C–H Activation

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(C₃) ligand 2-di(tert-butylphosphonamethyl)-6-phenylpyridine (1*) and its versatile coordination to a Rh center is described. Facile C–H activation occurs in the presence of a (internal) base, thus resulting in the new cyclometalated complex [Rh(CO)(κ²-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 [D₆]formic acid. The addition of HBF₄ to 3 leads to rapid net protonolysis of the Rh–C bond to produce [Rh(CO)(κ²-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)(κ²-P,N-1Me)] (5). Variable-temperature NMR spectroscopy indicates the involvement of a RhIII intermediate through formal oxidative addition to give trans-[Rh(C₃H₂)(CO)(κ²-P,N,C-1)] prior to C–C reductive elimination. The RhIII-trans-diiodide complex [Rh(CO)(κ²-P,N,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.² Reactivity studies have indicated that metal–arene 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 RhIII species.⁴ Isolated high-oxidation state RhIV complexes that feature a cyclometalated phenylpyridine ligand or substrate scaffold are well-documented.⁵ Well-characterized examples of low-oxidation state RhII cyclometalated complexes are rare (Figure 1).⁶ As a consequence, the potential reactivity of the metallacyclic RhIII-C bond and the scope for follow-up chemistry is unexplored.

![Figure 1. Overview of known cyclometalated Rh complexes.](image-url)

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 catalysts perspective. Herein, we describe our investigations toward the use of agostic interactions and reversible cyclometalation reactivity in the design of new flexideterminate 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(phosphonamethyl)benzene (PCP) pincer system reported by...
Milstein and co-workers, wherein a Rh(C<sub>Ph</sub>–H) bond was detected as an intermediate toward the oxidative addition of the C–H bond<sup>[8,9]</sup>. Examples of structurally characterized complexes with an agostic C<sub>aromatic</sub>–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<sup>[10–12]</sup>, and reversible cyclometalation has been postulated as a possible ligand-mediated mechanism in catalysis, primarily based on theoretical calculations<sup>[13]</sup>. 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<sup>[14–16]</sup>. 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<sup>+</sup> 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 an agostic C<sub>Ph</sub>–H complex. We also describe the first case of facile methylation of a cyclometalated Rh–arene through the reductive elimination of a [Rh(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<sup>+</sup> species**

Addition of ligand 1<sup>H</sup> to 0.5 molar equivalents of [Rh(μ-Cl)(CO)]<sub>2</sub> yielded a yellow solid, which displays a doublet in the <sup>31</sup>P NMR spectrum at <i>δ</i> = 104 ppm ([<i>J</i><sub>Rh–P</sub> = 160 Hz; Scheme 2]). X-ray crystal structure determination confirmed the square-planar geometry expected for this complex, formulated as [RhCl(CO)(μ<sup>2</sup>-PN–1<sup>H</sup>)]<sub>2</sub> (2; Figure 2). The most striking feature of the molecular structure is the fleeting pyridinyl ring that strongly points out of the Rh coordination plane (δ; Rh–N1–C5–C15 = 19.32(18)°) to accommodate the Cl ligand, which also results in a somewhat acute Rh1–Cl1 angle of 162.983(15)°.

Notably, the reaction of 1<sup>H</sup> with [Rh(acac)(CO)]<sub>2</sub> (acac = acetacetonate) results in the red complex 3 with very different spectroscopic features relative to 2. The <sup>31</sup>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 <sup>31</sup>P NMR spectrum showed a doublet at <i>δ</i> = 76 ppm with a significantly smaller coupling constant (<i>J</i><sub>Rh–P</sub> = 101 Hz), which indicates the presence of a strong o-donor trans to the phosphane group. Furthermore, the

---

**Scheme 1.** General concept for novel PN(C) ligand design and potential bond activation reactivity available through reversible cyclometalation.

**Scheme 2.** Synthesis of Rh<sup>+</sup> complexes 2 and 3 that display facile reversible metalation.

**Figure 2.** ORTEP (ellipsoids set at 50% probability) for complex 2 (front and side view). Selected bond lengths [Å] and angles [°]: Rh1–P1 2.2243(4), Rh1–N1 2.1546(12), Rh1–Cl1 2.4128(4), Rh1–C21 1.8039(16); P1–Rh1–Cl1 81.95(3), P1–Rh1–C11 84.64(3), N1–Rh1–Cl1 93.75(3); torsion: ± N1–C5–C15–C16 38.6(2).

**Figure 3.** <sup>31</sup>P NMR spectra with relevant <i>J</i><sub>Rh–P</sub> coupling constants for Rh<sup>+</sup> complexes 2–5.
$^{13}$C NMR spectrum contained a doublet of doublets at $\delta = 177$ ppm ($J_{HC} = 82, J_{CP} = 37$ Hz). The formation of free acacH was confirmed by using $^1$H NMR spectroscopy. These observations suggest efficient and selective C–H activation of the phenyl side arm of 1. The resulting $(k^3-P, N, C)$-coordination mode of the ligand in this unusual Rh$^ii$ cyclometalated complex was unambiguously confirmed by X-ray structure determination (Figure 4).$^{[5, 17, 18]}$ The cyclometalated ligand structure bears considerable strain, with $\pm$ P1-Rh1-C1 = 162.47(4) and $\pm$ N1-Rh1-C1 = 80.26(5). $^{[19]}

Influence of the base on the mechanism of cyclometalation

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$^iv$ catalysts, proceeds through a six-membered transition state where the non-coordinated acetate oxygen atom of the $k^1$-O ligated acetate deprotonates the C–H bond.$^{[19a]}$ 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$^ii$ and Ir$^iii$ species.$^{[19b, c]}$ Based on this precedent, we speculate that a similar mechanism is plausible for the Rh$^i$ 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 $-78^\circ$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(phospho)phenyl-lutidine (PnP) ligand.$^{[20]}$ Apart from a distinct darkening of the solution upon deprotonation of the pyridine fragment, deuterium experiments (that is, the use of DCI results in selective deuteration at the $-CH_{3}(P)$ position; see the Supporting Information) are indicative for methylene reactivity. However, this deamoratized species rapidly converts into 3 by proton transfer from the ortho-phenyl position to the CH backbone, even at $-78^\circ$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 $^1$H and $^1$H NMR spectroscopic analysis at $-78^\circ$C (see the Supporting Information). The cyclometalated complex 3 is still susceptible to deprotonation at the phosphane arm upon reaction with a strong base, according to in situ $^1$H and $^1$H NMR spectroscopic analysis (see the Supporting Information). Hence, this novel ligand scaffold displays two distinctly different modes of proton-responsive reactivity.$^{[21]}

We resorted to DFT calculations to understand the observed reaction sequence of the initial deprotonation at the $-CH_{3}(P)$ 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 $^{TS^2}_2$ 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$^{-1}$ ($^{TS^2}_1$-tBuOH$^{-}$). $^{[22]}

Reactivity of the cyclometalated Rh$^i$ complex toward acid: Formation of an aromatic C–H agostic Rh$^i$ species

As mentioned in the Introduction, pincer ligands with a flanking phenyl group are scarce, especially in contrast to the archetypical PCP pincers with a central phenyl ring. Isolated Rh complexes with an agostic interaction with an aromatic C–H group are very rare and limited to examples with PCP, wherein the C–H bond is forced within the coordination sphere of the Rh center.$^{[31]}$ The unique structure of ligand 1$^{iv}$ 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
The agostic interactions in solution may result in an upfield shift to about $\delta = 4$ ppm for the respective proton in the $^1$H NMR spectrum. Furthermore, the $J_{CH}$ value should decrease due to the weakening of the C–H bond. In case of 4, the phenyl group shows local C$_3$ symmetry by $^1$H NMR spectroscopic analysis, even at $-90\,^\circ$C, thus indicating fast rotation around the C$_{ph}$-C$_{py}$ bond. The signal for the two ortho-C$_{ph}$H$_2$ bonds does show an upfield shift to $\delta = 117$ ppm in the $^{13}$C NMR spectrum relative to complex 2, but the $J_{CH}$ 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.[7] 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 [(PCP)Rh(CO)][BF$_4$]$_2$, which was identified as an agostic Rh–(C–H) interaction by using DFT calculations. DFT (B3LYP-disp3) calculations for complex 4 reveal a Wiberg[23] 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 [(PCP)Rh(CO)][BF$_4$]$_2$, although the interactions in 4 are slightly weaker than in this PCP complex. Furthermore, the three-center bond order[23] 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).[24]

**Methylation of the cyclometalated Rh complex:**

**Involvement of a Rh$^{IV}$ intermediate**

Reactivity of a Rh–phenyl fragment toward Mel to induce selective methylation has been reported for a [(PCP)Rh(CO)] complex, but this reaction proved to be very sluggish by taking two weeks to complete.[25, 26] In contrast, species 3 reacts rapidly (<5 min) with Mel at room temperature to form 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.[7]
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 abase to ar hodacyclic species, based on preliminaryi nsitu major species, with adoublet at
exploring this reactivity in more detail. Rh
reductiveelimination process.

Reversible cyclometalation as potential for cooperative bond activation

During the course of our investigations, we noticed that the Rh1–C bond in complex 3 can be selectively activated, as illustrated by the smooth and facile reactions with HCl, HBF4, and Mel. This reactivity towards electrophiles could be caused by the ring strain (ΔN1-Rh1-C1 at 80.26(5)°) or the strong trans effect of the phosphane. We spectroscopically evaluated whether weaker acids could also cleave the Rh–C bond and found out that, amongst others, formic acid is a competent reagent, presumably generating the formate complex [Rh(CO)(CO)(HCOO)(I)] (7; see the Supporting Information). When [D3]formic acid (HCOOD) is used, both ortho positions of the phenyl group are deuterated within minutes, which indicates that the cyclometalation at the Rh center is reversible. This feature of reversible C–H bond activation might allow for cooperative catalysis with 3, as heterolytic cleavage of a suitable protic reagent or substrate could open up a coordination site at the Rh center upon dissociation of the regenerated phenyl group. Heterolytic activation of H2 (20 bar, room temperature) was not observed, thus suggesting that dehydrogenation of a putative Rh(PNC)−hydrate could be favorable. We are currently exploring this concept for catalytic applications, for example, in formic acid dehydrogenation.

Conclusion

We have described initial leads to exploit reversible cyclometalation as part of a reactive ligand concept in coordination chemistry. Ligand framework 1 can act as a reactive flexidentate 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 complex. The ligand backbone displays dual-site proton-responsive reactivity. The cyclometalated species reacts rapidly with various (protic) electrophiles. The Rh–Cn bond is selectively cleaved by one molar equivalent of HBF4 to result in the formation of the rare agostic

![Figure 7](https://example.com/image.png)
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-I1 2.054(3), Rh1–Cl1 2.054(3), Rh1–C1 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).

---

Scheme 5. Pathway for the conversion of 3 into 5 through the Rh8 intermediate A and synthesis of the Rh8 model species [Rh(CO)(I)][(I)] (6).

[Diagram of Scheme 5 is embedded here]
slowed warmed to room temperature overnight. The reaction mixture was stirred at 78 °C for 2 h and then became yellow. The product was washed with pentane to yield the desired complex in 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 solution of 3 in CHCl₃.

A synthetic alternative for 3: A solution of KOTBu in THF (1 mL, 11 mL, 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 ¹H NMR spectrum indicated full conversion into complex 3. ¹H NMR (300 MHz, [D₆]acetone): δ = 7.80 (app td, J = 7.8, 0.8 Hz, 2H, H4); 7.60 (J = 7.4 Hz, 1H, H5); 7.62–7.69 (m, 1H, H6); 7.40 (J = 7.7 Hz, 1H, H7); 7.02 (m, 1H, H8); 6.94 (J = 7.5, 7.5, J = 1.4 Hz, 1H, H7); 3.70 (d, J = 8.2 Hz, 2H, H2); 1.37 ppm (J = 13.3 Hz, 18H, H1); 1H NaP (400 MHz, [D₆]acetone): δ = 7.83 (app td, J = 7.8, 0.8 Hz, 2H, H4); 7.71 (d, J = 7.9 Hz, 1H, H5); 7.67 (J = 7.1, 1.7, 1.7 Hz, 1H, H9); 7.56 (dd, J = 7.7, 1.2 Hz, 2H, H6); 7.42 (d, J = 7.7 Hz, 1H, H7); 7.04 (dd, J = 7.2, 7.2, 1.3 Hz, 1H, H8); 6.96 (J = 7.5, 7.5, 1.4 Hz, 1H, H7); 3.73 (s, 2H, CH₃); 1.39 ppm (s, 18H, (CH₃)₂P); 1H NaP (121 MHz, [D₆]acetone): δ = 7.63 ppm (J = 101.0 Hz, 1H NaP (75 MHz, [D₆]acetone); δ = 162.99 ppm (J = 146.7 Hz, Py-C), 156.36 (J = 5.3 Hz, Py-C), 145.37 (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 = 8.1 Hz, Py-CH), 117.51 (s, Py-CH), 32.67 (d, J = 16.8 Hz, CH₃), 32.34 (d, J = 14.9 Hz, (CH₃)₂P), 30.10 ppm (d, J = 13.8 Hz, (CH₃)₂P); HRMS (FAB): m/z calced for C₆H₄O₂N₂P: 314.2025 [M⁺]H⁺; found: 314.2025.

Synthesis of [Rh(η⁵-C₆H₅)(η⁵-C₆H₅)]⁺ (2): A solution of [Rh(η⁵-C₆H₅)]⁺ (0.012 g, 0.032 mmol) in CH₂Cl₂ (2 mL) was added to a solution of 1⁺ (0.020 g, 0.064 mmol) in CH₂Cl₂ (3 mL), and the reaction mixture was stirred overnight. After evaporation of the solvent, the product was washed with pentane to yield the desired complex as a yellow solid. The yellow solution 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 an X-ray crystal structure determination were obtained by slow diffusion of pentane into a solution of 3 in CHCl₃.

Experimental Section

General methods

All the reactions were carried out in a nitrogen atmosphere by using standard Schlenk techniques. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane, and Et₂O were distilled from sodium benzophenone ketyl. CHCl₃ was distilled from CaH₂, toluene from sodium under nitrogen. NMR spectra (¹H, 13C, 31P, 19F, and 19B) were measured on a Varian INOVA 500 MHz, a Bruker AV400s or a Varian MERCURY 300 MHz spectrometer. IR spectra were recorded with a Bruker Alpha-P FTIR spectrometer. NMR spectra were measured on an ATR platinum diamond 1H, 13C, 19F, 31P, and 1H Cp NMR (121 MHz, [D₆]acetone): δ = 162.99 ppm (J = 146.7 Hz, Py-C), 156.36 (J = 5.3 Hz, Py-C), 145.37 (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 = 8.1 Hz, Py-CH), 117.51 (s, Py-CH), 32.67 (d, J = 16.8 Hz, CH₃), 32.34 (d, J = 14.9 Hz, (CH₃)₂P), 30.10 ppm (d, J = 13.8 Hz, (CH₃)₂P); HRMS (FAB): m/z calced for C₆H₄O₂N₂P: 314.2025 [M⁺]H⁺; found: 314.2025.
Characterization of [Rh(II)(Me)(κ2-PN-1-CO)] (A): Methyl iodide (3 μL, 23 μmol) was added to a solution of 3 (10 mg, 23 μmol) in [D₆]acetone (0.6 mL) at –78°C. The cold solution was transferred to a cold NMR tube and inserted in a precooled NMR machine. The temperature was slowly raised from –60 to –20°C, during which the Rh(II) intermediate formed. When the temperature was raised to 10°C, this intermediate converted into complex 5 within 60 min. H NMR (300 MHz, [D₆]acetone, 253 K): δ = 0.03–0.79 (m, 2H), 2.48 (t, J = 7.8 Hz, 2H, CH₂-P), 3.55 (s, J = 11.4 Hz, CH₂-P), 29.41 (d, J = 4.6 Hz, CH₃-C), 21.82 ppm (s, Ph-Me), signals for CO and CH₃P were not observed; IR (ATR): ν = 1952 cm⁻¹ (CO); HRMS (FAB): m/z calcd for C₆H₅ᵢNOPRh: 458.1120 (M–I)⁺; found: 458.1199.

Synthesis of Rh(III)(II)₆(P₂-N-2-P-1) (6): Li₆ (6 mg, 23 μmol) was added to a solution of 6 (10 mg, 23 μmol) in THF (1.5 mL), and the reaction mixture was stirred for 10 min. The solvent was evaporated to yield 6 as a dark-red solid in quantitative yield. Single crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of pentane into a solution of 6 in CH₂Cl₂. H NMR (300 MHz, CH₂Cl₂): δ = 7.87–7.69 (m, 4H), 7.38–7.25 (m, 2H), 6.94 (dd, J₁₂₂ = 7.8 Hz, J₂₃₄ = 6.1 Hz, 1.6 Hz), 3.91 (d, J₁₂₂ = 8.8 Hz, 2H, CH₂-P), 1.54 ppm (d, J₁₃₄ = 13.3 Hz, 18H; CH₂-P); ¹³C NMR (121 MHz, CH₂Cl₂): δ = 44.66 ppm (d, J₁₂₂ = 68.9 Hz); CT NMR (75 MHz, CH₂Cl₂): δ = 165.65 (d, J₁ = 6.2 Hz), 162.60 (d, J₁ = 6.3 Hz), 157.72 (dd, J₁₀₁ = 10.2, 18.1 Hz), 146.10, 141.76, 139.31, 132.19 (d, J₁ = 8.0 Hz), 125.16 (d, J₁ = 5.0 Hz), 123.57, 119.72 (d, J₁ = 8.4 Hz), 118.45, 38.51 (d, J₁ = 13.4 Hz), 38.06 (d, J₁ = 5.6 Hz), 31.93 ppm (d, J₁ = 3.4 Hz), signal for CO was not observed; IR (ATR): ν = 2049 cm⁻¹ (CO); HRMS (FD): m/z calcd for C₆H₅ᵢNOPRh: 696.8975 [M⁺]; found: 696.9002.

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 = 0.17103 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 software[26] or the Bruker APEX2 software.[21] Absorption correction and scaling was performed with SADAB,[21] The structures were solved with the programs SHELXT[28] for 2, SHELXS-97[24] for 3 and 4, or SHELXTL for 6.[31] Least-squares refinement was performed with SHELXL-2013[32] for 2, 4, 5 and 6 or SHELX-97[23] 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 program.[33] CCDC 966374 (2), 966375(3), 966376 (4), and CCDC 1038561 (6) contain the supplementary 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: C₂H₅ClNOPRh₂Cl₂, M = 564.70, yellow needle, 0.06 × 0.07 × 0.27 mm, monoclinic, P2₁/n (No: 14), a = 8.47689(19), b = 13.5740(5), c = 20.4259(5) Å, β = 101.2(1)°, V = 2468.41(1) Å³, Z = 4, Dc = 1.509 g cm⁻³, μ = 1.09 mm⁻¹, 46720 reflections were measured up to a resolution of (sin θ/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 = 0.0187; R = 0.0234; R1 = 0.0187 (all refl.): 0.0189/0.0459; R1 = 0.0223/0.0473; S = 1.051; twin fraction BASF = 0.0195(18); residual electron density between −0.60 and 0.68 e Å⁻³.

3: C₃H₅₃ClNOPRh₃, M = 443.32, red needle, 0.08 × 0.17 × 0.44 mm, monoclinic, C2/c (No: 15), a = 21.7218(5), b = 12.4865(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 θ/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 = 0.0161; R1 = 0.0187; R1 = 0.0187 (all refl.): 0.0189/0.0427; S = 1.047; residual electron density between −0.33 and 0.31 e Å⁻³.

4: [C₆H₅ᵢNOPRh(BF₄)₂], M = 531.13, orange block, 0.08 × 0.20 × 0.25 mm, triclinic, P11 (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 θ/λ)max = 0.81 Å⁻¹; 9822 reflections were unique (Rint = 0.020), of which 8640 were observed (I > 2σ(I)); 281 parameters were refined with no restraints; R₁ = 0.0206/0.0632; R1 = 0.020 (all refl.): 0.0331/0.0659; S = 1.034; residual electron density between −0.70 and 0.91 e Å⁻³.

5: C₆H₅ᵢNOPRh₂I, M = 697.11, red-orange block, 0.18 × 0.08 × 0.05 mm, triclinic, P11 (No: 2), a = 8.9530(4), b = 9.1338(4), c = 16.7107(7) Å, α = 102.541(2), β = 90.866(2), γ = 119.006(2)°, V = 11549.94(9) Å³, Z = 2, Dc = 2.050 g cm⁻³, μ = 3.493 mm⁻¹; 44618 reflections were measured up to a resolution of (sin θ/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;
DFT calculations were carried out with the Turbomole program package coupled to the PBI linker and the BP86 functional and the resolution-of-identity (RI) method.[40] We optimized the geometries of all stationary points at the def2-TZVP basis-set level by using the Grimme dispersion corrections (disp3 version) 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 were calculated from the Turbomole output by using the AOMix program.[41]

Acknowledgements

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

Keywords: C–H activation · metallaalloys · pincers · reactive ligands · rhodium
For the related Rh

At etradentate PNNP system with side-arm and backbone reactivity has

Chem. Eur. J.


C–C reductive elimination from the catonic \(\text{[Rh}^2\text{Me}^+(\text{PCP})]^{+}\) species usually requires exogenous coordination of CO: a) A. Vigalok, B. Rybicki-


