Facile Synthesis and Versatile Reactivity of an Unusual Cyclometalated Rhodium(I) Pincer Complex

Jongbloed, L.S.; de Bruin, B.; Reek, J.N.H.; Lutz, M.; van der Vlugt, J.I.

DOI
10.1002/chem.201406463

Publication date
2015

Published in
Chemistry - A European Journal

License
Article 25fa Dutch Copyright Act

Citation for published version (APA):
Facile Synthesis and Versatile Reactivity of an Unusual Cyclometalated Rhodium(I) Pincer Complex

Linda S. Jongbloed,[a] Bas de Bruin,[a] Joost N. H. Reek,[a] Martin Lutz,[b] and Jarl Ivar van der Vlugt*[a]

Abstract: The synthesis of the reactive PN(C^6) ligand 2-di((tert-butylphosphanomethyl)-6-phenylpyridine (1^m) and its versatile coordination to a Rh^I center is described. Facile C–H activation occurs in the presence of a (internal) base, thus resulting in the new cyclometalated complex [Rh(CO)(^2-PN,C-1)] (3), which has been structurally characterized. The resulting tridentate ligand framework was experimentally and computationally shown to display dual-site proton-responsive reactivity, including reversible cyclometalation. This feature was probed by selective H/D exchange with [D_5]formic acid. The addition of HBF_4 to 3 leads to rapid net protonolysis of the Rh–C bond to produce [Rh(CO)(^2-PN,(C–H=1)] (4). This species features a rare aryl C–H agostic interaction in the solid state, as shown by X-ray diffraction studies. The nature of this interaction was also studied computationally. Reaction of 3 with methyl iodide results in rapid and selective ortho-methylation of the phenyl ring, thus generating [Rh(CO)(^2-PN,1^me)] (5). Variable-temperature NMR spectroscopy indicates the involvement of a Rh^III intermediate through formal oxidative addition to give trans-[Rh(C)(CH_3)(CO)(^3-PN,C-1)] prior to C–C reductive elimination. The Rh^III-trans-diiodide complex [Rh(CO)(^3-PN,C-1)] (6) has been structurally characterized as a model compound for this elusive intermediate.

Introduction

Cyclometalated complexes are proposed to be intermediates in C–H functionalization reactions of aromatic substrates, mediated by directing-group ligation to a range of transition-metal species.[1,2] Reactivity studies have indicated that metal–arené bonds can interact with a variety of reagents. The site-specific cyclometalation of phenylpyridine, wherein pyridine acts as the directing group, and close analogues thereof has been explored extensively for synthetic purposes with several metals, including Rh^III species.[3] Isolated high-oxidation state Rh^III complexes that feature a cyclometalated phenylpyridine ligand or substrate scaffold are well-documented.[4] Well-characterized examples of low-oxidation state Rh^III cyclometalated complexes are rare (Figure 1).[5,6] As a consequence, the potential reactivity of the metallacyclic Rh^III–C bond and the scope for follow-up chemistry is unexplored.

Agostic metal–(C–H) bond interactions can stabilize coordinatively unsaturated, low-valent, and electron-deficient metal centers by donating some of the electron density from the C–H bond to the metal center to form a three-center two-electron (3c-2e) bond.[7] At the same time, π-back donation of π-type d-orbitals of low-valent transition-metal centers into the α* orbitals of agostic C–H bonds embedded in a chelating-ligand scaffold should enable facile and reversible cyclometalation. As such, chelating ligands that offer the possibility to both coordinate in a hemilabile (agostic) manner and easily switch between binding modes with either weak (agostic) or strong (cyclometalated) metal–ligand interactions are interesting, also from a catalysis perspective. Herein, we describe our investigations toward the use of agostic interactions and reversible cyclometalation reactivity in the design of new flexidenate ligands. Obviously, this concept requires ligand architectures that permit the agostic C–H bond to dissociate from the (low-valent) transition-metal center when needed. This scenario contrasts with reported examples wherein the agostic C–H bond interactions are enforced by geometric constraints imposed by other ligand donors, such as the phenyl-based 2,6-bis(phosphanomethyl)benzene (PCP) pincer system reported by...
Milstein and co-workers, wherein a Rh\(^{III}\)(C\(_{\text{Ph}}\)–H) bond was detected as an intermediate toward the oxidative addition of the C–H bond.\[^8,9\] Examples of structurally characterized complexes with an agostic C\(_{\text{aromatic}}\)–H bond bound to a Rh center wherein the arene moiety is not supported by flanking donors, but is itself a flanking group, have not been described to date to the best of our knowledge.

The reactivity of cyclometalated metal–carbon bonds toward acidic substrates has been discussed for a number of metal species,\[^10–12\] and reversible cyclometalation has been postulated as a possible ligand-mediated mechanism in catalysis,\[^13\] primarily based on theoretical calculations.\[^13\] 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.\[^14–16\] Understanding of and control over the reactivity of the metal–carbon fragment might ultimately enable the use of this bond type in cooperative catalysis.

Herein, we report the facile synthesis of a low-valent Rh\(^{III}\) cyclometalated complex bearing a phenylpyridine unit functionalized with an appended phosphane donor, thus creating an overall tridentate ligation to a Rh center (Scheme 1). The Rh–C bond can be selectively activated and functionalized, which has allowed the isolation and structural characterization of a novel Rh(C\(_{\text{Ph}}\)–C\(_{\text{aromatic}}\)) agostic complex. We also describe the first case of facile methylation of a cyclometalated Rh–arene through the reductive elimination of a Rh\(^{III}\)(Ph(Me)) species. Initial results into the potential activation of the Rh–C bond for small-molecule activation are also included.

**Results and Discussion**

**Bidentate versus tridentate coordination to a Rh\(^{III}\) species**

Addition of ligand 1\(^{\text{H}}\) to 0.5 molar equivalents of [Rh\((\mu-\text{Cl})(\text{CO})_2\)]\(_2\) yielded a yellow solid, which displays a doublet in the \(^{31}\text{P}\) NMR spectrum at \(\delta = 104\) ppm (\(^{1}J_{\text{Rh,P}} = 160\) Hz; Scheme 2). X-ray crystal structure determination confirmed the square-planar geometry expected for this complex, formulated as [RhCl(CO)(\(\text{C}^{\text{N}}\)(\text{Ph})\(_2\))]\(_2\) (Figure 2). The most striking feature of the molecular structure is the phenylpyridine ring that strongly points out of the Rh coordination plane (\(\chi,\text{Rh}–\text{N}1–\text{Cl}1=81.95(3)^{\circ}\)).

Notably, the reaction of 1\(^{\text{H}}\) with [Rh\((\text{acac})(\text{CO})_2\)]\(_2\) (acac = acetylacetonate) results in the red complex 3 with very different spectroscopic features relative to 2. \(^{31}\text{P}\) NMR spectroscopic analysis proved particularly insightful to probe the chemistry that occurs at the Rh center for the various reactions described herein (Figure 3). The \(^{31}\text{P}\) NMR spectrum showed a doublet at \(\delta = 76\) ppm with a significantly smaller coupling constant (\(^{1}J_{\text{Rh,P}} = 101\) Hz), which indicates the presence of a strong o-donor trans to the phosphane group. Furthermore, the C5-C15 = 19.32(18)\(^{\circ}\) to accommodate the Cl ligand, which also results in a somewhat acute P1-Rh1-C11 angle of 162.983(15)\(^{\circ}\).

![Scheme 2. Synthesis of Rh\(^{III}\) complexes 2 and 3 that display facile reversible metalation.](image-url)
The mechanism of acetate-assisted C=H activation, especially for Pd species, but may also be of relevance for Rh species, which was confirmed by using $^1$H NMR spectroscopy. These observations suggest efficient and selective C–H activation of the phenyl side arm of 1$^a$. The resulting (κ^1,PN,C)-coordination mode of the ligand in this unusual Rh cyclocatennated complex was unambiguously confirmed by X-ray structure determination (Figure 4).\textsuperscript{[5, 17, 18]} The cyclocatennated ligand structure bears considerable strain, with χ P1-Rh1-C1 = 162.47(4) and χ N1-Rh1-C1 = 80.26(5)$^b$.

**Figure 4.** 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 χ C1-C6-C7-N1 = −0.79(17).

**Influence of the base on the mechanism of cyclocatennation**

The mechanism of acetate-assisted C–H activation has been studied by DFT calculations. It is well-understood that the mechanism for electrophilic activation, especially for Pd\textsuperscript{4} catalyysts, proceeds through a six-membered transition state where-in the non-coordinated acetate oxygen atom of the κ^1-O ligated acetate deprotonates the C–H bond.\textsuperscript{[17a]} 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 Rh\textsuperscript{II} and Ir\textsuperscript{III} species.\textsuperscript{[18, 21]} Based on this precedent, we speculate that a similar mechanism is plausible for the Rh\textsuperscript{III} species with the acetate ion as an external base and with internal bases (for example, acac).

For this specific case, in which the ligand may be expected to be chemically noninnocent, we propose that the use of a strong base results in a different mechanism for C–H activation. The addition of KOtBu to 2 at −78 °C is proposed to result initially in deprotonation of the methylene unit of the ligand backbone, thus generating 2' (Scheme 3), in analogy to reported Rh chemistry with a structurally related 2,6-di(phosphanomethyl)lutidine (PNP) ligand.\textsuperscript{[20]} Apart from a distinct darkening of the solution upon deamortization of the pyridine fragment, deuteration experiments (that is, the use of DCI results in selective deuteration at the −CH$_2$(P) position; see the Supporting Information) are indicative for methylene reactivity. However, this deamortized species rapidly converts into 3 by proton transfer from the ortho-phenyl position to the CH backbone, even at −78 °C, thus preventing unambiguous spectroscopic identification of this transient species.

PMe$_3$ was added as a coligand to stabilize this putative 2' species, which gave complex 2-PMe$_3$ (Scheme 3). Although follow-up C–H activation to give 3 was impeded by exogenous phosphane coordination, this species was too unstable to be isolated under ambient conditions. Therefore, 2-PMe$_3$ was only characterized in situ by $^3$P and $^1$H NMR spectroscopic analysis at −78 °C (see the Supporting Information). The cyclocatennated complex 3 is still susceptible to deprotonation at the phosphane arm upon reaction with a strong base, according to in situ $^3$P and $^1$H NMR spectroscopic analysis (see the Supporting Information). Hence, this novel ligand scaffold displays two distinctly different modes of proton-responsive reactivity.\textsuperscript{[21]}

We resorted to DFT calculations to understand the observed reaction sequence of the initial deprotonation at the −CH$_2$P arm followed by C–H activation at the phenyl group and intramolecular proton transfer. The direct proton transfer from hydride species 2'' has a high lying transition state TS$_{2''-3}$ of 29.5 kcal mol$^{-1}$ (Figure 5). Therefore, the mechanism most likely involves proton shuttling through tBuOH; obtained from protonation of KOtBu, which gives a very low barrier of only approximately 1 kcal mol$^{-1}$ (TS$_{2''-2}$). The unique structure of ligand 1$^a$ allows us to uncover whether this interaction can also exist in less conformationally restrictive geometries. This discovery may not only broaden our understanding of this type of agostic C–H bond, particularly with Rh species, but may also be of relevance for mechanistic understanding related to Rh(C–H) species as catalytically relevant intermediates.

Upon the addition of ethereal HBF$_4$ to a red solution of species 3 in diethyl ether (Scheme 4), instantaneous precipitation of a yellow solid was observed. Redissolution of the yellow

\[ \text{Scheme 3. Deprotonation of the reactive side arm present in 2 concomitant with pyridine deamortization and subsequent intramolecular C–H activation of the phenyl arm to generate 3 in the absence and presence of PMe}_3 \text{ as a stabilizing coligand.} \]
solid in CD₂Cl₂ yielded a doublet at δ = 121 ppm (Δδ = 45.1 ppm vs. 3) in the ³¹P NMR spectrum, with a coupling constant ¹JₚRh of 202 Hz (ΔJ = 101 Hz vs. 3; see Figure 3). These data indicate the coordination of a weak α donor or a vacant site at the Rh center trans to the phosphorus atom. Yellow single crystals suitable for single-crystal X-ray structure determination were obtained from CH₂Cl₂/pentane, and the resulting X-ray structure of complex 4 (Figure 6) shows a distinct Rh(η¹-C–H) interaction, with a Rh–C=C bond length of 2.3750(12) Å. The Rh1–H11 distance 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.

The agostic interactions in solution may result in an upfield shift to about δ = 4 ppm for the respective proton in the ¹H NMR spectrum. Furthermore, the ¹JCH value should decrease due to the weakening of the C–H bond. In case of 4, the phenyl group shows local C₆ symmetry by ¹H NMR spectroscopic analysis, even at ~90 °C, thus indicating fast rotation around the C₆–C₄ bond. The signal for the two ortho-C4 atoms does show an upfield shift to δ = 117 ppm in the ¹C NMR spectrum relative to complex 2, but the ¹JCH value 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. Hence, the resulting interaction, if any, between the Rh center and the phenyl ortho-C–H protons is deemed to be much weaker in solution than in the solid state. The X-ray structure does not indicate any distortion in the aromaticity of the phenyl ring, excluding an arenium (Wheland-type) structure. However, 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 [(PC₃)Rh(CO)][BF₄]⁻ which was identified as an agostic Rh(C–H) interaction by using DFT calculations.

DFT (B3LYP-disp3) calculations for complex 4 reveal a Wiberg bond order of 0.241 between the Rh and C atoms and 0.098 between the Rh and H atoms. The bond order for the C–H bond is significantly lower than for the other C–H bonds (0.797 vs. 0.954), thus indicating weakening of this bond. These results are comparable with the bond orders found in [(PC₃)Rh(CO)][BF₄]⁻, although the interactions in 4 are slightly weaker than in this PCP complex. Furthermore, the three-center bond order between Rh–C–H is 0.041, thus indicating that the agostic interaction in 4 is rather weak (a three-center bond order of 0.10 was found for an agostic Pd complex).

**Methylation of the cyclometalated Rh complex:**

**Involvement of a Rh(II) intermediate**

Reactivity of a Rh–phenyl fragment toward Mel to induce selective methylation has been reported for a [(PC₃)Rh(II)]CO complex, but this reaction proved to be very sluggish by taking two weeks to complete. In contrast, species 3 reacts rapidly (< 5 min) with Mel at room temperature to form...
a single well-defined species (Scheme 5). Complex 5 resembles 2 in its composition and NMR features. In line with this finding, the addition of a base to 5 results in smooth regeneration of a rhodacyclic species, based on preliminary in situ $^{31}$P NMR spectroscopic analysis, with an almost identical chemical shift ($\delta = 105$ ppm) and coupling constant ($J_{\text{P},\text{P}} = 102$ Hz) as observed for cyclometalated complex 3. $^{1}H$ NMR spectroscopic and field-desorption (FD) mass-spectrometric analysis support the formulation of complex 5 as [Rh(CO)(I)(\(\kappa^1\)-P\(\kappa^3\)N\(\kappa^1\)Me)], in which 1\(\kappa^1\) is the ortho-tolyl variant of ligand 1\(\kappa^1\). The pathway for the formation of this complex presumably involves metal-centered oxidative addition of MeI to give [Rh\(^{4}\)(CO)(I)(Me\(\kappa^1\))] (A) as an intermediate, which subsequently undergoes C–C reductive elimination (Scheme 5). This pathway was supported by variable-temperature (VT) NMR spectroscopic investigations. The suggested Rh\(^{4}\) species could be detected at $-20$ °C as the major species, with a doublet at $\delta = 52$ ppm ($J_{\text{P},\text{P}} = 66$ Hz) in the $^{31}$P NMR spectrum and the methyl ligand appearing as a doublet of doublets at $\delta = 0.73$ ppm ($J_{\text{H},\text{H}} = 3.0$, $J_{\text{P},\text{H}} = 2.4$ Hz) in the $^{1}H$ NMR spectrum. Monitoring of the spectral changes over time resulted in clean first-order kinetics for the conversion into complex 5, thus indicating an intramolecular reductive elimination process.

To establish a more stable Rh\(^{4}\) derivative bearing ligand 1 as cyclometalated entity, 3 was treated with $I_{2}$, thus resulting in a clean and facile formation of a deep-red species that exhibited an upfield-shifted $^{31}$P NMR signal at $\delta = 45$ ppm ($\Delta \delta = 31$ ppm relative to 3) and a coupling constant $J_{\text{P},\text{P}}$ of 69 Hz. IR spectroscopic analysis showed a distinctly shifted CO band and at $\nu_{\text{CO}} = 2049$ cm$^{-1}$. These observations strongly support the presence of a Rh\(^{4}\) center (Scheme 5). The structure of the neutral complex [Rh\(^{4}\)(CO)(I\(\kappa^1\))\(\kappa^1\)](1\(\kappa^1\)) was confirmed by X-ray diffraction studies. The molecular structure (Figure 7) displays a distorted octahedral Rh\(^{4}\) center, with the two iodo ligands in the axial positions. The 1\(\kappa^1\)-Rh1-I2 angle is rather acute at 161.345(12)$^\circ$ as a result of steric interference with the bulky RBu groups of the phosphine arm. The Rh1–P1 bond length is significantly elongated relative to 3 ($\Delta \text{d} = 0.18 \text{Å}$). Heating of this species in toluene did not result in reductive elimination according to $^{31}$P NMR spectroscopic analysis. Initial attempts to react this Rh\(^{4}\) analogue by reaction with a base indicated dearomatization to occur for this high-valent complex in a similar fashion as documented for the low-valent situation. We are currently exploring this reactivity in more detail. Rh\(^{4}\) complex 6 does not react with, for example, HBF$_4$. 

### Conclusion

We have described initial leads to exploit reversible cyclometalation as part of a reactive ligand concept in coordination chemistry. Ligand framework 1\(\kappa^1\) can act as a reactive flexiblecate ligand, which switches between bi- and tridentate coordination in complexes 2 (yellow) and 3 (red), which have been fully characterized, including by UV/Vis spectroscopic analysis, DFT calculations, and single-crystal X-ray structure determination. Species 3 is the first example of a cyclometalated phenylpyridine fragment onto a low-valent Rh\(^{3}\) complex. The ligand backbone displays dual-site proton-responsive reactivity. The cyclometalated species reacts rapidly with various (protic) electrophiles. The Rh–C\(\kappa^1\) bond is selectively cleaved by one molar equivalent of HBF$_4$ to result in the formation of the rare agostic.

![Scheme 5. Pathway for the conversion of 3 into 5 through the Rh\(^{4}\) intermediate A and synthesis of the Rh\(^{3}\) model species [Rh(CO)(I\(\kappa^1\))\(\kappa^1\)](6).](image)

![Figure 7. ORTEP (ellipsoids set at 50% probability) for complex 6 (front and side view). Selected bond lengths (Å) and angles (°): Rh1–P1 2.4853(9), Rh1–N1 2.054(3), Rh1–C1 2.054(3), Rh1–C21 1.875(4), Rh1–I1 2.715(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).](image)
Slowly warmed to room temperature overnight. The reaction mixture and the organic phases were combined and dried over C\textsubscript{2}H\textsubscript{2} and P\textsubscript{2}P, 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 (H\textsubscript{1}, H\textsubscript{13}, \textit{J} = 10.1, 1.6 Hz; phen-C), 141.77 (s; Ph-C), 140.33 (d; Ph-CH), 135.36 (d; Ph-CH), 128.48 (s; Ph-CH), 125.16 (s; Ph-CH), 122.30 (d; Ph-CH) = 9.1 Hz; Ph-CH), 36.06 (dd; J\textsubscript{CP} = 20.2, J\textsubscript{CP} = 25.0 Hz, CH\textsubscript{2}P), 35.61 (d; J\textsubscript{CP} = 21.0 Hz; CH\textsubscript{2}P), 29.49 ppm (d; J\textsubscript{CP} = 4.5 Hz; CH\textsubscript{2}P); IR (ATR): v\textsubscript{f} = 1964 cm\textsuperscript{-1} (CO); UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}); \lambda\textsubscript{max} (e) = 287 (8.2 x 10\textsuperscript{4})<sup>-1</sup> cm\textsuperscript{-1}; HRMS (FAB); m/z calcd for C\textsubscript{25}H\textsubscript{34}N\textsubscript{2}O\textsubscript{2}P\textsubscript{2}Rh\textsubscript{2}: 451.0703 (M\textsuperscript{+}CO); found: 451.0688; elemental analysis (%) calcd for C\textsubscript{25}H\textsubscript{34}N\textsubscript{2}O\textsubscript{2}P\textsubscript{2}Rh\textsubscript{2}: CH\textsubscript{2}Cl\textsubscript{2}: C 48.88, H 5.55, N 2.64; found: C 48.86, H 5.46, N 2.63.

Synthesis of [Rh\textsuperscript{I}(c\textsuperscript{5-PN-C}(1-CO)]\textsuperscript{+} (3): [Rh(acac)(CO)]\textsuperscript{2+} (0.016 g, 0.064 mmol) was added to a solution of the ligand (0.020 g, 0.064 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (5 mL), and the reaction mixture was stirred overnight. After evaporation of the solvent under reduced pressure, the product was washed with pentane to yield 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 solution of 3 in CH\textsubscript{2}Cl\textsubscript{2}.

An alternative synthesis of 3: A solution of KO\textsubscript{t}Bu in THF (1 mL, 11.0, 0.011 mmol) was added to a solution of complex 2 (4.7 mg, 0.010 mmol) in THF (2 mL). The color immediately changed from yellow to red, and the \textsuperscript{13}C NMR spectrum indicated full conversion into complex 3. \textsuperscript{1}H NMR (300 MHz, [D\textsubscript{2}]acetone): \delta = 7.80 (app td, J = 7.8, 0.8 Hz, 1H; H\textsubscript{4}), 7.69 (dd, J\textsubscript{HH} = 7.4 Hz, 1H; H\textsubscript{5}), 7.62–7.69 (m, 1H; H\textsubscript{9}), 7.54 (m, 1H; H\textsubscript{6}), 7.40 (d, J\textsubscript{HH} = 7.7 Hz, 1H; H\textsubscript{8}), 7.02 (m, 1H; H\textsubscript{1}), 6.94 (ddd; J\textsubscript{CP} = 7.5, J\textsubscript{CP} = 1.4 Hz, 1H; H\textsubscript{7}), 3.70 (d; J\textsubscript{CP} = 8.2 Hz, 2H; H\textsubscript{2}), 1.37 ppm (d, J\textsubscript{CP} = 13.3 Hz, 18H; H\textsubscript{1}); \textsuperscript{31}P NMR (400 MHz, [D\textsubscript{2}]acetone): \delta = 7.83 (app t, J = 7.8 Hz, 1H; H\textsubscript{4}), 7.71 (d, J = 7.9 Hz, 1H; H\textsubscript{5}), 7.67 (ddd, J = 7.1, 1.7, 1.7 Hz, 1H; H\textsubscript{9}), 7.56 (dd, J = 7.7, 1.2 Hz, 1H; H\textsubscript{6}), 7.42 (d, J = 7.7 Hz, 1H; H\textsubscript{8}), 7.04 (ddd, J = 7.2, 7.2, 1.3 Hz, 1H; H\textsubscript{1}), 6.96 (ddd, J = 7.5, 1.4 Hz, 1H; H\textsubscript{7}), 3.73 (s, 2H; CH\textsubscript{2}P), 1.39 ppm (s, 18H; (CH\textsubscript{2})\textsubscript{3}CP); \textsuperscript{31}P NMR (121 MHz, [D\textsubscript{2}]acetone): \delta = 76.31 ppm (d, J\textsubscript{PP} = 101.0 Hz); \textsuperscript{13}C NMR (75 MHz, [D\textsubscript{2}]acetone): \delta = 201.01 (dd; J\textsubscript{CP} = 78.8, J\textsubscript{CP} = 11.1 Hz; CO), 176.93 (dd; J\textsubscript{CP} = 81.8, J\textsubscript{CP} = 36.5 Hz; Ph-C\textsubscript{n}; Rh-C\textsubscript{R}), 168.06 (dd, J = 6.7, 3.0 Hz; Ph-C), 165.20 (dd, J = 10.1, 1.6 Hz; Ph-C), 150.35 (s; Ph-C), 140.33 (d; J\textsubscript{CP} = 7.6, 1.6 Hz; Ph-C), 136.99 (s; Ph-C), 130.36 (d; J = 5.6, 2.5 Hz; Ph-C), 124.46 (d; J = 3.5 Hz; Ph-C), 123.58 (s; Ph-C), 120.62 (d; J = 9.3 Hz), 116.41 (s; Ph-C), 125.03 (d; J\textsubscript{CP} = 14.0 Hz; Ph-C); 35.25 (dd; J\textsubscript{CP} = 12.0, J\textsubscript{CP} = 0.8 Hz; (CH\textsubscript{2})\textsubscript{3}CP); IR (ATR): v\textsubscript{f} = 1933 cm\textsuperscript{-1} (CO); UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}); \lambda\textsubscript{max} (e) = 250 (2.4 x 10\textsuperscript{4})<sup>-1</sup> cm\textsuperscript{-1}; HRMS (FAB); m/z calcd for C\textsubscript{25}H\textsubscript{34}N\textsubscript{2}O\textsubscript{2}P\textsubscript{2}Rh\textsubscript{2}: 444.0964 (M\textsuperscript{+}H); found: 444.0970; elemental analysis (%) calcd for C\textsubscript{25}H\textsubscript{34}N\textsubscript{2}O\textsubscript{2}P\textsubscript{2}Rh\textsubscript{2}: C 56.89, H 6.14, N 3.16; found: C 56.62, H 6.11, N 3.13.

Synthesis of [Rh\textsuperscript{I}(c\textsuperscript{5-PN-C}(1-CO)]\textsuperscript{+}BF\textsubscript{4}\textsuperscript{+} (4): HBF\textsubscript{4} (54 wt% in Et\textsubscript{2}O, 3.7 mg, 23 \mu mol) was added to a solution of 3 (10 mg, 23 \mu mol) in Et\textsubscript{2}O (5 mL), thus resulting in immediate precipitation of a yellow solid. The supernatant was removed and the product was washed with diethyl ether (1 mL) to yield 4 as a yellow solid in quantitative yield. Single crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of pentane into a solution of 4 in THF. \textsuperscript{1}H NMR (500 MHz;
Synthesis of [Rh(CO)(CN)2]Cl2 (5): Methyl iodide (6 mL, 45 µmol) was added to a solution of 3 (20 mg, 45 µmol) in acetonitrile (5 mL), thus resulting in a color change from red to brown within minutes at room temperature. Removal of the solvent in vacuo resulted in the isolation of 5 as a brown solid in quantitative yield.19

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Yield %</th>
<th>Color</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(CO)(CN)2]Cl2</td>
<td>C2H18Cl2NO2</td>
<td>60</td>
<td>Dark-red</td>
<td>Crystal yield</td>
</tr>
</tbody>
</table>

Characterization of [Rh(CO)(CN)2]Cl2 (5): Methyl iodide (3 µL, 23 µmol) was added to a solution of 3 (10 mg, 23 µmol) in D2O (0.6 mL) at -78 °C. The cold solution was transferred to a cold NMR tube and inserted in a precooled NMR machine.

X-ray crystallography studies

X-ray intensities were measured on either a Bruker Kappa APEX II diffractometer with a sealed tube and Triumph monochromator (λ = 0.71073 Å) at 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 150(2) K for 6. The intensity data were integrated with the Eval15 software20 or the Bruker APEX2 software.21 Absorption correction and scaling were performed with SADABS.22 The structures were solved with the programs SHELXT23 for 2, SHELXS-9724 for 3 and 4, or SHELXTL for 6.25 Least-squares refinement was performed with SHELXL-201326 for 2, 4, and 6 or SHELXL-9727 for 3 against F2 of all the reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All of the hydrogen atoms were located in difference Fourier maps. The metal-bound hydrogen atom H11 in complex 4 was refined freely with an isotropic displacement parameter, whereas all the other hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program28

CCDC 696373 (2), 696375(3), 696376 (4), and CCDC 1035861 (6) contain the supplemental crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2: C2H18Cl2NOPRh·CH2Cl2, M. = 564.70, yellow needle, 0.06 x 0.07 x 0.27 mm, monoclinic, P2/c (No: 14), a = 8.47689(19), b = 13.4570(4), c = 20.4259(5) Å, β = 90.149(1)°, V = 2468.41(11) Å³, Z = 4, Dc = 1.509 g cm⁻³, µ = 0.09 mm⁻¹; 46702 reflections were measured up to a resolution of (sin ω/λ)max = 0.65 Å⁻¹; 5708 reflections were unique (Rint = 0.024), of which 5253 were observed (I > 2σ(I)); the structure was refined as a pseudo-orthorhombic twin with a two-fold rotation about hkl = (0,0,1) as a twin operation; 269 parameters were refined with no restraints; R1/wR2 (I > 2σ(I)): 0.0189/0.0459; R1/wR2 (all refls.): 0.0223/0.0473; S = 1.051; twin fraction BASF = 0.1995(18); residual electron density between −0.60 and 0.68 e Å⁻³.

3: C2H18Cl2NOPRh, M. = 443.32, red needle, 0.08 x 0.17 x 0.44 mm, monoclinic, C2/c (No: 15), a = 21.7218(5), b = 12.4856(3), c = 16.3022(4) Å, β = 113.853(1)°, V = 4043.71(17) Å³, Z = 8, Dc = 1.456 g cm⁻³, µ = 0.93 mm⁻¹; 32483 reflections were measured up to a resolution of (sin ω/λ)max = 0.65 Å⁻¹; 4641 reflections were unique (Rint = 0.017) of which 4230 were observed (I > 2σ(I)); 232 parameters were refined with no restraints; R1/wR2 (I > 2σ(I)): 0.0161/0.0418; R1/wR2 (all refls.): 0.0189/0.0427; S = 1.047; residual electron density between −0.33 and 0.31 e Å⁻³.

4: [C3H18Cl2NOPRh(BF4)], M. = 531.13, orange block, 0.08 x 0.20 x 0.25 mm, triclinic, P1 (No: 2), a = 8.0624(3), b = 11.5108(4), c = 12.8859(3) Å, α = 108.143(1)°, β = 95.856(1)°, γ = 96.480(1)°, V = 1117.18(6) Å³, Z = 2, Dc = 1.579 g cm⁻³, µ = 0.88 mm⁻¹; 40925 reflections were measured up to a resolution of (sin ω/λ)max = 0.81 Å⁻¹; 6922 reflections were unique (Rint = 0.020), of which 8640 were observed (I > 2σ(I)); 281 parameters were refined with no restraints; R1/wR2 (I > 2σ(I)): 0.0260/0.0632; R1/wR2 (all refls.): 0.0331/0.0659; S = 1.034; residual electron density between −0.70 and 0.91 e Å⁻³.

5: C3H18Cl2NOPRh, M. = 697.11, red-orange block, 0.18 x 0.08 x 0.05 mm, triclinic, P1 (No: 2), a = 8.9530(4), b = 9.1338(4), c = 16.7107(7) Å, α = 102.5412(1)°, β = 90.8662(1)°, γ = 119.0062(1)°, V = 1154.94(9) Å³, Z = 2, Dc = 2.095 g cm⁻³, µ = 3.493 mm⁻¹; 44618 reflections were measured up to a resolution of (sin ω/λ)max = 0.81 Å⁻¹; 4059 reflections were unique, of which 3590 were observed (I > 2σ(I)); 250 parameters were refined with no restraints;
Geometric optimizations were carried out using the Turbomole program package[30] coupled to the PQR Baker optimizer[31] via the BOP package[32] at the spin unrestricted ri-DFT level using the BP86[33] functional and the resolution-of-identity (Ri) method.[34] We optimized the geometries of all stationary points at the def2-TZVP basis-set level[35] by using the Grimme dispersion corrections (disp3 version)[36] and a tight energy grid (m5). The identity of the transition state 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. Zero-point energy (ZPE) and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) were calculated from these analyses by using standard thermodynamics. The optimized geometries of all the species are supplied as separate .pdb and .xyz files. Wiberg bond orders[37] were calculated from the Turbomole output files by using the AOMix program.[38]

Acknowledgements

This work was funded by the European Research Council (ERC, Starting Grant 279097, EuReCat to J.l.v.d.V.).

Keywords: C–H activation • metallacycles • pincer • reactive ligands • rhodium


For the related Rh
Chem. Eur. J.

[17] Rh–N and Rh–C bond lengths are similar to Rh3+-pyridylpyridine and Rh3+-phenylpyridine (2 eq) in RhCl(CO)3(pyridine)264; or reaction was observed upon mixing [Rh(acac)(CO)3] with MeI to an on-cyclometalated [{RhCl(CO)3(PPh)}2] species.


Received: December 12, 2014
Revised: January 23, 2015
Published online on March 24, 2015

www.chemeurj.org
7305 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim