J_{Rh-P}$
coupling constant suggest formation of a Rh\textsuperscript{I} complex similar to complex 2. However, this putative species could not be isolated in pure form and no unambiguous analytical data could be obtained to support the C-CF\textsubscript{3} coupling.

### 2.3 Conclusion

A new strategy to utilize both hemilabile agostic interactions and reversible cyclometalation as part of a reactive ligand concept in coordination chemistry is reported in this Chapter. The results discussed show that ligand framework 1\textsuperscript{H} can act as a reactive flexidentate ligand, switching between bi- and tridentate coordination in complexes 2 and 3.

The cyclometalation of ligand 1\textsuperscript{H} to Rh\textsuperscript{I} is smooth and can proceed with weak bases such as acac\textsuperscript{-} or KOAc. When a stronger base (KOTBu) is used, the C-H activation follows a different mechanism through initial deprotonation of the -CH\textsubscript{2}P arm resulting in dearomatization.

The cyclometalated species reacts rapidly with strong acids and the addition of HCl shows that the cyclometalation is completely reversible. Moreover, the Rh-C\textsubscript{Ph} bond is selectively cleaved by HB\textsubscript{F}\textsubscript{4}, resulting in formation of cationic [Rh\textsuperscript{I}(1\textsuperscript{H})(CO)]\textsuperscript{+} species 4 that shows a Rh-(C-H) interaction in the solid state as proven by X-ray analysis. Various NMR experiments and DFT calculations show that the M-(C-H) interaction is weak and can not be clearly assigned as agostic.

Complex 3 also reacts very smoothly with carbon-based electrophiles. Very rapid methylation of the phenyl ring was observed by reaction of 3 with Mel to selectively give species 5. This reaction proceeds via oxidative addition to generate a Rh\textsuperscript{II}(Me)(I) intermediate. Similar oxidation with CF\textsubscript{3}\textsuperscript{+} reagents resulted in stable Rh\textsuperscript{III} complex 7 that does not undergo facile C-CF\textsubscript{3} reductive elimination.

In this Chapter, the flexidentate properties of ligand 1\textsuperscript{H} and the reactivity of the M-C bond in Rh\textsuperscript{I} complex 3 were established with stoichiometric reactions. Whether Rh\textsuperscript{I} systems bearing the reactive ligand 1\textsuperscript{H} are competent species in metal-ligand bifunctional catalysis is discussed in Chapter 3.

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Bas de Bruin is thanked for all the DFT calculations that were performed in this Chapter. Martin Lutz is thanked for the crystallographic measurements for complexes 2, 3 and 4.

### 2.4 Experimental section

**General Methods.** All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and Et\textsubscript{2}O were distilled from sodium benzophenone ketyl. CH\textsubscript{2}Cl\textsubscript{2} was distilled from CaH\textsubscript{2}, toluene from sodium under nitrogen. NMR spectra (\textsuperscript{1}H, \textsuperscript{1}H\{\textsuperscript{31}P\}, \textsuperscript{31}P, \textsuperscript{31}P\{\textsuperscript{1}H\}, \textsuperscript{31}P\textsuperscript{-}\textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\})
Synthesis of ligand 1\(^{1}\): This is a modified procedure. A solution of 2-phenyl-6-methyl-pyridine (0.26 g, 1.54 mmol) in THF (10 mL) was cooled to -78 °C, and 1 equiv. of tBuLi (1.6 M in pentane, 0.96 mL, 1.54 mmol) was added. After the solution was stirred at -78 °C for 2 h, ClP(tBu)\(_{2}\) (0.29 mL, 1.54 mmol) was added dropwise. The solution was stirred at -78 °C for another 2 h, after which it was slowly warmed to RT overnight. The reaction mixture was hydrolyzed with degassed water (10 mL) and the organic phase was separated. The water layer was washed with pentane two times and the organic phases were combined and dried over MgSO\(_{4}\). The product was washed with pentane, yielding the desired complex as yellow-white powder (0.47 g, 97%). Single crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of pentane into a CH\(_{2}\)Cl\(_{2}\)-solution of 2. 1H NMR (300 MHz, acetone-d\(_{6}\), ppm): \(\delta\) 8.15-8.07 (m, 2H, Ph), 7.98 (ddd, \(J = 7.8, 7.8, 0.9\) Hz, 1H, Py), 7.65 (dd, \(J = 7.8, 1.1\) Hz, 1H, Py), 7.58 (d, \(J = 7.9\) Hz, 1H, Py), 7.44-7.39 (m, 3H, Ph), 4.03 (d, \(J_{\text{CP}} = 9.3\) Hz, 2H, CH\(_{2}\)P), 1.41 (d, \(J_{\text{CP}} = 13.7\) Hz, 18H, (CH\(_{3}\))\(_{3}\)CP). 31P NMR (121 MHz, DMSO-d\(_{6}\), ppm): \(\delta\) 36.88. 13C NMR (75 MHz, acetone-d\(_{6}\), ppm): \(\delta\) 162.99 (d, \(J_{\text{CP}} = 14.6\) Hz, Py-C), 156.36 (d, \(J_{\text{CP}} = 5.3\) Hz, Py-C), 140.37 (s, Ph-C), 137.67 (s, Py-CH), 129.52 (Ph-CH), 129.38 (s, 2C, Ph-CH), 127.45 (s, 2C, Ph-CH), 123.18 (d, \(J_{\text{CP}} = 8.1\) Hz, Py-CH), 117.51 (s, Py-CH), 32.67 (d, \(J_{\text{CP}} = 16.8\) Hz, CH\(_{2}\)P), 32.34 (d, \(J_{\text{CP}} = 14.9\) (CH\(_{3}\))CP), 30.10 (d, \(J = 13.8\) Hz, (CH\(_{3}\))CP). HR-MS (FAB) calcd for [M+H]\(^{+}\) C\(_{20}\)H\(_{29}\)NP m/z 314.2038; found, 314.2035.

Synthesis of Rh(\(\mu\)-Cl)(CO)(\(\kappa^{2}-\text{P.N.1}\)) (2). To a solution of 1\(^{1}\) (0.020 g, 0.064 mmol) in CH\(_{2}\)Cl\(_{2}\) (3 mL) was added a solution of [Rh(\(\mu\)-Cl)(CO)]\(_{2}\) (0.012 g, 0.032 mmol) in CH\(_{2}\)Cl\(_{2}\) (2 mL) and the reaction mixture was stirred overnight. After evaporation of the solvent, the product was washed with pentane, yielding the desired complex as yellow powder (0.022 g, 72%). Single crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of pentane into a CH\(_{2}\)Cl\(_{2}\)-solution of 2. 1H NMR (300 MHz, acetone-d\(_{6}\), ppm): \(\delta\) 8.15-8.07 (m, 2H, Ph), 7.98 (ddd, \(J = 7.8, 7.8, 0.9\) Hz, 1H, Py), 7.65 (dd, \(J = 7.8, 1.1\) Hz, 1H, Py), 7.58 (d, \(J = 7.9\) Hz, 1H, Py), 7.44-7.39 (m, 3H, Ph), 4.03 (d, \(J_{\text{CP}} = 9.3\) Hz, 2H, CH\(_{2}\)P), 1.41 (d, \(J_{\text{CP}} = 13.7\) Hz, 18H, (CH\(_{3}\))\(_{3}\)CP). 31P NMR (121 MHz, acetone-d\(_{6}\), ppm): \(\delta\) 104.23 (d, \(J_{\text{CP}} = 160.1\) Hz). 13C NMR (75 MHz, acetone-d\(_{6}\), ppm): \(\delta\) 192.31 (dd, \(J_{\text{RhC}} = 72.5\) Hz, \(J_{\text{CP}} = 14.0\) Hz, CO), 163.27 (d, \(J_{\text{CP}} = 1.3\) Hz, Py-C), 162.98 (dd, \(J_{\text{CP}} = 4.5\) Hz, \(J_{\text{RhC}} = 1.6\) Hz, Py-C), 141.77 (s, Ph-C), 139.75 (s, Py-CH), 130.24 (s, 2C, Ph-CH), 129.95 (s, Ph-CH), 128.48 (s, 2C, Ph-CH), 125.16 (s, Py-CH), 122.30 (d, \(J_{\text{CP}} = 9.1\) Hz, Py-CH), 36.06 (dd, \(J_{\text{RhC}} = 20.2\) Hz, \(J_{\text{CP}} = 2.5\) Hz, CH\(_{2}\)P), 35.61 (d, \(J_{\text{CP}} = 21.0\) Hz, (CH\(_{3}\))CP) 29.49 (d, \(J_{\text{CP}} = 4.5\) Hz, (CH\(_{3}\))CP). IR (ATR, cm\(^{-1}\)): \(\nu_{\text{CO}} = 1924\). UV-vis (CH\(_{2}\)Cl\(_{2}\), nm): \(\lambda_{287} (\varepsilon = 8.2 \times 10^{3}\) L·mol\(^{-1}\)·cm\(^{-1}\)) 406 (\(\varepsilon = 1.1 \times 10^{3}\) L·mol\(^{-1}\)·cm\(^{-1}\)). HR-MS (FAB) calcd for [M-CO]\(^{+}\) C\(_{20}\)H\(_{28}\)N\(_{3}\)ClPRh m/z 451.0703; found, 451.0698. El. Anal. calcd. for C\(_{21}\)H\(_{28}\)N\(_{3}\)Cl: C, 48.88; H, 5.55; N, 2.64. Found: C, 48.86; H, 5.46; N, 2.63.

Synthesis of Rh(\(\kappa^{3}-\text{P.N.C.1}\))(CO) (3). To a solution of ligand 1\(^{1}\) (0.020 g, 0.064 mmol) in CH\(_{2}\)Cl\(_{2}\) (5 mL) was added Rh(acac)(CO)\(_{2}\) (0.016 g, 0.064 mmol) and the reaction mixture was stirred overnight. After evaporation of the solvent under reduced pressure, the product was washed with pentane, yielding the desired complex as a red
crystalline solid (0.025 g, 0.057 mmol, 89%). Single crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of pentane into a CH₂Cl₂-solution of 3. Alternative synthesis: to a solution of complex 2 (4.7 mg, 0.010 mmol) in THF (2 ml) was added a 1M solution of KOTBu in THF (11 μL, 0.011 mmol). The color immediately changed from yellow to red and the ³¹P NMR spectrum indicated full conversion to complex 3. ¹H NMR (300 MHz, acetone-d₆, ppm): δ 7.80 (app td, J = 7.8, 0.8 Hz, 1H, H4), 7.69 (d, J⁵⁰₀ = 7.4 Hz, 1H, H5), 7.62-7.69 (m, 1H, H9), 7.54 (m, 1H, H6), 7.40 (d, J⁵⁰₀ = 7.7 Hz, 1H, H3), 7.02 (m, 1H, H8), 6.94 (ddd, J⁵⁰₀ = 7.5, 7.5, 4J = 1.4 Hz, 1H, H7), 3.70 (d, J = 8.2 Hz, 2H, H2), 1.37 (d, J = 13.3 Hz, 18H, H1). ³¹P NMR (400 MHz, acetone-d₆, ppm): δ 78.33 (app t, J = 7.8 Hz, 1H, H4), 7.71 (d, J = 7.9 Hz, 1H, H5), 7.67 (ddd, J = 7.1, 1.7, 1.7 Hz, 1H, H9), 7.56 (dd, J = 7.7, 1.2 Hz, 1H, H6), 7.42 (d, J = 7.7 Hz, 1H, H3), 7.04 (ddd, J = 7.2, 7.2, 1.3 Hz, 1H, H8), 6.96 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H, H7), 3.73 (s, 2H, CH₂P), 1.39 (s, 18H, (CH₃)₂CP). ³¹P NMR (121 MHz, acetone-d₆, ppm): δ 76.31 (d, Jᵣᵢₚ = 101.0 Hz). ¹³C NMR (75 MHz, acetone-d₆, ppm): δ 201.01 (dd, Jᵣᵢₚ = 78.8 Hz, JCP = 11.1 Hz, CO), 176.93 (dd, Jᵣᵢₚ = 81.8 Hz, JCP = 36.5 Hz, Ph-C(Rh)), 168.06 (dd, J = 6.7, 3.0 Hz, Py-C), 165.20 (dd, J = 10.1, 1.6 Hz, Py-C), 150.35 (s, Ph-C), 140.33 (d, J = 4.7 Hz), 139.99 (s, Py-CH), 130.36 (dd, J = 5.6, 2.5 Hz, Ph-CH), 124.46 (d, J = 3.5 Hz, Ph-CH), 123.58 (s, Ph-CH), 120.62 (d, J = 9.3 Hz), 116.41 (s, Py-CH), 36.03 (d, Jᵣᵢₚ = 14.0 Hz, CH₂P), 35.25 (dd, Jᵣᵢₚ = 12.0 Hz, JCP = 0.8 Hz, (CH₃)₂CP), 29.73 (d, Jᵣᵢₚ = 6.7 Hz, (CH₃)₂CP). IR (ATR, cm⁻¹): νCO 1933. UV-vis (CH₂Cl₂, nm): λ 250 (ε = 2.4 × 10⁴ L·mol⁻¹·cm⁻¹), 277 (ε = 1.7 × 10⁴ L·mol⁻¹·cm⁻¹), 321 (ε = 2.1 × 10⁴ L·mol⁻¹·cm⁻¹), 457 (ε = 2.7 × 10⁵ L·mol⁻¹·cm⁻¹). HR-MS (FAB) calcd for [M+H]⁺ C₃₁H₃₂ONPRh m/z 444.0964; found, 444.0970. El. Anal. calcd. for C₃₁H₃₂ONPRh: C, 56.89; H, 6.14; N, 3.16. Found: C, 56.62; H, 6.11; N 3.13.

Stabilization of 2′ with PMe₃ (2′-PMe₃). A solution of complex 2 (10 mg, 21 μmmol) in THF-d₈ (0.6 ml) was cooled to -60 °C and PMe₃ (2.1 μL, 21 μmmol) and a 1M solution of KOtBu in THF (21 μL, 21 μmmol) were added sequentially. An immediate color change from yellow to dark red was observed. The solution was quickly transferred to an NMR-tube and placed in the pre-cooled NMR machine. Due to its unstable nature, this species was only characterized in situ. ¹H NMR (500 MHz, THF-d₈, ppm, 243 K) δ 8.50-7.30 (m, 5H, Ph), 6.39-6.33 (m, 1H, Py), 5.98 (d, J = 8.7 Hz, 1H, Py), 5.62 (d, J = 6.5 Hz, 1H, Py), 3.36 (d, J = 6.2 Hz, 1H, CH₂P), 1.33 (d, J = 5.4 Hz, 9H, (CH₃)₃CP), 1.30 (d, J = 5.5 Hz, 9H, (CH₃)₃CP), 0.73 (d, J = 8.4 Hz, 3H, P(CH₃)₃). ³¹P NMR (202 MHz, THF-d₈, ppm, 243 K) δ 86.50 (dd, J₀ = 279.2 Hz, Jᵣᵢₚ = 125.1 Hz, (CH₃)₃CP) -15.05 (dd, J₀ = 297.7 Hz, Jᵣᵢₚ = 130.7 Hz, P(CH₃)₃).

Deprotonation of 3 to form K[Rh(μ₃-PP,N,C(1))(CO)]. To a solution of complex 3 (7 mg, 16 μmol) in THF-d₈ (0.6 ml) was added a 1M solution of KOTBu in THF (16 μL, 16 μmol). An immediate color change from red to very dark red was visible. No full conversion was observed, since still 30% of the starting material was present. Due to its unstable nature, this species was only characterized in situ using NMR spectroscopy. ¹H NMR (500 MHz, THF-d₈, ppm, 243 K) δ 7.49-7.45 (m, 1H, Ph), 6.96 (d, J = 7.6 Hz, 1H, Ph), 6.67 (m, 1H, Ph), 661 (ddd, J = 7.4, 7.4, 1.5 Hz, 1H, Ph), 6.08 (ddd, J = 8.6, 6.8, 1.8 Hz, 1H, Py), 5.70 (d, J = 8.7 Hz, 1H, Py), 5.35 (d, J = 6.4 Hz, 1H, Py), 3.02 (s, 1H, CH₂P), 1.26 (dd, J = 12.4 Hz, 18H, (CH₃)₃CP). ³¹P NMR (202 MHz, THF-d₈, ppm, 243 K) δ 69.20 (d, Jᵣᵢₚ = 102.1 Hz).
Synthesis of [Rh(κ³-P,N-(CH)-1¹) (CO)]BF₄ (4). To a solution of 3 (10 mg, 23 μmol) in Et₂O (5 mL) was added HB₄F (54 wt% in Et₂O, 3.7 mg, 23 μmol), resulting in immediate precipitation of a yellow solid. The supernatant was removed and the product was washed with diethyl ether (1 mL), yielding 4 as a yellow solid in quantitative yield. Single crystals suitable for an X-ray crystal structure determination were obtained by slow diffusion of pentane into a THF-solution of 4. ¹H NMR (500 MHz, CD₂Cl₂, ppm): δ 8.23-8.15 (m, 3H), 7.93-7.84 (m, 3H), 7.83-7.77 (m, 2H), 3.89 (d, 2JPh = 10.0 Hz, 2H, CH₂P), 1.43 (d, 3JPh = 15.6 Hz, 18H, (CH₃)₂CP). ³¹P NMR (121 MHz, CD₂Cl₂, ppm): δ 121.40 (d, J = 202.3 Hz). ¹³C NMR (126 MHz, CD₂Cl₂, ppm): δ 190.19 (dd, 1JRhC = 70.2, 2JCP = 16.1 Hz), 162.57 (m, Py-C), 159.27 (s, Py-C), 142.46 (m, Py-CH), 141.14 (s, Ph-C), 139.23 (m, (CH₃)CP). ¹⁹F NMR (282 MHz, CD₂Cl₂, ppm): δ -152.20. IR (ATR, cm⁻¹): νCO 1986. HR-MS (FAB) calcld for [M-BF₄]⁺ C₂H₂₈NOPrH m/z 444.0964; found, 444.1031. El. Anal. calcd. for C₂H₂₈BF₄NOPrH: C, 47.49; H, 5.31; N, 2.64. Found: C, 46.73; H, 5.24; N, 2.81.

Synthesis of Rh(I)(CO)(κ²-P,N-1¹Me) (5). To a solution of 3 (20 mg, 45 μmol) in acetone (5 mL) was added methyl iodide (6 μL, 45 μmol), resulting in a color change from red to brown within minutes at room temperature. Removal of solvent in vacuo resulted in the isolation of 5 as a brown solid in quantitative yield. ¹H NMR (300 MHz, acetone-d₆, ppm): δ 7.99 (dd, J = 7.3, 1.8 Hz, 1H, Ph), 7.92 (dd, J = 7.8, 7.8, 0.8 Hz, 1H, Py), 7.67 (d, J = 7.7 Hz, 1H, Py), 7.42 (d, J = 7.7 Hz, 1H, Py), 7.36-7.19 (m, 3H, Ph), 3.98 (d, 2JPh = 9.6 Hz, 2H, CH₂P), 2.42 (s, 3H, Ph-CH₃), 1.56-1.23 (m, 18H, (CH₃)₂CP). ³¹P NMR (121 MHz, acetone-d₆, ppm): δ 109.25 (d, 1JRhP = 169.8 Hz). ¹³C NMR (75 MHz, acetone-d₆, ppm): δ 163.40 (d, J = 4.6 Hz, Py-C), 163.17 (s, Py-C), 142.74 (s, Ph-C), 138.77 (s, Py-CH), 137.34 (s, Ph-C), 132.07 (s, Ph-CH), 130.46 (s, Ph-CH), 129.78 (s, Ph-CH), 126.63 (s, Ph-CH), 125.96 (s, Ph-CH), 122.20 (d, 2JCP = 9.3 Hz, Py-CH), 35.58 (d, 1JCP = 19.4 Hz, (CH₃)CP), 29.41 (d, 2JCP = 4.6 Hz, (CH₃)CP), 21.82 (s, Ph-Me). Signals for CO and CH₂P were not observed. IR (ATR, cm⁻¹): νCO 1952. HR-MS (FAB) calcd for [M-I]⁺ C₂₂H₃₀NOPrH m/z 458.1120; found, 458.1199.

Characterization of Rh(III)(Me)(κ³-P,N-(CH)-1) (CO) (A). Methyl iodide (3 μL, 23 μmol) was added to a cold solution of 3 (10 mg, 23 μmol) in acetone-d₆ (0.6 mL) at -78 °C. The cold solution was transferred to a cold NMR tube and inserted in a pre-cooled NMR machine. The temperature was slowly raised from -60 °C to -20 °C during which the Rh(III) intermediate formed. When the temperature was raised to 10 °C, this intermediate converted to complex 5 within 60 min. ¹H NMR (300 MHz, acetone-d₆, ppm, 253 K) δ 8.03-7.89 (m, 2H), 7.80 (ddd, J = 7.8, 2.9, 1.5 Hz, 1H), 7.63 (tt, J = 7.5, 1.3 Hz, 1H), 7.54 (dd, J = 7.2, 1.5 Hz, 1H), 7.18 (tt, J = 7.5, 1.6 Hz, 1H), 7.03-6.94 (m, 1H), 4.08-3.89 (m, 2H, CH₂P), 1.56 (d, 3JPh = 13.2 Hz, 9H, (CH₃)₂CP), 1.39 (d, 3JPh = 12.5 Hz, 9H, (CH₃)₃CP), 0.73 (dd, 3JPh = 5.0, 1JRhH = 2.4 Hz, 3H, Rh-CH₃). ³¹P NMR (122 MHz, acetone-d₆, ppm, 253 K) δ 52.22 (d, 1JRhP = 65.6 Hz).

Synthesis of Rh(κ²-P,N-1) (CO)(I)₂ (6). To a solution of complex 3 (10 mg, 23 μmol) in THF (1.5 mL) was added I₂ (6 mg, 23 μmol) and the reaction was stirred for 10 min.
The solvent was evaporated, yielding 7 as a dark red solid in quantitative yield. Single crystals suitable for an X-ray crystal structure determination were obtained by slow diffusion of pentane into a CH₂Cl₂-solution of 7. ¹H NMR (300 MHz, CD₂Cl₂, ppm) δ 7.87-7.69 (m, 4H), 7.38-7.25 (m, 2H), 6.94 (dddd, 3JH = 7.8, 3JH = 7.2, 1.1, 0.6 Hz, 1H), 3.91 (d, 2JPH = 8.8 Hz, 2H, CH₂P), 1.54 (d, 3JPH = 13.3 Hz, 18H, (CH₃)₃CP), ¹³P NMR (121 MHz, CD₂Cl₂, ppm) δ 44.66 (d, 1JRP = 68.9 Hz). ¹³C NMR (75 MHz, CD₂Cl₂, ppm) δ 165.65 (d, J = 6.2 Hz, Py-C), 162.60 (d, J = 6.3 Hz, Py-C), 157.72 (dd, 2JRH = 101.2 Hz, 2JCP = 18.1 Hz, Rh-C), 146.10 (s, Ph-C), 141.76 (s, Py-CH), 139.51 (s, Ph-CH), 132.19 (d, J = 8.0 Hz, Ph-CH), 125.16 (d, J = 5.0 Hz, Ph-CH), 123.57 (s, Ph-CH), 119.72 (d, J = 8.4 Hz, Py-CH), 118.45 (s, Py-CH), 38.51 (d, J = 13.4 Hz), 38.06 (d, J = 5.6 Hz), 31.93 (d, J = 3.4 Hz, (CH₃)₃CP), signal for CO was not observed. IR (ATR, cm⁻¹): νCO 2049. HR-MS (FD) calcld for [M⁺ C₂₃H₂₇F₃NORh] m/z 696.8975; found, 696.9002.

Synthesis of cis-Rh(CF₃)(OTf)(κ³-P,N,C-1)(CO) (7). To a solution of complex 3 (20 mg, 45 μmol) in MeCN (1 mL) was added [5-(trifluoromethyl)dibenzothiophenium](OTf) (18 mg, 45 μmol) which caused an immediate color change from red to pale yellow. The product that is formed, presumably trans-Rh(CF₃)(OTf)(κ³-P,N,C-1)(CO) was only characterized in situ due to the instability in solution. NMR showed full conversion to intermediate B. ¹H NMR(300 MHz, MeCN-d₂, ppm) δ 8.12-7.98 (m, 2H), 7.92-7.86 (m, 1H), 7.80 (t, J = 8.0 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.41 (tt, J = 7.5, 1. Hz), 7.34 (t, J = 7.3 Hz, 1H), 3.98-3.89 (m, 2H, CH₂P), 1.49 (d, J = 14.6 Hz, 9H, (CH₃)₃CP), 1.29 (d, J = 13.4 Hz, 9H, (CH₃)₃CP). ³¹P NMR (121 MHz, MeCN-d₃, ppm) δ 64.76 (dq, J = 62.7 Hz, J = 7.7 Hz). ¹⁹F NMR (282 MHz, MeCN-d₃, ppm): -5.57 (dd, 3JRF = 19.0, 3JFP = 7.5, CF₃), -79.31 (OTf). This product converts to the thermodynamic cis-complex in 3 days in MeCN. When the same reaction is carried out in CH₂Cl₂ the product can be isolated by crystallization from layering with CH₂Cl₂/pentane (21 mg, 7%). Upon dissolving in MeCN-d₃ and standing for 3 days, the cis-complex is selectively formed. ¹H NMR (500 MHz, MeCN-d₃, ppm) δ 8.13-7.93 (m, 4H), 7.59 (d, J = 7.3 Hz, 1H), 7.52 (tt, J = 7.5, 2.1 Hz, 1H), 7.48-7.42 (m, 1H), 3.90 (qd, J = 17.4, 9.8 Hz, 2H), 1.42 (d, J = 8.0 Hz, 9H), 1.40 (d, J = 7.7 Hz, 9H). ³¹P NMR (121 MHz, MeCN-d₃, ppm): δ 55.40 (dq, 1JRP = 69.2 Hz, 3JFP = 19.8 Hz). ¹⁹F NMR (282 MHz, MeCN-d₃, ppm): δ -7.10 (dd, 3JFP = 20.4 Hz, 2JRF = 10.7 Hz, CF₃), -79.34 (OTf). ¹³C NMR (126 MHz, MeCN-d₃, ppm): δ 162.23 (d, J = 6.2 Hz, Py-C), 161.34 (d, J = 3.0 Hz, Py-C), 151.59 (d, 1JRC = 90.1, 2JCP = 21.0 Hz, Rh-C), 146.77 (s, Ph-C), 141.32 (s, Py-CH), 136.90 (s, Ph-CH), 132.30 (d, J = 7.8 Hz, Ph-CH), 127.02 (s, Ph-CH), 126.80 (d, J = 4.5 Hz, Ph-CH), 122.59 (d, 3J = 7.8 Hz, Py-CH), 118.94 (s, Py-CH), 36.72 (d, 1J = 7.2 Hz, (CH₃)₃CP), 35.65 (d, 1J = 10.1 Hz, (CH₃)₃CP), 34.86 (d, 1J = 17.8 Hz, H₂P), 28.40 (d, 2J = 4.1 Hz, (CH₃)₃CP), 28.16 (d, 2J = 3.6 Hz, (CH₃)₃CP). Signals for CO, CF₃ and OTf were not observed. HRMS(): m/z calcd. for C₂₂H₂₇F₃NORh: 512.0837 [M⁺]; found: 512.0820.

X-ray crystallography studies. X-ray intensities were measured on either a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K for 2-4 or on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 50 detector at a temperature of 150(2) K for 6. Intensity data were integrated with the EvalI5 software or the Bruker APEXII software. Absorption correction and scaling was performed with SADABS. The structures were solved with the programs SHELXTL.
1.018. Residual electron density between -0.629 and 0.686 e/Å
3
no restraints.
R
of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. Metal bound hydrogen atom H11 in complex 4 was refined freely with an isotropic displacement parameter, all other hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program. Crystallographic data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2: C\textsubscript{2}H\textsubscript{28}CINOPRh-CH\textsubscript{2}Cl\textsubscript{2}, \textit{M} = 564.70, yellow needle, 0.06×0.07×0.27 mm, monoclinic, \textit{P}2\textsubscript{1}/c (No: 14), \textit{a} = 8.47689(19), \textit{b} = 14.3570(4), \textit{c} = 20.42595(9) Å, \textit{β} = 90.149(1)°, \textit{V} = 2486.41(11) Å\textsuperscript{3}, \textit{Z} = 4, \textit{Dx} = 1.509 g cm\textsuperscript{-3}, \textit{µ} = 1.09 mm\textsuperscript{-1}. 46702 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ Å}^{-1}\). 5708 Reflections were unique \((R_{\text{int}} = 0.024)\), of which 5253 were observed \([I > 2\sigma(I)]\). The structure was refined as a pseudo-orthorhombic twin with a twofold rotation about \(hkl = (0,0,1)\) as twin operation. 269 Parameters were refined with no restraints. \(R/I\text{w}R\ [I > 2\sigma(I)]: 0.0189 / 0.0459\). \(R/I\text{r}wR\ [\text{all refl.}]: 0.0223 / 0.0473\). \textit{S} = 1.051. Twin fraction BASF = 0.01995(18). Residual electron density between -0.60 and 0.68 e/Å\textsuperscript{3}. CCDC 966374.

3: C\textsubscript{2}H\textsubscript{27}NOPRh, \textit{M} = 443.32, red needle, 0.08×0.17×0.44 mm\textsuperscript{3}, monoclinic, \textit{C}2\textsubscript{1}/c (No: 15), \textit{a} = 21.7218(5), \textit{b} = 12.4856(3), \textit{c} = 16.3022(4) Å, \textit{β} = 113.853(1)°, \textit{V} = 4043.71(17) Å\textsuperscript{3}, \textit{Z} = 8, \textit{Dx} = 1.456 g cm\textsuperscript{-3}, \textit{µ} = 0.93 mm\textsuperscript{-1}. 32483 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ Å}^{-1}\). 4641 Reflections were unique \((R_{\text{int}} = 0.017)\), of which 4230 were observed \([I > 2\sigma(I)]\). 232 parameters were refined with no restraints. \(R/I\text{w}R\ [I > 2\sigma(I)]: 0.0161 / 0.0418\). \(R/I\text{r}wR\ [\text{all refl.}]: 0.0189 / 0.0427\). \textit{S} = 1.047. Residual electron density between -0.33 and 0.31 e/Å\textsuperscript{3}. CCDC 966375.

4: [C\textsubscript{2}H\textsubscript{28}NOPRh\textsubscript{3}](BF\textsubscript{4}), \textit{M} = 531.13, orange block, 0.08×0.20×0.25 mm, triclinic, \textit{P}\textsubscript{T} (No: 2), \textit{a} = 8.0624(3), \textit{b} = 11.5108(4), \textit{c} = 12.8859(3) Å, \textit{α} = 108.143(1), \textit{β} = 95.856(1), \textit{γ} = 96.480(1)°, \textit{V} = 1117.18(6) Å\textsuperscript{3}, \textit{Z} = 2, \textit{Dx} = 1.579 g cm\textsuperscript{-3}, \textit{µ} = 0.08 mm\textsuperscript{-1}. 40925 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.81 \text{ Å}^{-1}\). 9822 Reflections were unique \((R_{\text{int}} = 0.020)\), of which 8640 were observed \([I > 2\sigma(I)]\). 281 Parameters were refined with no restraints. \(R/I\text{w}R\ [I > 2\sigma(I)]: 0.0260 / 0.0632\). \(R/I\text{r}wR\ [\text{all refl.}]: 0.0331 / 0.0659\). \textit{S} = 1.034. Residual electron density between -0.70 and 0.91 e/Å\textsuperscript{3}. CCDC 966376.

5: [C\textsubscript{2}H\textsubscript{27}NOPRh\textsubscript{3}]\textsubscript{2}Cl\textsubscript{2}, \textit{M} = 697.11, red-orange block, 0.18×0.08×0.05 mm, triclinic, \textit{P}\textsubscript{T} (No: 2), \textit{a} = 8.9530(4), \textit{b} = 9.1338(4), \textit{c} = 16.7107(7) Å, \textit{α} = 102.541(2), \textit{β} = 90.866(2), \textit{γ} = 119.006(2)°, \textit{V} = 1154.94(9) Å\textsuperscript{3}, \textit{Z} = 2, \textit{Dx} = 2.005 g cm\textsuperscript{-3}, \textit{µ} = 3.493 mm\textsuperscript{-1}. 44618 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.81 \text{ Å}^{-1}\). 4059 Reflections were unique, of which 3590 were observed \([I > 2\sigma(I)]\). 250 Parameters were refined with no restraints. \(R/I\text{w}R\ [I > 2\sigma(I)]: 0.0203 / 0.0429\). \(R/I\text{r}wR\ [\text{all refl.}]: 0.0274 / 0.0451\). \textit{S} = 1.018. Residual electron density between -0.629 and 0.686 e/Å\textsuperscript{3}. CCDC 1038561.

DFT calculations. Geometry optimizations were carried out with the Turbomole program package couped to the PQS Baker optimize via the BOpt package at
the spin unrestricted ri-DFT level using the BP86\textsuperscript{97,98} functional and the resolution-of-identity (ri) method.\textsuperscript{99} We optimized the geometries of all stationary points at the def2-TZVP basis set level,\textsuperscript{100} using Grimme’s dispersion corrections (disp3 version)\textsuperscript{101} and a tight energy grid (m5). The identity of the transition states was confirmed by following the imaginary frequency in both directions (IRC). All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated using standard thermodynamics. Wiberg bond orders\textsuperscript{63} were calculated from the Turbomole output files using the AOMix program.\textsuperscript{102,103}

Table 2.1: Comparison of bond distances (nm) of selected bonds in complex 4-PMe\textsubscript{2} calculated with two different functionals, with and without dispersion corrections.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Bond distance (nm)</th>
<th>BP86</th>
<th>BP86-disp3</th>
<th>B3LYP</th>
<th>B3LYP-disp3</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-H35</td>
<td>2.025</td>
<td>2.050</td>
<td>2.144</td>
<td>2.176</td>
<td>2.19(2)</td>
</tr>
<tr>
<td>Rh-C25</td>
<td>2.367</td>
<td>2.353</td>
<td>2.461</td>
<td>2.451</td>
<td>2.3750(15)</td>
</tr>
<tr>
<td>C25-H29</td>
<td>1.123</td>
<td>1.120</td>
<td>1.101</td>
<td>1.099</td>
<td>0.926(19)</td>
</tr>
<tr>
<td>C26-H29</td>
<td>1.090</td>
<td>1.090</td>
<td>1.082</td>
<td>1.082</td>
<td>0.98</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The (def2-)TZVP basis set was used for all atoms in all calculations.

Table 2.2: Comparison of Wiberg bond orders of selected bond in complex 4.\textsuperscript{a}

<table>
<thead>
<tr>
<th>BO</th>
<th>BP86</th>
<th>BP86-disp3</th>
<th>B3LYP</th>
<th>B3LYP-disp3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-H35</td>
<td>0.171</td>
<td>0.158</td>
<td>0.111</td>
<td>0.093</td>
</tr>
<tr>
<td>Rh-C25</td>
<td>0.290</td>
<td>0.298</td>
<td>0.236</td>
<td>0.241</td>
</tr>
<tr>
<td>C25-H29</td>
<td>0.749</td>
<td>0.751</td>
<td>0.792</td>
<td>0.797</td>
</tr>
<tr>
<td>C26-H29</td>
<td>0.942</td>
<td>0.944</td>
<td>0.953</td>
<td>0.954</td>
</tr>
<tr>
<td>Rh-H35-C35</td>
<td>0.052</td>
<td>0.050</td>
<td>0.045</td>
<td>0.041</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The (def2-)TZVP basis set was used for all atoms in all calculations.

References

Cyclometalation at Rh